Abstract

Charvet, Richard André. Ring-Opening Metathesis Polymerization of Functionalized Cyclobutene Derivatives. (Under the direction of Bruce M. Novak)

The field of ring-opening metathesis polymerization has known a growing interest in the last twenty years due to the development of well-defined carbene catalysts with an improved tolerance toward functional groups and the ability to promote living polymerizations. Also, little attention has been paid to monomer design for ROMP. To further extend the field of applications of ROMP polymers, a new family of functionalized polycyclic monomers based on the endo-tricyclo[4.2.2.02,5]deca-3,9-diene structure bearing anhydride, N-alkyl or N-phenyl substituted succinimides at the 7,8 positions has been prepared. Monomers functionalized with a N-phenyl succinimide moiety bearing an ortho substituent were shown to exist as atropisomeric mixtures.

Polymerization studies were performed with well-defined Schrock's molybdenum catalysts and a variety of Grubb's ruthenium carbene catalysts. A living polymerization was obtained with Cl2Ru(=CHPh)(PCy3)2 (Ru-III).

19F NMR analysis indicated that the ortho and meta fluorinated substituents of the N-phenyl succinimide moiety could be regarded as sensitive reporters vis-à-vis the microstructure of the polymer. "Blocky" copolymers from a mixture of cis-cyclooctene and the penta-fluorinated monomer M-7 could be prepared with Ru-III. The presence of cis-cyclooctene was shown to have an influence on the kinetics of the polymerization and the polymer microstructure.
Kinetic studies with Ru-III indicated that faster polymerizations were obtained with more electron donating substituents at the 7,8-positions. The functionalization of the monomer structure with bulky polyaryl ether dendritic molecules had a remarkable effect on the catalysts' activity. The incorporation of two dendrons per monomer unit led to significant decrease in the rates of polymerization and a controlled polymerization was obtained with the very active Ru(=CHPh)Cl2(PCy3)(1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) (Ru-VI). This control behavior was explained by the decrease of the propagation rate due to the bulkiness of the dendritic functional groups.

Polymers functionalized with a simple N-succinimide moiety displayed a remarkable thermal stability with decomposition temperatures above 300°C. No T_g was observed below decomposition temperature, indicated the generation of a very rigid polymer backbone. Upon hydrogenation of poly-2, a T_g was present at 285°C and the thermal stability increased by 100°C, both data consistent with the generation of a saturated polymer backbone.

Graft copolymers based on a ROMP polymer skeleton and with poly(methylmethacrylate) branches could be prepared in a one-pot procedure using the single catalyst Ru-III and monomers based on the endo-tricyclo[4.2.2.02,5]deca-3,9-diene structure functionalized with a tertiary alkyl bromide, present as an ATRP initiator. Both distinct polymerization processes seem to occur in tandem and in a controlled fashion. 1H NMR analysis suggested the formation of a specific morphology in solution and DSC analysis confirmed the presence of phase segregation between the different polymer backbones.
RING-OPENING METATHESIS POLYMERIZATION OF FUNCTIONALIZED CYCLOBUTENE DERIVATIVES

by

RICHARD ANDRE CHARVET

A dissertation submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy

DEPARTMENT OF CHEMISTRY

Raleigh

2002

APPROVED BY:

_________________________________________  ________________________________

_________________________________________

Chairman of Advisory Committee
Biography

The author was born on February 7, 1975 in Rillieux la Pape, France. After completing his primary and secondary education in Rillieux la Pape, Richard was selected to attend the Preparatory Classes for the "Grandes Ecoles" at "Lycée du Parc" in Lyon. After two years of intensive studies in maths, physics and chemistry, he successfully passed the competitive entrance exam for the School of Chemistry, Physics and Electronics of Lyon (CPE Lyon) in 1995. After two years of studies in chemistry and engineering processes, he did an optional one-year internship in a company and in a public research laboratory. He then began his graduate education at North Carolina State University in 1998 with Dr. Bruce M. Novak. His first year of studies and first results in research allowed him to fulfill the requirements for CPE Lyon from which he graduated with a Diploma in chemistry and engineering process in 2000.

Aside from chemistry, the author enjoys sport: skiing, triathlon (swimming, cycling, running) hiking in the Alpes and music. He also has a particular interest for foreign languages, other cultures and international political economy.
Acknowledgements

Completing a PhD. in chemistry was a very intense experience. The last four years have included some moments of serious doubts and I would like to say thanks to those who helped me along the way.

I would like to thank my parents, Marcelle and Gilbert and my two young brothers, Claude and Michel who offered me their love and unending support through the years. They have always believed in me and encouraged me to go for my dreams. I would also like to thank my grand father, Guy who always supported me and inspired me through his strong personality. Your disappearance during my stay was heartbreaking but further reinforced my determination and ambition.

I would like to thank Prof. Bruce Novak for the financial support and remarkable working conditions that generated a perfect atmosphere to make progress in research. I am also very thankful to "Bruce" for the independence I had in conducting research and for his scarce but real encouragements. He gave me the opportunity to pursue the projects I found the most interesting. Though I had some very tough times, I guess I have learnt a lot by myself and I have grown from that.

I would like to thank all past and present members of Novak group. I enjoyed the international atmosphere of our group. I am particularly thankful to the first group members who moved from UMass and helped to set up the lab in the 1999 summer. I appreciated the guidance of Dr. Toshifumi Satoh when I started working in the lab. I also
enjoyed sharing interesting discussions with the various "company guys" who stayed in our group and with Dr Gonglu Tian, my hood's neighbor.

Finally, I would like to express my deepest gratitude to the open-minded and lively few friends I had in this country. Their presence and support were very precious and wherever I am, they will always be welcome.
# Table of Contents

List of Figures viii
List of Tables xiv
List of Schemes xvi

## Chapter I

### Introduction to Ring-Opening Metathesis Polymerization

1.1. Olefin metathesis and ROMP 1
1.2. From ill-defined to well-defined ROMP catalysts 12
1.3. A quest for new ROMP monomers
   1.3.1. Few industrial applications 25
   1.3.2. Norbornene: the traditional ROMP monomer 28
   1.3.3. The original family of cyclobutene containing monomers
      1.3.3.1. Monocyclic monomers 30
      1.3.3.2. Monomers containing a fused cyclobutene ring 33
1.4. References 36

## Chapter II

### Preparation of New ROMP Polymers from Cyclobutene Derivatives

2.1. A new family of monomers
   2.1.1. Choice of the monomer structure 43
   2.1.2. Monomer synthesis 47
   2.1.3. Observation of atropisomers 51
   2.1.4. Experimental section 57
2.2. Polymerization studies
Chapter III

Variation of the Monomer Functionality

3.1. Variation of the electronic character of the monomer substituents
3.2. Monomers functionalized with polyaryl ether dendrimers
   3.2.1. Motivations
   3.2.2. Monomer synthesis
   3.2.3. Kinetic studies of the polymerization
   3.2.4. Conclusions
3.3. Thermal properties
3.4. Experimental section
3.5. References

Chapter IV

Investigations on the Preparation of Graft Copolymers via ROMP-ATRP Catalysis

4.1. Introduction
4.2. Results
4.2.1. Monomer design 174
4.2.2. Polymerization studies 175
4.2.3. Conclusions 184
4.3. Experimental section 185
4.4. References 191

Appendices

A.1. $^1$H and $^{13}$C NMR spectra of monomers M-1 to M-22 194
A.2. $^1$H and $^{13}$C NMR spectra of the dendritic monomers DM-1 to DM-8 217
A.3. DSC thermograms of the dendritic monomers DM-1 to DM-8 226
A.4. $^1$H and $^{13}$C NMR spectra of poly-2 and hydrogenated poly-2 235
A.5. TGA thermograms of poly-2 and hydrogenated poly-2 237
A.6. DSC thermogram of hydrogenated poly-2 239
List of Figures

Figure 1.1. Metal halide-metal alkyl ROMP initiating systems 12
Figure 1.2. Initiators with no obvious metal alkyls and metal carbenes 14
Figure 1.3. Industrially useful polymers via ROMP 26
Figure 1.4. Water-soluble catalysts for ROMP in emulsion 27
Figure 1.5. Recyclable dendritic Ru-based metathesis catalyst 28
Figure 2.1. Structures of monomers used in this study and compound numbering cross reference 48
Figure 2.2. Endo-exo and endo-endo conformations 52
Figure 2.3. $^1$H NMR spectrum of M-11 54
Figure 2.4. $^1$H NMR spectrum of M-8 54
Figure 2.5. Zoom on the $^1$H NMR spectra of the two atropisomers of M-13 56
Figure 2.6. Molecular weight of poly-2 samples 82
Figure 2.7. Plot of kinetic data for the polymerization of M-2 initiated by Ru-III 83
Figure 2.8. Plot of kinetic data for the polymerization of M-4 initiated by Ru-III 83
Figure 2.9. Determination of the second order rate constant of polymerization for M-2 initiated by Ru-III 84
Figure 2.10. $^{19}$F NMR spectra of poly-8 prepared with Ru-III and Ru-VI 94
Figure 2.11. $^{19}$F NMR spectra of poly-7 prepared with Ru-III and Ru-VI

Figure 2.12. Polymerization of M-7 with Ru-III followed by $^{19}$F NMR

Figure 2.13. $^{19}$F NMR spectra of poly-12 prepared with Ru-III and Ru-VI

Figure 2.14. The $^1$H NMR spectrum of an on-going copolymerization of M-7 / COE

Figure 2.15. Dependence of the $^{19}$F NMR spectrum on the copolymer composition

Figure 2.16. Kinetic data plots of the copolymerization of a M-7 / COE mixture using Ru-III

Figure 2.17. Logarithm plot of the disappearance of M-7 versus time before and after addition of COE

Figure 2.18. $^{19}$F NMR spectra of copolymers with addition of COE at different times

Figure 2.19. $^{19}$F NMR spectra of a M-7 / COE copolymer (20% M-7) in C$_6$D$_6$ and in CDCl$_3$

Figure 3.1. Neighboring chelation effect in the ROMP of 3-substituted cyclobutenes

Figure 3.2. $^1$H NMR spectrum of a block copolymer (M-7 / M-19) prepared with Ru-III

Figure 3.3. 7-Oxanorbornene functionalized with "zero-generation" dendrons

Figure 3.4. Dendritic monomers used in this study

Figure 3.5. Dendritic compounds used for the functionalization of the monomer
Figure 3.6. Kinetic plots of the polymerization of DM-7 with Ru-III and Ru-VI

Figure 3.7. Kinetic plots of the polymerization of DM-7 and DM-8 with Ru-III

Figure 3.8. Kinetic plots of the polymerization of DM-1, DM-4 and DM-6 with Ru-VI

Figure 3.9. Kinetic plots of the polymerization of DM-3, DM-4 and DM-5 with Ru-VI

Figure 4.1. $^1$H NMR spectrum of poly-21 (20-mer) prepared with Ru-III

Figure 4.2. The $^1$H NMR spectrum (CDCl$_3$) of a copolymer (poly-22)-$^{\text{graft}}$-PMMA

Figure 4.3. $^1$H NMR spectrum of a graft copolymer in toluene-d$_8$ and in CDCl$_3$

Figure 4.4. Logarithm plot of the kinetic data of the ATRP of MMA during a copolymerization with M-22 and Ru-III

Figure 4.5. The $^1$H and $^{13}$C NMR spectra of a (poly-21)-$^{\text{graft}}$-PMMA copolymer

Figure A1.1. $^1$H (in CDCl$_3$) and $^{13}$C NMR (in DMSO-d$_6$) spectra of M-1

Figure A1.2. $^1$H and $^{13}$C NMR spectra of M-2 in CDCl$_3$

Figure A1.3. $^1$H and $^{13}$C NMR spectra of M-3 in CDCl$_3$
Figure A1.4. $^1$H and $^{13}$C NMR spectra of M-4 in CDCl$_3$ 197
Figure A1.5. $^1$H and $^{13}$C NMR spectra of M-5 in CDCl$_3$ 198
Figure A1.6. $^1$H and $^{13}$C NMR spectra of M-6 in CDCl$_3$ 199
Figure A1.7. $^1$H and $^{13}$C NMR spectra of M-7 in CDCl$_3$ 200
Figure A1.8. $^1$H and $^{13}$C NMR spectra of M-8 in CDCl$_3$ 201
Figure A1.9. $^1$H and $^{13}$C NMR spectra of M-9 in CDCl$_3$ 202
Figure A1.10. $^1$H and $^{13}$C NMR spectra of M-10 in CDCl$_3$ 203
Figure A1.11. $^1$H and $^{13}$C NMR spectra of M-11 in CDCl$_3$ 204
Figure A1.12. $^1$H and $^{13}$C NMR spectra of M-12 in CDCl$_3$ 205
Figure A1.13. $^1$H and $^{13}$C NMR spectra of M-13 (major isomer) in CDCl$_3$ 206
Figure A1.14. $^1$H NMR spectrum of M-13 (minor isomer) in CDCl$_3$ 207
Figure A1.15. $^1$H and $^{13}$C NMR spectra of M-14 in CDCl$_3$ 208
Figure A1.16. $^1$H and $^{13}$C NMR spectra of M-15 in CDCl$_3$ 209
Figure A1.17. $^1$H and $^{13}$C NMR spectra of M-16 in CDCl$_3$ 210
Figure A1.18. $^1$H (in CD$_3$OD) and $^{13}$C NMR (in DMSO-d$_6$) spectra of M-17 211
Figure A1.19. $^1$H and $^{13}$C NMR spectra of M-18 in CDCl$_3$ 212
Figure A1.20. $^1$H and $^{13}$C NMR spectra of M-19 in CDCl$_3$ 213
Figure A1.21. $^1$H and $^{13}$C NMR spectra of M-20 in CDCl$_3$ 214
Figure A1.22. $^1$H and $^{13}$C NMR spectra of M-21 in CDCl$_3$ 215
Figure A1.23. $^1$H and $^{13}$C NMR spectra of M-22 in CDCl$_3$ 216
Figure A2.1. $^1$H and $^{13}$C NMR spectra of DM-1 in CDCl$_3$ 217
Figure A2.2. $^1$H and $^{13}$C NMR spectra of DM-1B in CDCl$_3$ 218
Figure A2.3. $^1$H and $^{13}$C NMR spectra of DM-2 in CDCl$_3$ 219
Figure A2.4. $^1$H and $^{13}$C NMR spectra of DM-3 in CDCl$_3$ 220
Figure A2.5. $^1$H and $^{13}$C NMR spectra of DM-4 in CDCl$_3$ 221
Figure A2.6. $^1$H and $^{13}$C NMR spectra of DM-5 in CDCl$_3$ 222
Figure A2.7. $^1$H and $^{13}$C NMR spectra of DM-6 in CDCl$_3$ 223
Figure A2.8. $^1$H and $^{13}$C NMR spectra of DM-7 in CDCl$_3$ 224
Figure A2.9. $^1$H and $^{13}$C NMR spectra of DM-8 in CDCl$_3$ 225
Figure A3.1. DSC Thermogram of DM-1 226
Figure A3.2. DSC Thermogram of DM-1B 227
Figure A3.3. DSC Thermogram of DM-2 228
Figure A3.4. DSC Thermogram of DM-3 229
Figure A3.5. DSC Thermogram of DM-4 230
Figure A3.6. DSC Thermogram of DM-5 231
Figure A3.7. DSC Thermogram of DM-6 232
Figure A3.8. DSC Thermogram of DM-7 233
Figure A3.9. DSC Thermogram of DM-8 234
Figure A4.1. $^1$H NMR spectra of poly-2 and hydrogenated poly-2 in CDCl$_3$ 235
Figure A4.2. $^{13}$C NMR spectra of poly-2 and hydrogenated poly-2 in CDCl$_3$ 236
Figure A5.1. TGA Thermogram of poly-2 237
Figure A5.2. TGA Thermogram of hydrogenated poly-2 238
Figure A6. DSC Thermogram of hydrogenated poly-2
List of Tables

Table 2.1  Prepared maleimides-reagents used for the condensation reaction 49
Table 2.2  Succinimide functionalized monomers 50
Table 2.3  Catalyst activity comparison for the ROMP of M-4 73
Table 2.4  Molecular weight data for the polymerization of M-16 with Ru-III 76
Table 2.5  Comparison of the well-defined catalysts' activity 78
Table 2.6  Polymer molecular weight at various [M-2] / [Ru-III] ratios 82
Table 2.7  Examples of well-defined block copolymers prepared with Ru-III 85
Table 2.8  Investigated fluorinated monomers 91
Table 2.9  Analysis of copolymers produced from different M-7 / COE mixtures 103
Table 3.1  Relative polymerization rates of various succinimide functionalized monomers 119
Table 3.2  Structures of polyaryl ether dendritic building blocks 125
Table 3.3  Dendritic monomers prepared by a one-step coupling 132
Table 3.4  Yields of the esterification for the coupling of the dendritic side-chains 134
Table 3.5  DSC analysis of the dendritic monomers and precursors 135
Table 3.6  Kinetic data of the polymerization of DM-1 with Ru-III and Ru-VI 137
Table 3.7. Thermal transitions of the polymers functionalized with dendritic side-chains 141

Table 4.1. Graft copolymerization Results 177

Table 4.2. Analysis of poly(M-22-co-M-2)-graft-PMMA 183
List of Schemes

Scheme 1.1. Experiments supporting a double bond cleavage in the metathesis reaction 3

Scheme 1.2. The experiment of Chauvin supporting the metal carbene mechanism 4

Scheme 1.3. Ring-opening and cross metathesis reactions 5

Scheme 1.4. RCM, ADMET and ROMP reactions 6

Scheme 1.5. Key step in Danishefsky's synthesis of Radicicol Dimethyl Ether 6

Scheme 1.6. Acyclic diene metathesis polymerization of 1,9-decadiene 7

Scheme 1.7. ROMP of bicyclo[2.2.1]hept-5-ene 8

Scheme 1.8. Secondary metathesis reactions in ROMP 9

Scheme 1.9. Quenching of a molybdenum carbene by an aldehyde 9

Scheme 1.10. Possible stereochemistry of the polymer backbone 10

Scheme 1.11. All-HT polymer of 1-methylnorbornene 12

Scheme 1.12. The first isolated titanocyclobutane 13

Scheme 1.13 Early transition metal well-defined ROMP catalysts 16

Scheme 1.14. Synthetic route to the Schrock's molybdenum catalysts 18

Scheme 1.15. Well-defined ruthenium carbene catalysts 20

Scheme 1.16 Synthesis of the first ruthenium carbene Ru-I 20

Scheme 1.17. Synthesis of the benzylidene catalysts Ru-II and Ru-III 21
Scheme 1.18. Synthesis of homo- and hetero bimetallic ruthenium catalysts  
22

Scheme 1.19. Preparation of ruthenium catalysts bearing N-heterocyclic 
carben ligands  
23

Scheme 1.20. The last generation Grubb's catalyst  
24

Scheme 1.21. The first ROMP of 1,5-dimethyl-1,5-cyclooctadiene  
24

Scheme 1.22. Applications of the stereoselective ROMP of 
1-methylcyclobutene  
31

Scheme 1.23. Preparation of well-defined acid-functionalized 
polybutadiene  
34

Scheme 1.24. The Durham route to polyacetylene  
34

Scheme 1.25. The "photoisomer" route to polyacetylene  
35

Scheme 2.1. Preparation of soluble functionalized polyacetylenes  
44

Scheme 2.2. Synthesis of soluble, ionically functionalized polyacetylenes  
45

Scheme 2.3. Polyacetylene from saturated polymer precursors  
46

Scheme 2.4. A possible new route to polyacetylene  
46

Scheme 2.5. The synthesis of anhydride functionalized monomer, M-1, and its 
modification  
47

Scheme 2.6. Synthesis of maleimides  
49

Scheme 2.7. Alternating ROMP copolymers from non-polar and polar olefins  
102

Scheme 3.1. Synthesis of O-benzyl and N-benzyl functionalized monomers  
120

Scheme 3.2. Synthetic route to polyaryl ether dendrons  
130

Scheme 3.3. Procedure used for the functionalization of the 7-oxanorbornene
moiety

Scheme 3.4. Functionalization of the *endo*-tricyclo[4.2.2.0\(^2,5\)]deca-3,9-diene structure with two polyaryl ether dendrons

Scheme 3.5. Preparation of a dendritic monomer carrying two different dendrons

Scheme 3.6. Synthetic route to monomers carrying one dendritic side-chain

Scheme 4.1. General ATRP mechanism

Scheme 4.2. Proposed mechanism for the polymerization of MMA with the ternary system CCl\(_4\), RuCl\(_2\)(PPh\(_3\))\(_3\), MeAl(ODBp)\(_2\)

Scheme 4.3. Tandem ROMP and ATRP with a single modified Ru-carbene catalyst

Scheme 4.4. Synthesis of monomers functionalized with an ATRP initiator
CHAPTER I.
INTRODUCTION TO RING-OPENING METATHESIS POLYMERIZATION

1.1. Olefin metathesis and ROMP

The word metathesis comes from the Greek meta (change) and tithemi (place).\(^1\) In olefin chemistry, it refers to the pair-wise exchange of substituents on a carbon-carbon double bond (Equation 1.1).

\[
\text{A} - \text{B} + \text{E} - \text{F} \rightleftharpoons \text{A} - \text{E} + \text{C} - \text{G} \tag{1.1}
\]

It was not until 1967 that the phrase olefin metathesis was used.\(^2\) Prior to this time, this transformation was actually present in two chemical processes that were believed to be mechanistically different. The first one was referred as a disproportionation (or dismutation) reaction and leads to the formation of substituted olefins and ethylene from propylene using supported oxide catalyst at elevated temperatures (Equation 1.2).\(^3\)

\[
\text{MoO}_3 - \text{Al}_2\text{O}_3 \quad \xrightarrow{160 \degree C} \quad \text{ } + \quad \text{ } \tag{1.2}
\]

The second one was identified as a ring-opening polymerization process when an unusual unsaturated polymer was obtained upon polymerization of the cyclic norbornene olefin with a traditional Ziegler-Natta 1,2-olefin catalyst at room temperature (Equation
The similarity of the overall reaction was not obvious as different catalysts and reactions conditions were involved.

\[
\begin{align*}
\text{TiCl}_4 - \text{LiAlR}_4 & \quad \xrightarrow[n]{n} \\
\text{Cycloalkene} & \quad \xrightarrow[n]{n} \\
\text{Copolymer}
\end{align*}
\] (1.3)

The connection between those two overall similar reactions was made by Calderon in 1967 with the discovery that the system \( \text{WCl}_6/\text{EtAlCl}_2/\text{EtOH} \) \((1/4/1)\) was effective for the ring-opening metathesis polymerization of cyclooctene and cycloocta-1,5-diene\(^{2c}\), and would also promote the cross-metathesis (disproportionation) of pent-2-ene at room temperature.\(^{2a,c,d}\) The finding that a unique catalytic system could provide those two dissimilar reactions suggested that there was one olefin metathesis process.

Evidence that the double bonds were completely broken in the cross-metathesis reaction was provided by two independent studies. Calderon observed that the exchange between but-2-ene\(\text{-}d_8\) and but-2-ene only led to but-2-ene\(\text{-}d_4\)\(^{2b,d}\) whereas Mol reported that in the cross-metathesis of radioactive [2-\(^{14}\text{C}\)]propene, the formed but-2-ene had twice the radioactivity of the starting propene whereas no radioactivity was present in the ethene product\(^3\) (Scheme 1.1). In the ring-opening metathesis polymerization of cycloalkenes, evidence was found by analysing the degradation products of [1-\(^{14}\text{C}\)]cyclopentene/cyclooctene copolymers prepared with the system.
WOCl₄/Et₂AlCl₃/(PhCOO)₂. Upon ozonolysis and transformation to the α,ω-diol acetates, radioactivity was only detected in AcO(CH₂)₅OAc.  

Scheme 1.1. Experiments supporting a double bond cleavage in the metathesis reaction.

\[
\begin{align*}
CD₃CD=CDCD₃ + CH₃CH=CHCH₃ &\rightleftharpoons CD₃CD=CHCH₃ \\
CH₃¹⁴CH=CH₂ + CH₃¹⁴CH=CH₂ &\rightleftharpoons CH₃¹⁴CH + CH₂ + CH₂
\end{align*}
\]

Initially, the mechanism of the reaction was not well understood. How could the catalyst facilitate the exchange of alkylidene moieties? At first, a "pair-wise" mechanism was proposed: the double bonds would come together in the vicinity of the metal complex and orbital overlap would occur between the metal and the two olefins in a way that would allow the exchange. But, this mechanism was eventually ruled out and replaced by a "metal carbene chain mechanism" (or "metal carbene mechanism") in which the propagating species is a metal carbene complex formed in some way, and the reaction occurs via the formation of a metallocyclobutane intermediate (Equation 1.4).

\[
\begin{align*}
\begin{array}{c}
R_1 \\
[M]
\end{array} &+ &\begin{array}{c}
R_3 \\
[M]
\end{array} &\rightleftharpoons &\begin{array}{c}
R_1 \\
[M]
\end{array} \begin{array}{c}
R_3 \\
[M]
\end{array} &\rightleftharpoons &\begin{array}{c}
R_1 \\
[M]
\end{array} \begin{array}{c}
R_3 \\
[M]
\end{array} &\rightleftharpoons &\begin{array}{c}
R_1 \\
[M]
\end{array} \begin{array}{c}
R_3 \\
[M]
\end{array} &\rightleftharpoons &\begin{array}{c}
R_1 \\
[M]
\end{array} \begin{array}{c}
R_3 \\
[M]
\end{array} &\rightleftharpoons &\begin{array}{c}
R_1 \\
[M]
\end{array} \begin{array}{c}
R_3 \\
[M]
\end{array}
\end{align*}
\]

The metal carbene mechanism was first supported by Hérisson and Chauvin in 1971. While studying the cross-metathesis of cyclopentene with unsymmetrical olefins
using WOCl₄/Bu₄Sn or WOCl₄/Et₂AlCl, they observed that the reaction with pent-2-ene was leading to three series of compounds: EMₙE, EMₙP and PMₙP (n = 1-4) where E = ethyldene, P = propyldene and Mₙ represents ring-opened units of cyclopentene (Scheme 1.2). A 1:2:1 statistical ratio was found. Similar results were obtained with other cyclic olefins (cyclooctene, cycloocta-1,5-diene, cyclododeca-1,5,9-triene) in place of cyclopentene. Those data supported the metal carbene mechanism as pair-wise exchange would only have lead to the unsymmetrical series.

**Scheme 1.2.** The experiment of Chauvin supporting the metal carbene mechanism.

\[
\begin{align*}
[M_i]=E & + nM \quad \rightarrow \quad [M_i]=M_nE \\
[M_i]=M_nE & + EP \quad \leftrightarrow \quad [M_i]=E + EM_nP \\
[M_i]=P & + nM \quad \rightarrow \quad [M_i]=M_nP \\
[M_i]=M_nP & + EP \quad \leftrightarrow \quad [M_i]=P + EM_nP
\end{align*}
\]

catalytic system: WOCl₄/ Bu₄Sn or WOCl₄/ Et₂AlCl

Further studies by Katz⁶ with various long chain olefins and Grubbs⁷ with deuterated dienes supported the currently accepted carbene mechanism. Nevertheless, no metal carbene was observed in the catalytic systems used in the early age of the metathesis reaction. In the eighties, progress made in both the preparation of well-defined metallocyclobutanes and the synthesis of well-defined metal carbene complexes led to a better understanding of the metathesis mechanism.¹ The availability of well-defined
catalysts provided the possibility of catalyst activity tuning. Through the use of these complexes, the metathesis reaction proved to be a powerful and practical tool to generate carbon-carbon bonds and its use has expanded in several areas of organic and polymer chemistry.

In a metathesis reaction, either two different olefinic substrates or only one substrate can be involved. In the first case, those reactions are known as either ring-opening metathesis (ROM) or cross-metathesis (CM) reactions (Scheme 1.3).

**Scheme 1.3.** Ring-opening and cross metathesis reactions.

Efforts towards the preparation of very active well-defined catalysts have recently allowed the cross-metathesis of $\alpha, \beta$-unsaturated carbonyl olefins$^8$, vinylphosphonates$^9$ and vinyl sulfones$^{10}$. The tandem ring opening-cross metathesis reaction has also been reported for the preparation of trisubstituted olefins$^{11}$ and a combination of ring-opening, cross and ring-closing metathesis was used for the preparation of macrocyclic rings from bis-vinyl ketones and cyclic olefins.$^{12}$ Other metathesis reactions involve a unique olefinic substrate and are known as ring-closing metathesis (RCM), acyclic diene metathesis polymerization (ADMET) and ring-opening metathesis polymerization (ROMP) (Scheme 1.4).
Scheme 1.4. RCM, ADMET and ROMP reactions.

RCM has recently found some very promising applications in the challenging problem of macrocyclisation in natural product synthesis as the last generation catalyst displays higher activity and stereoselectivity while low catalyst loading is necessary.\textsuperscript{71}

Scheme 1.5. Key step in Danishefsky's synthesis of Radicicol Dimethyl Ether.\textsuperscript{13}

ADMET and ROMP are two polymerization processes that differ in their polymerization mechanism. First proposed long ago, ADMET has recently been reconsidered by Wagener\textsuperscript{14} due to the availability of active metal carbene catalysts leading to controlled polymerizations. ADMET is a step-growth polymerization similar to a polycondensation reaction that is driven by the removal of ethylene (Scheme 1.6).
Scheme 1.6. Acyclic diene metathesis polymerization of 1,9-decadiene.

ADMET has been shown to be an efficient technique for the preparation of unsaturated polyethers,\textsuperscript{15} unsaturated polyesters,\textsuperscript{16} as well as a variety of functionalized polyethylenes,\textsuperscript{17} and polyalkenylenes containing heteroatoms (N\textsuperscript{18a}, Si\textsuperscript{18b}) in the polymer main chain.

Like ADMET, the ROMP technique is a powerful tool for transferring the unsaturation present in the monomer into the polymer backbone, but polymerization occurs through a chain-growth mechanism. It was shown that the first step involves a sigmatropic coordination of a "carbene organometallic complex" to a cyclic olefin. The highly strained metallocyclobutane can open to give either the starting materials or to relieve the ring strain and position the active metal center at the end of the chain (Scheme 1.7).\textsuperscript{1} The propagation involves the repeated coordination of monomer units to the active center followed by their insertion into the main chain.
The coordination of the olefin to the active center involves a reciprocal affinity between the metal center and the olefinic substrate whereas the main driving force for the propagation step is the energy released upon opening of the strained olefin (highly negative free energy). Therefore, ROMP is most effective for the polymerization of monomers containing C₄, C₇, C₈ and higher rings. The polymerization of cyclopentene (strain energy of about 17 kJ.mol⁻¹) is usually slow and competition between the formation of cyclic oligomers and linear polymer occurs. The thermodynamically disfavored ROMP of cyclohexene has not been achieved in a practical way: only small oligomers have been produced. Another way to push the polymerization requires the preparation of monomers containing fused rings or rings incorporated in polycyclic structures that lead to increased ring strain.

Like most polymerization process, side-reactions or undesirable reactions can happen. The most common one is a secondary metathesis reaction that can occur during the propagation step. For example, intramolecular metathesis reactions (back-biting) will lead to the formation of small cyclic molecules or cyclic oligomers and decrease of the molecular weight whereas intermolecular metathesis reactions (chain transfer) will broaden the molecular weight (Scheme 1.8). These reactions can mostly be avoided by
increasing the steric hindrance between the catalyst and enchained olefins either through catalyst design (ligands) or monomer design (polycyclic structure, substituents), the latter leading to less flexible, stiffer chains.

**Scheme 1.8.** Secondary metathesis reactions in ROMP.

Termination reactions can occur between the active metal center and polar functional groups such as aldehyde or ketones. Trace oxygen is also a very effective terminating agent. These termination steps are particularly important when dealing with the more oxophilic early transition metal catalysts (Ti, Mo, W) and lead to the formation of metal oxo complexes. Interestingly, this sensitivity can be used to terminate the polymerization: polymerizations performed with well-defined molybdenum carbene catalysts are quenched by addition of an aldehyde compound to form end-functionalized polymers (Scheme 1.9).

**Scheme 1.9.** Quenching of a molybdenum carbene by an aldehyde.
ROMP polymers can display a very rich microstructure. Depending on the monomer, three main characteristics can be observed: cis/trans isomerism, tacticity, and head-to-tail bias. Cis/trans isomerism is present in all ROMP polymers and relatively easy to quantify using spectroscopic techniques. Analysis of tacticity has only been successful with polymers made from prochiral monomers (Scheme 1.10). Head-to-tail bias can be observed with non-symmetrical monomers.

**Scheme 1.10.** Possible stereochemistry of the polynorbornene backbone.

The cis/trans isomerism is hard to predict as it results from the specific interaction between the metal complex and the monomer, and therefore can depend on the geometry of the metal center, the bulkiness of the metal substituents, and also the properties of the cyclic monomer (sterics and electronics). The reactions conditions (temperature, solvent) are also important as they can affect the organization of the ligands around the metal center. All these factors will influence the relative ease of formation of the intermediate cis and trans metallacyclobutanes. The use of well-defined metal carbene catalysts provided a better understanding of the factors influencing the cis/trans isomerism and
stereoselective polymerizations have been achieved in some particular cases.\textsuperscript{1} The cis/trans content of a ROMP polymer is usually evaluated using NMR techniques. Atoms located next to the main chain unsaturation (α position) are sensitive to the double bond stereochemistry and distinguishable, whereas peak overlap usually occurs in the olefinic region. Also, quantitative $^{13}$C NMR is commonly used: α-trans carbons appear 5 ppm downfield from α-cis carbons in simple olefins.

The understanding and control of tacticity is a complex issue and no general prediction can be made. Tacticity is associated with the polymerization of prochiral monomers, i.e., when stereogenic centers are generated in the polymer backbone. The stereochemistry of those chiral centers is related to the specific way that the coordination of the monomer to the metal center occurs. The amount of tacticity control observed depends mostly on the degree of specificity present in the coordination step leading to the formation of the metallocyclobutane intermediate. Indeed, it really reflects an individualized catalyst to monomer interaction as a given catalyst rarely leads to a given type of tacticity, and factors that affect the cis/trans content will also be crucial. It has also been shown that the stereochemistry of the growing polymer chain itself could affect the tacticity bias.\textsuperscript{1}

Head-to-tail isomerism is observed in the polymers of unsymmetrical substituted cycloalkenes. The extent of HT bias is very dependent on the location and nature of the substituents, and on the catalyst. The preparation of fully-HT biased polymers has been reported (Scheme 1.11).
Head-to-tail isomerism is observed in the polymers of unsymmetrical substituted cycloalkenes. The extent of HT bias is very dependent on the location and nature of the substituents, and on the catalyst. The preparation of fully-HT biased polymers has been reported (Scheme 1.11).

1.2. From ill-defined to well-defined ROMP catalysts

Ring-opening metathesis polymerization has been shown to occur via the formation of a metallocyclobutane intermediate but in most active catalytic systems, no such intermediate has been isolated or identified. According to the current understanding of ROMP, the active systems can be divided into three main groups.

The first active catalysts (Group 1) initially identified in the early 60s were composed of several components: a metal halide, a cocatalyst and sometimes a third component such as an alcohol (Figure 1.1).

\[
\text{TiCl}_4 - \text{LiAl(C}_7\text{H}_{15})_4 \quad \text{MoCl}_5 - \text{EtAlCl}_2 \\
\text{TiCl}_4 - \text{Et}_3\text{Al} \quad \text{WCl}_6 - \text{Et}_2\text{AlCl} - \text{EtOH} \\
\text{NbCl}_5 - \text{Et}_2\text{AlCl} \quad \text{WCl}_6 - \text{Sn(CH}_3)_4 \\
\text{TaCl}_5 - \text{EtAlCl}_2
\]

**Figure 1.1.** Metal halide-metal alkyl ROMP initiating systems (Group 1).
The cocatalyst was usually a metal alkyl and was assumed to participate in the generation of a metal carbene ligand. Mounting evidence such as the evolution of methane from Sn(CH₃)₄ cocatalyzed systems, suggested the formation of a metal carbene intermediate in these systems.¹ The main advantages of those systems are the readily availability of the chemicals, the low processing cost and their relatively good stability. Hence, they are still used in industry, especially the WCl₆/Sn(CH₃)₄ system. Nevertheless, the reactive species is not well-defined and polydisperse polymer samples are usually obtained. Also, the reactions must be performed with extreme care as catalyst activity depends on many factors: proportions, order of addition of the reactants (the olefin is not always added last), temperature and incubation time (before the addition of the olefin). All these factors have an influence on the nature and concentration of the active species. The first isolated metallocyclobutane in those multi-component-systems came from the treatment of a metallocene catalyst, Cp₂TiCl₂, with 2 equivalents of AlMe₃.²⁰ The cyclic intermediate could subsequently react with norbornene and the titanocyclobutane be isolated (Scheme 1.12). This is the first example of living ring-opening metathesis polymerization of norbornene (Gilliom, 1986).²¹

**Scheme 1.12.** The first isolated titanocyclobutane.

\[
\text{Cp}_2\text{TiCl}_2 + 2 \text{Me}_3\text{Al} \rightarrow \text{CH}_4 + \text{Me}_2\text{AlCl} + \text{Cp}_2\text{Ti} \begin{array}{c} \text{CH}_2 \\ \text{Cl} \end{array} \quad \text{AlMe}_2
\]

amine base

\[
\text{Cp}_2\text{Ti}
\]
The activity of the second group (Group 2) of catalysts only relies on the interaction between the metal complex and the olefin while no well-defined metal carbene is present (Figure 1.2).

- MoO₃ - Al₂O₃
- IrCl₃ - 3H₂O
- RuCl₃ - 3H₂O
- Ru(H₂O)₆(OTs)₂
- OsCl₃ - 3H₂O

**Figure 1.2.** Initiators with no obvious metal alkyls and metal carbenes (Group 2).

Driven by the industrial research, intensive studies have been done on systems based on supported molybdenum oxides.¹ Diverse kinds (Al₂O₃, SiO₂, TiO₂) and combinations of supports can be used. Those heterogeneous systems require a pretreatment procedure (~ activation) that usually consists of heating cycles with additive in the gas phase. The pretreatment has a great influence on the metathesis activity. Those systems are recyclable, easy to handle on large scale and metathesis can be performed in the gas phase. Therefore, they are very attractive for industry. Nevertheless, a precise control of the reaction conditions is required and their use is limited to the cross-metathesis of unsymmetrical alkenes with ethylene gas (neohexene process) or the preparation of internal alkenes in the Shell Higher Olefin Process (SHOP process) for example.¹

Other members of the second group are particularly interesting as they are active in aqueous emulsion, and solvent-free polymerizations can be performed. The active species is unknown, and an induction period that can be very long (24 h) is usually present. Late transition metals have been shown to be more tolerant of polar substrates
than their early transition metal counterparts.\textsuperscript{1} The activity of RuCl$_3$-3H$_2$O vis-à-vis a variety of functionalized 7-oxanorbornenes has been investigated by Novak and Grubbs.\textsuperscript{22} Early experiments indicated that in organic solvents, water could act as a catalyst with the presence of air, reducing the induction period from 24 h to 30-35 min.\textsuperscript{23} Interestingly, the aqueous ruthenium solution could be recycled (up to 14 times) with no loss but improvement of the activity (\textasciitilde catalyst aging). A more defined ruthenium catalyst, Ru(H$_2$O)$_6$(OTs)$_2$ (OTs = \textit{p}-toluene sulphonate) displayed a higher activity with functionalized 7-oxanorbornenes (induction time < 1 min) and upon polymerization a mono-olefin adduct was also isolated (Equation 1.5).\textsuperscript{23} With this catalyst, aqueous ROMP was possible.\textsuperscript{24}

\begin{equation}
\text{Ru(H}_2\text{O)}_6(\text{OTs})_2 \quad \text{O} \quad \text{n O} \quad (n-1) \quad \text{OMe} \quad \text{OMe} \\
(\text{OMeMeO})_5\text{Ru}^{2+} \quad \text{OMe} \quad \text{OMe}
\end{equation}

(1.5)

While no control over the polymerization was possible with the ill-defined systems, some of them lead to highly stereoselective polymerizations. This specific behavior was used to precisely characterize the polymer microstructure with respect to the cis/trans content, tacticity and head-to-tail bias with norbornene derivatives using NMR techniques.\textsuperscript{1}

To better understand the ROMP mechanism, the catalyst's activity, and to develop living systems, tremendous efforts were made toward the preparation of well-defined
metallocyclobutane and metal carbene catalysts firstly based on early transition metals (Scheme 1.13).

**Scheme 1.13.** Early transition metal well-defined ROMP catalysts.

![Scheme 1.13](image)

In 1976, the high activity of (CO)_5W=C(Ph)_2 (the Casey carbene) activated by heat was reported by Katz. Interestingly, the quantitative ROMP of a wide variety of non-functionalized cyclic olefins was possible: norbornene, strained trisubstituted olefins (2-methynorbornene, 2-methycyclobutene) and cis-cyclic olefins (cyclopentene, cycloheptene). While high molecular weight polymers were usually obtained, the polymerization was highly stereoselective (cis content > 90%). The chromium analog, (CO)_5Cr=C(Ph)_2, displayed a very specific behavior and is still the only catalyst active for the ROMP of 2,3-dihydrofuran. In 1984, it was shown that a titanacycle could insert a norbornene molecule at 20°C and by increasing the temperature at 65°C, the controlled
polymerization of norbornene was observed. Nevertheless, the high oxophilic character of titanium limits its use to non-functionalized olefins.

Metal tungsten had been known as interested substrates for the metathesis reaction but research progress really intensified in the early 1980's. In 1982, Osborn reported and observed via NMR techniques the metathesis activity of the tungsten (VI) carbene W(CH\text{tBu})(OCH_2\text{tBu})_2(X)_2 (X = Cl, Br) activated by aluminium halides. Upon use of GaBr_3, the mechanism could be specified: the carbene complex can form an adduct with the Lewis acid that abstracts one halogen, and the generated cationic tungsten carbene is responsible for the metathesis activity. In 1985, Basset and co-workers reported the synthesis of the first single component highly active tungsten carbene. With the chloro-aryloxide carbene W(OAr)_2Cl(CHCMe_3)(OR_2) (Ar = 2,6-(Ph)_2-C_6H_3, R = Et, iPr), norbornene and functionalized norbornenes (ester and nitrile groups) could be quantitatively polymerized in 10 s at room temperature. The bulky aryloxide ligands were considered as protecting groups with respect to carbene dimerization and coordination of functional groups (poisoning). In 1986, Schrock and co-workers reported the synthesis of the first imido-alkoxy catalyst of the type W(CHR')(N-2,6-C_6H_3-i-Pr_2)(OR_2) (R' = tBu, R = OCMe(CF_3)_2) that displayed a higher activity than the titanacyclobutane / titanium carbene complex in cross-metathesis, but chain transfer between polymer chains was observed in the ROMP of norbornene upon warming of the reaction mixture (from -80°C to room temperature). Changing the alkoxide ligands to OC(Me)_2CF_3, i.e., making the metal less electrophilic, lead to the preparation of monodisperse polynorbornene samples with no secondary metathesis reactions occurring at room temperature. In this catalyst,
the bulky imido ligand (dianion) acts as a protecting group and the neutral metal keeps its high oxidation state (+VI) while being part of a four-coordinate complex. Variation of the alkoxide ligands was used to tune the activity and reactivity of the catalyst. Substitution with electron withdrawing alkoxides (RO\(^-\) = (CF\(_3\))\(_2\)(CH\(_3\))CO\(^-\)\) increased the catalyst's activity such that strained olefins such as norbornene were polymerized uncontrollably and a high activity for the metathesis of acyclic olefins was observed. On the other hand, the living polymerization of norbornene and poor metathesis activity with acyclic olefins were achieved with the non-fluorinated analog (RO\(^-\) = (CH\(_3\))\(_3\)CO\(^-\)). To circumvent the high sensitivity of tungsten towards functional group, the molybdenum analogs were prepared via a slightly different 4-step sequence (Scheme 1.14).31

**Scheme 1.14** Synthetic route to the Schrock's molybdenum catalysts.
The development of this new family of molybdenum catalysts usually referred as "Schrock's type catalyst" had a major impact on the field of ROMP.\textsuperscript{32} Mo-I could be used for the living polymerizations of 2,3-disubstituted 7-oxanorbornenes and 7-oxanorbornadienes\textsuperscript{33} whereas functionalized norbornenes\textsuperscript{34} and 2,3-difunctionalized norbornadienes\textsuperscript{35} could be polymerized in a living fashion with Mo-II. Indeed, fine-tuning of the ROMP activity was possible by varying the alkoxide substituents. Both electron donating and electron withdrawing alkoxides could be used for ROMP but better control was obtained with Mo-II. Also, a high degree of stereoselectivity was observed in those polymerizations: initiator Mo-II showed a strong tendency toward forming trans chains whereas Mo-I lead to high cis chains. While the development of those well-defined catalysts lead to key observations to better understand the driving forces of the catalysts' activity and stereoselectivity, the major drawback also present with Ti, Ta and W initiators remained their complete intolerance of protic functionalities, including minor traces of moisture. Hydroxyl-, acid- or unsubstituted amine-functionalized monomers have never been shown to polymerize with the molybdenum Schrock's catalysts. Also, the monomers that did polymerize required tedious air-free purification and extreme care had to be taken in the catalyst's synthesis, all those conditions making the reaction tedious as compared to benchtop-stable chemistry. In 1988, Novak and Grubbs had shown the way to a highly tolerant system with the RuCl\textsubscript{3}-3H\textsubscript{2}O catalyst: the aerobic polymerization of functionalized 7-oxanorbornenes could be performed in alcoholic solutions and aqueous emulsions in high yield.\textsuperscript{22-24} Research for tolerant catalyst really intensified in
the early 1990's and turned toward the less oxophilic ruthenium late transition metal (Scheme 1.15).

**Scheme 1.15.** Well-defined ruthenium carbene catalysts.

![Scheme 1.15](image)

In 1992, Grubbs and co-workers reported the synthesis of the first well-defined ruthenium carbene (Scheme 1.16).36

**Scheme 1.16.** Synthesis of the first ruthenium carbene Ru-I.

![Scheme 1.16](image)
The controlled polymerization of norbornene was observed, and the presence of protic solvents (ethanol, water) had no effect on the polymerization activity of the vinylalkyldiene catalyst that was limited to highly strained cyclic olefins. The substitution of PPh$_3$ by the more $\sigma$-donating phosphines PCy$_3$ (Cy = cyclohexyl) or P(iPr)$_3$ lead to an increased activity so that the ROMP of norbornene was no longer controlled but the ROMP of low-strained cyclic olefins and metathesis of functionalized acyclic olefins were possible.\textsuperscript{37} Those results suggested that the catalyst's activity was driven by the electronic density on the metal. But in contrast to the Schrock's catalysts, a more electron rich metal center was displaying a higher metathesis activity. Also, the multi-step synthesis of the diphenyl cyclopropene reactant and the slow rate of initiation (relative to propagation) of those catalysts limited their use. In 1995, a series of novel benzylidene ruthenium complexes $[\text{RuCl}_2(=\text{CHR'})(\text{PR}_3)_2]$ ($R' = \text{alkyl, aryl}; R = \text{Ph, Cy}$) was reported (Scheme 1.17).\textsuperscript{38}

**Scheme 1.17.** Synthesis of the benzylidene catalysts **Ru-II** and **Ru-III**.

In comparison with **Ru-I**, they were 20-10$^3$ times more active. Upon substitution of PPh$_3$ by PCy$_3$, the stability of the catalyst in solution and toward temperature was
improved. Monodisperse (PDI = 1.04) polynorbornene samples with a highly trans content (≈ 90%) could be prepared with Ru-II (R' = R = Ph). The electronic character of X in RuCl2(=CH-p-C₆H₄X)(PPh₃)₂ was shown to not have a major effect on the catalyst activity, whereas incorporation of PCy₃ (Ru-III, R' = Ph, R = Cy) lead to increased activity and the presence of back-biting was observed (polynorbornene with PDI = 2.0-2.5).³⁹ This high activity was particularly interesting for the metathesis of acyclic olefins. In comparison with the molybdenum carbenes, those catalysts were much more tolerant towards oxygen and moisture. But their activity in ROMP and cross-metathesis reactions were much lower. In the hope of increased activity, homo- and heterobimetallic ruthenium carbenes were prepared from Ru-III and the bridged chloride dimers [(p-cymene)RuCl₂], [(p-cymene)OsCl₂]₂ and [(tBu₂C₂)RhCl₂]₂ (Scheme 1.18).⁴⁰

**Scheme 1.18.** Synthesis of homo- and heterobimetallic ruthenium catalysts.

![Scheme 1.18](image)

Those catalysts displayed a higher activity than their parents (20-100 times) for the metathesis of low ring-strained cyclic or acyclic olefins. Also, it was shown that olefin methathesis with Ru-IV proceeded through an associative mechanism contrary to the dissociative mechanism proposed for the Ru-III parent.⁴¹-⁴³
The most recent modifications of the Grubbs' catalyst Ru-III have led to a significant increase in the metathesis activity. First, in 1998, both phosphine ligands were substituted by two imidazolin-2-ylidene ligands (Scheme 1.19).

Scheme 1.19. Preparation of ruthenium catalysts bearing N-heterocyclic carbene ligands.

The new catalyst bearing two N-heterocyclic carbene ligands (NHC) could quantitatively and rapidly polymerize norbornene (100 eq., 1 min) and cyclooctene (500 eq., 1h) in a non-controlled fashion while the RCM of 1,7-octadiene was quantitative within 10 min. One year later, mixed NHC/phosphine complexes were reported with the advantage of being air-stable compound. The NHC ligand is a better σ-donor and much less labile than PCy₃. The increased steric hindrance with the introduction of mesitylene substituents (Ru-V) proved to be crucial to avoid carbene dimerization and conduct polymerizations at high temperature. One more step towards higher metathesis activity was made in 2000 by the introduction of the saturated NHC version of Ru-V (Scheme 1.20).
Scheme 1.20. The last generation Grubbs' catalyst.

\[
\begin{align*}
\text{Cl} & \quad \text{PCy}_3 \quad \text{Ru} \quad \text{Mes} \quad \text{Cl} \\
\text{Cl} & \quad \text{PCy}_3 \quad \text{Ph} \quad \text{PCy}_3 \\
\text{Mes} & \quad \text{NN} \quad \text{Mes} \quad \text{Bu} \\
\text{Ru-VI} & \\
\text{Mes} & \quad \text{C}_6\text{H}_{12}-2,4,6-(\text{CH}_3)_3
\end{align*}
\]

The superiority of Ru-VI includes high rates of ROMP for low-strain substrates and even the ROMP of sterically hindered substrates containing tri-substituted olefins. The ROMP of 1,5-dimethyl-1,5-cyclooctadiene afforded polyisoprene and upon hydrogenation an ethylene-propylene copolymer was obtained (Scheme 1.21).

Scheme 1.21. The first ROMP of 1,5-dimethyl-1,5-cyclooctadiene.

Whereas those catalysts are stable in air and tolerant towards most functional groups, activities for ROMP also become competitive with the Schrock's catalysts but the polymerizations are not controlled. The last generation Grubb's catalyst is particularly useful for the metathesis (CM, RCM) of acyclic olefins but displays uncontrolled high activities (\(k_p >> k_i\)) with strained cyclic olefins for which molecular weight regulation requires the use of a chain transfer agent.46
The challenge in catalyst design for ROMP ideally remains the finding of a highly active tunable catalyst for the living polymerization of any cyclic olefins in aerobic conditions and in the presence of protic and heteroatom functionalities (particularly nitrile, 1° and 2° amines with ruthenium-based catalysts). Achieving high stereoselectivity with Grubbs' type catalysts is also a matter of concern. Nevertheless, the shift towards the ruthenium late transition metal has revolutionized the area of olefin metathesis as highly tolerant well-defined catalysts active for a specific metathesis reaction are now available.  

1.3. A quest for new ROMP monomers

1.3.1. Few industrial applications

Despite the tremendous litterature related to ROMP in the last 30 years, very few ROMP polymers are produced in industry (Figure 1.3).

Poly(dicyclopentadiene) (PDCP) has been profitably produced for several years by a reaction injection molding process (RIM), a fast and bulk polymerization technique. High trans (90%) polynorbornene produced with a RuCl3/HCl catalyst in butanol is commercialized as a moulding powder under the trade name Norsorex® and is an attractive material due to its high oil and plasticizers trapping properties. Trans-polyoctenamer, known a Vestenamer®, is used as a blending material for the improvement of properties of elastomers.
Figure 1.3. Industrially useful polymers via ROMP.$^{1,23}$

The interest in fully hydrocarbon ROMP polymers lies in their usually high glass transition temperatures (up to 150°C), their hydrophobic character and good thermal stability (>400°C). Nevertheless, a major concern with ROMP polymers is the unsaturation present in the polymer backbone responsible for their fast degradation. In the absence of antioxidant, the stability of the polymers is usually limited.

The currently used catalytic systems are bi-component systems (Group 1) or metal oxide supported catalysts from Group 2. Due to their low cost, possible recycling, well-documented preparation and characterization, those systems are attractive for industry. Nevertheless, the major drawbacks concern their high sensitivity toward functional groups as they are based on early transition metals. Also, while stereospecific polymerizations have been reported,$^1$ those usually rely on a specific catalyst / monomer combination and particular reaction conditions. The main polymer stereochemistry is of
primary importance for the polymer properties and resulting process and applications. The absence of specific control can limit the versatility of any developed catalytic platform.

The development of well-defined ROMP catalysts had a major impact on polymerization control and functional group tolerance, especially with ruthenium-based catalysts. While their cost is a possible limitation on large-scale synthesis, they also require the use of organic solvents and the polymerization control is usually lost in bulk condition. The recent development of ROMP with well-defined catalysts in emulsion is worth noticing. The emulsion polymerization of norbornene was performed with a water-soluble version of Ru-III whereas 1,5-cyclooctadiene and cyclooctene could be polymerized with Ru-III using a mini-emulsion technique (Figure 1.4).50

![Figure 1.4. Water soluble catalysts for ROMP in emulsion.](image)

As compared to industrially used catalysts, the removal and recycling of well-defined catalysts are two other issues of concern. On small scale polymerization, traces of catalyst are typically removed by passing a polymer solution on a silica gel column and by multiple precipitations. Such work-up is not viable in industry whereas removal of
catalyst is crucial for the properties and stability of the resulting polymer. Recently, Hoveyda and co-workers have addressed the problem of catalyst recycling. Substitution of one phosphine ligand in Ru-III and Ru-V by a styrenyl ether ligand leads to air-stable catalysts that can be purified by silica gel column chromatography. The catalysts are particularly useful for RCM reactions and can be subsequently recovered after the reaction but the separation can sometimes be difficult. Upon functionalization of a tetraalkylsilyl dendron with those catalysts (Figure 1.5), a highly active (CM, RCM) and recyclable system was obtained.

![Figure 1.5. Recyclable dendritic Ru-based metathesis catalyst.](image)

**1.3.2. Norbornene: the traditional ROMP-monomer**

Another explanation for the minor industrial development of ROMP polymers deals with the limited number of monomer cyclic structures available. Indeed, many of the important polymer properties (e.g., chain entanglement lengths, glass transition temperatures, etc.) are determined by the backbone structure that is set by the monomer and a small monomer pool limits the number of possible applications.
Most common ROMP polymers are derived from norbornene-type monomers. The norbornene structure has recently been used extensively to introduce a variety of functional groups into polymers. Two main reasons can explain this trend.

First of all, the development of well-defined catalysts has lead to the controlled polymerization of the readily available norbornene moiety and stereoregular polymer backbones can be prepared. Therefore, a wide range of molecular weight polymers is rapidly available and the properties associated with the introduced functionality (liquid crystal, ferro-electric, etc.) can be broadly studied. Those catalysts also display a fairly good tolerance toward functional groups. For example, DNA-block copolymer conjugates were recently prepared by ROMP.

Secondly, interesting properties are associated with the polynorbornene backbone itself: high glass transition temperature and good thermal stability for example. One disadvantage could be its tendency to easily oxidize in air, but the unsaturation can be removed by hydrogenation.

Also, as compared to other commercial polymerization techniques such as free radical polymerizations, the current ROMP-norbornene system is very attractive. One major problem of radical polymerization is molecular weight control because of chain transfer and termination processes. Controlled/"living" free radical polymerization can now be obtained by nitroxy radical-mediated polymerization and atom transfer radical polymerization (ATRP). But, those living polymerizations usually require long reaction time for completion. Molecular weight control can also be achieved with living ionic
polymerizations but the stringent conditions limit their utility to non-functionalized monomers.

1.3.3. The original family of cyclobutene containing monomers

1.3.3.1 Monocyclic monomers

The ROMP of cyclobutene leads to a perfect Poly(1,4-butadiene), a perfection never obtained by anionic polymerization, and upon hydrogenation perfectly linear polyethylene is obtained. Its high ring strain and low boiling point (2°C) makes cyclobutene an attractive substrate even if it is not readily available. First polymerization trials were reported by Dall'Asta in 1962 using Ziegler-Natta type catalysts and limited success was obtained. The living polymerization of cyclobutene was reported in 1992. While using the very active W(CHtBu)(NAr)(OtBu)2 (Ar = 2,6-(iPr)2-C6H3), a controlled polymerization was obtained by addition of PMe3 which was shown to reversibly binds to the propagating alkylidene complex. The presence of the phosphine additive slowed down the typical fast propagation.

Few reports have appeared on the polymerization of simple substituted cyclobutenes, mostly because their preparation requires a lot of steps and only small-scale applications are possible. For example, the preparation of 3-methylcyclobutene and 3,3-dimethylcyclobutene is an 8-step synthesis with an overall yield of less than 10%. Furthermore, those compounds must be handled at low temperature due to their low
stability. But substituted cyclobutenes are interesting materials for the preparation of functionalized polybutadienes with specific applications.

The polymerization of 1-methylcyclobutene with Mo(=CH(CH₃)₂Ph)(NAr)(OC(CH₃)₂CF₃) was shown to be highly stereospecific (only cis isomerism) and regiospecific (100% head-to-tail configuration). The resulting polymer, cis-1,4-polyisoprene (natural rubber), could be obtained with relatively narrow molecular weight distribution (PDI ≥ 1.46) and for the first time, perfectly alternating cis-1,4-polyisoprene could be prepared. Upon hydrogenation, a perfectly alternating copolymer of ethylene and propylene was obtained (Scheme 1.22).

Scheme 1.22. Applications of the stereoselective ROMP of 1-methylcyclobutene.

The same catalyst was also effective for the stereoselective polymerization of 3,3-dipropylcyclobutene.

Well-defined Schrock's catalysts were also used for the regiospecific polymerization of 3-methylcyclobutene and 3,3-dimethylcyclobutene. Upon hydrogenation, those polymers are equivalent to alternating copolymers of poly(ethylene-alt-propylene) and poly(ethylene-alt-isobutylene).

The polymerization of a family of cyclobutenes bearing various functional groups (ether, ester, alcohol, amine, carboxylic acid) connected to the 3-position by various
linkers was investigated with the PCy₃ disubstituted analog catalyst of **Ru-I** and **Ru-III**. Functional groups connected with a simple methylene spacer could bind to the propagating mono-phosphine complex when the initiation was slow, as it is with the vinylbenzylidene initiator. This reversible chelation was leading to loss of polymerization control (PDI >1.5). A living polymerization was observed upon use of a longer spacer (4 C) and use of **Ru-III**, which is known for its higher initiation rate as compared to the vinylbenzylidene analog. In this study, monomer design proved to be crucial to get control over the polymerization. Interestingly, the functionality present on the side chain had a major influence on the phase transitions of those poly(butadiene)s (-46.6 °C < Tg < 69.4 °C). The same monomer structure was also functionalized with various substituted triphenylene mesogens. Polybutadienes displaying a discotic columnar mesophase were obtained.

The system WCl₆ / Sn(CH₃)₄ was effective for the polymerization of 3,4-diisopropylcyclobutene whereas low polymer yields were obtained with cis-3,4-dichlorocyclobutene, low yield that may result from the formation of conjugated sequences (HCl loss) during the polymerization (catalyst deactivation).

A cross-conjugated polymer was synthesized by ROMP of 3,4-diisopropylidenecyclobutene with a titanocene methylidene carbene precursor. Upon oxidative treatment with iodine, conductivities of 10⁻³-10⁻⁴ S / cm⁻¹ were measured from polymer films.

The ROMP of 3,4-disubstituted cyclobutenes containing various functional groups (ether, ester) was reported by Perrott and Novak in the 1990's. Using **Mo-II**, a
living behavior was observed and therefore well-defined block copolymers could be prepared. Also, the polymerization was shown to be stereoselective with the fluorinated Mo-I ($\sigma_c > 0.9$) whereas a trans bias was seen with Mo-II (55-70%). No polymer was obtained with the ill-defined catalysts (Group 1) and the well-defined ruthenium carbene Ru-I.

1.3.3.2. Monomers containing a fused cyclobutene ring

The Casey carbene (CO)$_5$W=(C$_6$H$_5$)$_2$ was effective for the polymerization of bicyclo[4.2.0]octa-7-ene (A). The highly reactive bicyclo[3.2.0]heptene (B) was polymerized in a living fashion using Ru-I. A 58% cis configuration was observed and block copolymers with norbornene could be prepared.

Perrott used a bicyclic structure that incorporated a cyclobutene ring fused with cyclic ether, anhydride or succinimide functional groups (C). Highly functionalized polybutadiene derivatives were achieved in a control fashion using Mo-I or Mo-II. Nevertheless, the anhydride functionalized polymers proved to be unstable. It was proposed that the presence of the anhydride at two allylic positions could result in elimination reactions to form conjugate segments presumably responsible for the poor
solubility and observed color change. The use of protection / deprotection chemistry also lead to the preparation of monodisperse alcohol and acid-functionalized polybutadienes, which are not directly available from the functionalized precursors due to the high sensitivity of the molydenum catalysts to protic functionalities (Scheme 1.23).

**Scheme 1.23.** Preparation of well-defined acid-functionalized polybutadiene.

![](image1)

A polycyclic structure incorporating a cyclobutene ring can readily be obtained by a Diels-Alder reaction between 1,3,5,7-cyclooctatetrene (COT) and electron-deficient disubstituted acetylenes (dienophiles). In the early 1980s, the resulting adducts based on the *endo*-tricyclic[4.2.2.0\(^{2,5}\)]deca-3,7,9-triene (TCDT) structure with ester (TCDT-(CO\(_2\)Me)\(_2\)) or fluorine groups (the "Feast monomer", TCDT-(CF\(_3\))\(_2\)) at the 7,8-positions (D) were polymerized using the WCl\(_6\)/Sn(CH\(_3\))\(_4\) initiator in a non-controlled fashion (PDI > 3). Named the "Durham route" to polyacetylene, those polymers were shown to produce polyacetylene by retro Diels-Alder reaction upon slight heating (50-100°C) (Scheme 1.24).

**Scheme 1.24.** The Durham route to polyacetylene.

![](image2)
The driving force for the retro Diels-Alder in those systems is the liberation of an aromatic compound upon elimination and this compound is volatile at mild temperature. In 1989, the same polycyclic monomers were polymerized in a controlled fashion with a well-defined tungsten carbene and later with the molybdenum analog Mo-II.\textsuperscript{69a} In both cases, oligomeric polyene chains could be obtained upon heating. Norbornene-polyene block copolymers\textsuperscript{69b} and a variety of diblock copolymers films containing self-assembled polyacetylene structures were also prepared and the microphase separation characterized by SAXS and TEM.\textsuperscript{69c}

**Scheme 1.25.** The "photoisomer" route to polyacetylene.

TCDT-(CF$_3$)$_2$ was also modified by photoisomerization to get a precursor with improved thermal stability as the conversion to polyacetylene occurred between 100 and 120°C (Scheme 1.25).\textsuperscript{70}

ROMP is a powerful tool to prepare functionalized polybutadienes not available with other polymerization techniques. With the advent of well-defined carbene catalysts, monodisperse polybutadienes with control architectures can be prepared for targeted applications.
1.4. References


(9) Chatterjee, A.K.; Choi, T.-L.; Grubbs, R.H. *Synlett* **2001**, 1034


(17) Watson, M.D.; Wagener, K.B. Macromolecules 2000, 33, 8963


(b) Wagener, K.B.; Smith, D.W. Macromolecules 1991, 24, 6073


(20) Tebbe, F.N.; Parshall, G.W.; Reddy, G. J. Am. Chem. Soc. 1978, 100, 3611


Katz, T.J.; Acton, N. Tetrahedron Lett. 1976, 47, 4251


(c) DiMare, M.; Schofield, M.; Anhaus, J.; Walborsky, E.; Evitt, E.; Krüger, C.; Betz, P. *Organometallics* **1990**, *9*, 2262


38


(42) Sanford, M.S.; Ulman, M.; Grubbs, R.H. *J. Am. Chem. Soc.* **2001**, *123*, 749


(45) Scholl, M.; Ding, S.; Lee, C.W.; Grubbs, R.H. *Org. Lett.* **1999**, *1*, 953


(49) Mohr, B.; Lynn, D.M.; Grubbs, R.H. Organometallics 1996, 15, 4317


(b) Garber, S.B.; Kingsbury, J.S.; Gray, B.L.; Hoveyda, A.H. J. Am. Chem. Soc. 2000, 122, 8168

(52) Buchmeiser, M.R. Chem. Rev. 2000, 100, 1565


(54) ACS Symp Series 685, Controlled radical polymerization, Matyjaszewski, K, Ed.; 1998

(55) Dall'Asta, G.; Mazzanti, G.; Natta, G.; Porri, L. Makromol. Chem. 1962, 56, 224

Natta, G.; Dall'Asta, G.; Mazzanti, G.; Motroni, G. Makromol. Chem. 1963, 69, 163


(64) (a) Perrott, M.G.; Novak, B.M. *Macromolecules* **1995**, *28*, 3492

(b) Perrott, M.G.; Novak, B.M. *Macromolecules* **1996**, *29*, 1817


(67)


CHAPTER II.

PREPARATION OF NEW ROMP POLYMERS FROM CYCLOBUTENE DERIVATIVES

2.1. A new family of monomers

2.1.1. Choice of the monomer structure

As previously discussed, few cyclic olefin monomers are currently available for ROMP. The norbornene structure has been extensively functionalized and can be regarded as a functional group "carrier". The more tolerant well-defined carbene catalysts have lead to controlled and stereoselective polymerizations in some cases, which makes it easier to establish structure-property relationships. Polynorbornene has been precisely characterized and is therefore a well-known polymeric backbone.

Cyclobutenes represent a marginal family but the resulting poly(butadiene)s are of particular interests for their properties as they are not available with other polymerization techniques. ROMP can lead to highly stereoregular backbone with no defects, which is a crucial factor for determining properties in subsequent structure-property relationship studies.

In the last twenty years, there has been a growing interest for the preparation of conducting polymers due to their attractive optical and electronic properties. The simplest conjugated polymer is polyacetylene (PA). The morphology of the conjugated backbone has a great influence on various properties such as density, conductivity and tensile strength. The intractability and bad solubility of this conjugated polymer make
characterization and processing difficult tasks and limits its range of applications. The major breakthrough in the PA preparation was made by Shirakawa and co-workers in 1971.\textsuperscript{1} Polymerization of acetylene at the gas / liquid interface of a concentrated catalyst solution lead to free-standing films.

Nevertheless, routes using acetylene gas directly lead to the conjugated backbone with no control over molecular weight but various qualities of polyacetylenes (low-density, high-density, etc.) have been prepared. There is a need for the development of routes that display a control over molecular weight and stereoselectivity, two crucial factors for polymer properties.

The preparation of polyacetylene via ROMP of 1,3,5,7-cyclooctatetraene (COT) was first reported by Höcker \textit{et al.} using the W\textsubscript{Cl\textsubscript{6}} / AlEt\textsubscript{2}Cl system in 1985.\textsuperscript{2} Oligomers along with black insoluble polymer were obtained in low yields. In 1988, the neat polymerization of COT using a well-defined imido-alkoxide Schrock-type tungsten carbene gave high quality shiny silver films (Klavetter, Grubbs) when low monomer / catalyst ratios were used (50-150).\textsuperscript{3} Backbiting reactions leading to the formation of benzene were observed via NMR. Later, it was discovered that soluble polyacetylenes could be obtained via the ROMP of functionalized cyclooctatetraenes (Scheme 2.1).\textsuperscript{4}

\textbf{Scheme 2.1.} Preparation of soluble functionalized polyacetylenes.
With the improved solubility, precise polymer characterization was possible. Also, the *cis/trans* isomerization via photolysis and structure-property relationships could be evaluated. COT has recently been functionalized with ionic functional groups for the preparation of highly conjugated soluble polyelectrolytes (Scheme 2.2). Ion-pairing to the catalyst center affected the kinetics of polymerization.

**Scheme 2.2.** Synthesis of soluble, ionically functionalized polyacetylenes.

![Scheme 2.2](image)

R = \(-\text{N}(\text{CH}_3)_3\text{OTf}\)
\(-\text{SO}_3\text{N}(\text{CH}_3)_4\)

The COT route to polyacetylene displays two major drawbacks: the absence of stereoselectivity and molecular weight control. While the first one is complicated and involved many factors hardly understood yet, the latter one could be tackled via the preparation of well-defined polymer precursors. The Durham route to polyacetylene developed by Edwards and Feast was a major breakthrough in this regard. The precursor polymers could be processed and the aromatic by-product of the retro Diels-Alder reaction was easily removed due to its high volatility. Despite the initial lack of polymerization control, well-defined oligomers and copolymers could be prepared by the use of the Schrock catalysts.
Safir and Novak reported the preparation of saturated polymer precursors to polyacetylene by the 1,2-vinyl-insertion polymerization of functionalized norbornadiene and 7-oxanorbornadiene using palladium (II) complexes (Scheme 2.3). All-trans-polyacetylene was obtained by a retro Diels-Alder reaction that liberated the more stable cyclopentadiene or furan monomer precursors.7

**Scheme 2.3.** Polyacetylene from saturated polymer precursors.

While those routes to polyacetylene may exhibit some advantages as compared to the COT route (easy processing and/or molecular weight control), the major problem is the weight loss associated with the generation of the conjugated backbone as only one double bond is formed per elimination. In the Durham route, the weight loss accounts for 60-80% per double bond introduced whereas in the latter case, it reaches 90%.

**Scheme 2.4.** A possible new route to polyacetylene.

Determined to minimize the weight loss from these precursor polymers, the ROMP of *endo*-tricyclo[4.2.2.02,5]deca-3,9-diene derivatives with fused functionalized
rings at the 7- and 8- positions was investigated. A pericyclic elimination from the resultant materials would also yield polyacetylene (Scheme 2.4). The advantage here is that for each elimination three new double bonds are generated.

### 2.1.2. Monomer synthesis

The *endo*-tricyclo[4.2.2.0^2,5]deca-3,9-diene structure is obtained via the [4+2] Diels-Alder reaction between COT and the desired dienophile. In 1948, this reaction was first reported by Reppe and co-workers who prepared Diels-Alder adducts of COT with maleic anhydride, acrylic acid and quinone.\(^8\) The reaction is performed in neat conditions or in a high-boiling point solvent (chlorobenzene, \(o\)-dichlorobenzene) and at high temperature (160-170ºC). This reaction has been shown to be stereospecific: only the *endo* isomer is formed as expected from pericyclic rules.\(^9\)

The first adduct (**M-1**) was made using maleic anhydride as a dienophile. The anhydride functionality was used as a precursor to alcohol and acid functional groups that can be protected in various ways (Scheme 2.5).

**Scheme 2.5.** The synthesis of anhydride functionalized monomer, **M-1**, and its modification.
Figure 2.1. Structures of monomers used in this study and compound numbering cross reference.
As difficulties were met in the polymerization studies with the anhydride adduct, a variety of functionalized maleimides were prepared and used for the preparation of monomers containing the N-succinimide (or N-dicarboximide) moiety. Maleimides are well-known dienophiles for [4+2] Diels Alder reactions and have been used for the preparation of 7-oxanorbornene monomers. Maleimides are prepared from maleic anhydride and the desired amino containing compound. A one or two-step procedure can be used. In all cases, the first intermediate is the maleamic acid and with the help of a dehydrating reagent, ring-closure occurs through elimination of water (Scheme 2.6).

Scheme 2.6. Synthesis of maleimides.

Depending of the functionality carried by the amine, the conditions and reagents for the second step can vary (Table 2.1) and the yields also depend on the substituents (30-95%).

Table 2.1. Prepared maleimides-reagents used for the condensation reaction.

<table>
<thead>
<tr>
<th>Group carried by the maleimide (R)</th>
<th>Reagents used for the condensation step</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Tert-butylphenyl</td>
<td>Neat reaction</td>
</tr>
<tr>
<td>Tert-butyl</td>
<td></td>
</tr>
<tr>
<td>2,3,4,5,6-pentafluorophenyl</td>
<td></td>
</tr>
<tr>
<td>2-fluorophenyl, 4-fluorophenyl</td>
<td></td>
</tr>
<tr>
<td>2-trifluoromethylphenyl, 4-methoxyphenyl</td>
<td></td>
</tr>
<tr>
<td>3-trifluoromethylphenyl, 4-nitrophenyl</td>
<td></td>
</tr>
<tr>
<td>3,5-ditri fluoromethylphenyl</td>
<td></td>
</tr>
<tr>
<td>2-trifluoromethoxyphenyl</td>
<td></td>
</tr>
<tr>
<td>4-hydroxyphenyl</td>
<td></td>
</tr>
<tr>
<td>CH₃COONa / acetic anhydride</td>
<td></td>
</tr>
<tr>
<td>P₂O₅ / H₂SO₄</td>
<td></td>
</tr>
</tbody>
</table>
The N-succinimide moiety could have been introduced by using the anhydride adduct M-1 as a precursor to the maleamic acid and subsequent water elimination. This procedure has been used to prepare some N-phenylsuccinimide functionalized norbornene in moderate yields. But for practical and cost reasons, the N-succinimide moiety was introduced via the direct reaction of the maleimide with COT.

The yield of the Diels-Alder reaction appeared to depend on the electronic and steric character of the maleimide substituents (Table 2.2).

Table 2.2. Succinimide functionalized monomers.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Succinimide substituent</th>
<th>Isolated yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-2</td>
<td>methyl</td>
<td>74</td>
</tr>
<tr>
<td>M-3</td>
<td>tert-butyl</td>
<td>27</td>
</tr>
<tr>
<td>M-4</td>
<td>phenyl</td>
<td>90</td>
</tr>
<tr>
<td>M-5</td>
<td>2-fluorophenyl</td>
<td>75</td>
</tr>
<tr>
<td>M-6</td>
<td>4-fluorophenyl</td>
<td>70</td>
</tr>
<tr>
<td>M-7</td>
<td>2,3,4,5,6-pentafluorophenyl</td>
<td>70</td>
</tr>
<tr>
<td>M-8</td>
<td>2-trifluoromethylphenyl</td>
<td>74</td>
</tr>
<tr>
<td>M-9</td>
<td>3-trifluoromethylphenyl</td>
<td>64</td>
</tr>
<tr>
<td>M-10</td>
<td>4-trifluoromethylphenyl</td>
<td>60</td>
</tr>
<tr>
<td>M-11</td>
<td>2-trifluoromethoxyphenyl</td>
<td>80</td>
</tr>
<tr>
<td>M-12</td>
<td>3,5-ditrifluoromethylphenyl</td>
<td>45</td>
</tr>
<tr>
<td>M-13</td>
<td>2-tert-butyl phenyl</td>
<td>46</td>
</tr>
<tr>
<td>M-14</td>
<td>4-methoxyphenyl</td>
<td>75</td>
</tr>
<tr>
<td>M-15</td>
<td>4-nitrophenyl</td>
<td>84</td>
</tr>
<tr>
<td>M-16</td>
<td>4-bromophenyl</td>
<td>62</td>
</tr>
<tr>
<td>M-17</td>
<td>4-hydroxyphenyl</td>
<td>60</td>
</tr>
</tbody>
</table>

Lower yields were observed for the more electron-rich N-alkyl dienophiles. For the reactions involving N-phenyl maleimides, the presence of a very bulky and electron donating substituent (tert-butyl) at the ortho position and the substitution of the
deactivating meta positions by trifluoromethyl groups lead to lower reaction's yields. Even if the ortho bulky substituent constrains the phenyl ring to lie in a plane perpendicular to the maleimide ring, it does not interfere so much in the approach of the dienophile toward COT. The inductive electron donating character of the tert-butyl group is a more credible reason for the low yield of the reaction. With the exception of the tert-butyl group, no specific trend can be seen when the electronic character of the substituents at the ortho and para positions varies. A lack of more complete set of derivatives prevented us from observing more specific trends in the cycloaddition reaction. Our results are consistent with what is already known: the HOMO of the "more electron-rich" COT will have a stronger interaction with the LUMO of an electron-poor dienophile, which will facilitate the cycloaddition.12

The prepared monomers are all solids that were purified by sublimation, recrystallization or column chromatography. They exhibit relatively high melting points (M_p > 100ºC) with apparent decomposition as evidenced by TGA analysis. Their solubility properties depend on the functionality present. With the exception of M-17, they are all soluble in chlorinated aliphatic solvents, acetone and DMSO.

2.1.3. Observation of atropisomers

The NMR spectra of compounds M-5, M-8, M-11 and M-13 bearing substituents at the ortho-positions(s) of the diimide ring indicated the presence of rotamers. The presence of an ortho substituent slows down the rotation of the N_sp2-C_sp2 bond as steric interactions occur between the ortho substituent and one of the imide carbonyl groups. As
a result, the aromatic ring lies in a plane perpendicular to the flat succinimide ring. Since the cyclic structure is asymmetric about the succinimide ring plane, two non-planar conformations of different energies will result. Therefore, the incorporation of a substituent at the ortho position allows to differentiate the two possible positions of the phenyl ring vis-à-vis the diimide plane. Even when the phenyl ring bears no substituent, it is known that it does not lie in the same plane as the diimide moiety in the ground state but instead adopts a twisted conformation to relieve the unfavorable steric interactions between the ortho-hydrogens and the diimide substituents. N-phenyl imides and amides with bulky substituent(s) at the ortho positions have been used by Curran to induce diastereoselectivity in different reactions including Diels-Alder reactions. An ortho bulky group will prevent the $N_{sp2}-C_{sp2}$ from rotating at room temperature and/or above, therefore interesting levels of asymmetric induction can be observed when using those compounds.

In our case, the rotamers, or atropisomers, "endo-endo" and "endo-exo", were conveniently observed using $^{19}F$ NMR: two equal signals for the ortho substituent of the compound M-5 (Figure 2.2), indicating that neither of the two conformations is favored. For M-7, the two ortho fluorine groups are not equivalent because the phenyl ring adopts a twisted geometry vis-à-vis the diimide ring.

![Endo-exo and endo-endo conformations.](image)

**Figure 2.2.** Endo-exo and endo-endo conformations.
The same observation is valid for **M-11**: two rotamers can be detected in the single compound purified by column chromatography in a 1.4:1.0 ratio in solution at 25°C. While only peak broadening could be seen on the $^{19}$F NMR spectrum of **M-5**, possessing a OCF$_3$ substituent, the ratio of isomers could be determined using $^1$H NMR and measuring the relative intensity of the ortho proton for each conformation, which are resolved in the spectrum. On compound **M-11**, the ortho proton is more shielded in the minor conformation (Figure 2.3). This contrasts with the trend reported for the norbornene systems wherein the o-proton is more shielded in the major conformation (endo-exo).$^{13,14}$ The fact that the major conformation adopted by **M-11** is the endo-endo one (the opposite trend) could result from orbital overlap between the oxygen atom of the OCF$_3$ moiety and the double bond of the [2.2.2] ring. Actually, the trifluromethoxy group is not very bulky but very flexible. As more bulky substituents were introduced, this distribution of isomers changed, favoring the "endo-exo" configuration.
Figure 2.3. $^1$H NMR spectrum of M-11.

Figure 2.4. $^1$H NMR spectrum of M-8.
For compounds **M-8** and **M-13**, the two isomers could be seen by TLC analysis. The attempted separation by column chromatography failed with **M-8** as isomerization occurred readily in solution at room temperature. The isolated major isomer (endo-exo) equilibrated to a 10.5 to 1 ratio. After annealing for 24 hours at 50°C in chloroform, the rotamer ratio equilibrated to 2.6 to 1. The observed ratio of isomers are determined kinetically and depended on the "history" of the compound: lower ratios were observed at room temperature when the compound was purified by recrystallization (once or twice). For instance, for the second crop recovered by recrystallization, a 1.6:1.0 ratio was found. Actually, the Diels-Alder reaction certainly occurs with a certain degree of diastereoselectivity but as it is performed at 165°C, isomerization may also occur *in-situ*. As the isomers could not be separated, polymerizations were conducted on the atropisomeric mixture. As reported with the norbornene system, the *o*-proton was shielded in the major conformation (Figure 2.4).

The two conformers of **M-13**, possessing the bulky t-butyl group could be separated using column chromatography and characterized independently and no isomerization was observed in solution, indicative of a higher activation energy for the rotation of the \( \text{N}_{\text{sp2}}-\text{C}_{\text{sp2}} \). A 3.6 to 1 ratio was found. Slight differences can be seen when comparing the \(^1\text{H} \) NMR spectra (Figure 2.5). The main difference concerns the chemical shift of the olefinic protons of the 8 carbon bicyclic structure: these protons are more deshielded in the endo-exo isomer (6.08 vs 6.04 ppm) whereas the major *o*-proton is still more shielded.
Interestingly, only one compound has been reported upon Diels-Alder cycloaddition of cyclopentadiene and N-2-tert-butylphenyl maleimide.\textsuperscript{11c} The main difference is that this reaction is performed at room temperature and the major endo-exo isomer is isolated as the kinetic product. Nevertheless, it did not equilibrate to an isomeric mixture up to 150°C. The fact that the Diels-Alder reaction is performed at 165°C in our case may explain the presence of the two atropisomers. Upon annealing at 50°C, the ratio of isomers did not change.

\textbf{Figure 2.5.} Zoom on the \textsuperscript{1}H NMR spectra of the two atropisomers of M-13.
2.1.4 Experimental section

General procedures and characterizations

All manipulations involving air- and moisture-sensitive compounds were carried under an atmosphere of prepurified nitrogen using standard Schlenk techniques.

$^1$H NMR spectra were obtained at 300 MHz with GE NMR Omega spectrometer and at 300, 400 MHz with Varian-Mercury NMR spectrometers. Chemical shifts for $^1$H NMR spectra are reported in $\delta$ (ppm), positive values indicating shifts downfield of tetramethylsilane and are referenced to selected residual proton peaks of the solvent as follows: CDCl$_3$, 7.27, singlet; DMSO-d$_6$, 2.50, quintet; CD$_3$OD, 3.31, quintet. Significant $^1$H NMR data are tabulated in order: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, bs = broad singlet, m = multiplet), coupling constant in Hertz, number of protons. $^{13}$C{$^1$H} proton decoupled NMR were measured at 75 MHz with a GE NMR Omega spectrometer and at 100 MHz on a Varian-Mercury spectrometer. Chemical shifts for $^{13}$C{$^1$H} NMR spectra are reported in $\delta$ (ppm), positive values indicating shifts downfield of tetramethylsilane, and are referenced to selected residual peaks of the solvents as followed: CDCl$_3$, 77.23, triplet; DMSO-d$_6$, 39.51, septet; CD$_3$OD, 49.15, septet. $^{19}$F NMR spectra were measured at MHz using a Varian Gemini spectrometer and $^{19}$F NMR spectra are referenced to C$_6$F$_6$ used as an external 0 ppm reference.

Infrared spectra were obtained using a Jasco FT/IR-410 spectrometer as thin films on NaCl disks or neat samples between NaCl disks and are uncalibrated. IR data are
reported in units of wavenumber (cm\(^{-1}\)) for characteristic peaks. Elemental analyses were performed by Atlantic Microlab, Inc.

Before sample analysis, solvents were removed with a rotary evaporator and under Schlenk line vacuum (approximately 0.05 Torr). Column chromatography was carried out with Selecto Scientific 63-200 mesh silica gel.

**Reagents**

Unless indicated, all materials were purchased from Aldrich Chemical Company or TCI America. 1,3,5,7-cyclooctatetraene was purchased from Strem Chemical.

N-2-fluorophenyl maleimide, N-4-fluorophenyl maleimide, N-2,3,4,5,6-pentafluorophenyl maleimide, N-2-trifluoromethylphenyl maleimide were prepared by a two-step procedure.\(^{11a}\) N-2-tert-butylphenyl maleimide was prepared by a known one-step procedure.\(^{11b}\)

**Experimental procedures and characterizations**

**4-Methoxyphenyl maleamic acid.** By a similar procedure reported by Sanchez Chavez et al.,\(^{11a}\) powdered maleic anhydride (9.8 g, 0.1 mol) was dissolved in 40 mL of chloroform in a 3-neck flask equipped with a mechanical stirrer, thermometer and gas inlet (N\(_2\)). Then a solution of \(p\)-anisidine (12.32 g, 0.1 mol) in 40 mL of chloroform was added dropwise using a dropping funnel and under vigorous stirring. Precipitation of a yellow solid readily occurs. At half addition, 40 mL of chloroform is added. After complete addition, the mixture is stirred for 1 h. A green/khaki solid is recovered by filtration. After drying under vaccum, the desired compound is recovered as green/khaki needles upon recrystallization with ethanol/water (18.45 g, 83.4%). \(^1\)H NMR (DMSO-d\(_6\))
δ: 13.5-12.5 (sh, 1H), 10.39 (s, 1H), 7.54 (d, J = 9 Hz, 2H), 6.91 (d, J = 9 Hz, 2H), 6.46 (d, J = 12 Hz, 1H), 6.30 (d, J = 12 Hz, 1H), 3.73 (s, 3H).

3,5-Ditritfluoromethylphenyl maleamic acid. By a similar procedure as above, from maleic anhydride (4.9 g, 0.05 mol) and 3,5-ditritfluoromethyl aniline (7.8 mL, 0.5 mol), the desired compound was recovered as a white powder (15.8 g, 96.6%). ¹H NMR (DMSO-d₆) δ: 12.9 (sh, 1H), 10.63 (s, 1H), 8.12 (s, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.57 (t, J = 8.1 Hz, 1H), 7.42 (d, J = 8.1 Hz, 1H), 6.48 (d, J = 11.7 Hz, 1H), 6.33 (d, J = 11.7 Hz).

4-Trifluoromethylphenyl maleamic acid By a similar procedure as above, from maleic anhydride (9.8 g, 0.1 mol) and 4-trifluoromethylaniline (7.8 mL, 0.1 mol), the desired compound was recovered as a white powder (15.8 g, 96.6%). ¹H NMR (DMSO-d₆) δ: ;

4 Nitrophenyl maleamic acid. By a similar procedure as above, from maleic anhydride (9.8 g, 0.1 mol) and 4-nitroaniline (6.91 g, 0.1 mol), the desired compound was recovered as a fine yellow-green powder (2.39 g, 15%). ¹H NMR (DMSO-d₆) δ: 13.8-12.0 (sh, 1H), 10.86 (s, 1H), 8.23 (d, J = 9 Hz, 2H), 7.86 (d, J = 9 Hz, 2H), 6.52 (d, J = 11.7 Hz, 1H), 6.35 (d, J = 11.7 Hz, 1H).

N-4-Bromophenyl maleamic acid. By a similar procedure as above, from maleic anhydride (4.9 g, 0.05 mol) and 4-bromoaniline (8.6 g, 0.05 mol), the desired compound was recovered as a fine white/green very pale powder (13.27 g, 98.3%). ¹H NMR (DMSO-d₆) δ: 10.47 (s, 1 H), 7.59 (d, J = 8.4 Hz, 2 H), 7.50 (d, J = 8.4 Hz, 2 H), 6.45 (d, J = 12.3 Hz, 1 H), 6.30 (d, J = 12 Hz, 1 H).
3-Trifluoromethylphenyl maleamic acid. By a similar procedure as above, from maleic anhydride (9.8 g, 0.1 mol) and 3-trifluoromethylaniline (12.5 mL, 0.1 mol), the desired compound was recovered as a white powder (25.2 g, 97.1%). $^1$H NMR (DMSO-d$_6$) $\delta$: 12.9 (sh, 1H), 10.63 (s, 1H), 8.12 (s, 1H), 7.78 (d, $J = 8.1$ Hz, 1H), 7.57 (t, $J = 8.1$ Hz, 1H), 7.42 (d, $J = 8.1$ Hz, 1H), 6.48 (d, $J = 11.7$ Hz, 1H), 6.33 (d, $J = 11.7$ Hz).

2-Trifluoromethoxyphenyl maleamic acid. A solution of 2-trifluoromethoxyaniline (2.5 g, 0.014 mol) in CHCl$_3$ (6 mL) was added dropwise to a chloroform (7 mL) solution of maleic anhydride (1.372 g, 0.014 mol) under vigorous mechanical stirring at RT. The solution turned yellow pale and precipitation occurred after 2/3 addition. After complete addition, 4 mL of CHCl$_3$ were added and stirring was continued for 3 hours. A fine white powder, pure N-2-trifluoromethoxyphenyl maleamic acid, was recovered by filtration, washed with chloroform and dried under vacuum (3.49 g, 91%). $^1$H NMR (DMSO-d$_6$) $\delta$: 13.5-12.5 (sh, 1H), 10.31 (s, 1H), 7.97 (d, $J = 7.2$ Hz, 1H), 7.39 (m, 2H), 7.28 (t, $J = 7.6$ Hz, 1H), 6.55 (d, $J = 12.3$ Hz, 1H), 6.35 (d, $J = 12.3$ Hz, 1H).

N-4-Methoxyphenyl maleimide. 4-Methoxyphenyl maleamic acid (11.06 g, 0.05 mol) was added under vigorous stirring to a solution of acetic anhydride (47.1 mL, 0.5 mol) containing 2.54 g (0.031 mol) of sodium acetate in a 3-neck flask equipped with a mechanical stirrer, a condenser and a thermometer. After heating for 1 h at 90$^\circ$C, the mixture was stirred at RT for 2 h. The orange solution was slowly poured in 400 mL of iced water and stirred for 1 h. A yellow solid is recovered by filtration and dried. The desired compound was recovered as dark yellow duvet solid (7.85 g, 78%) upon
recrystallization with ethanol/water. $^1$H NMR $\delta$: 7.24 (d, J = 9 Hz, 2H), 6.99 (d, J = 9 Hz, 2H), 6.84 (s, 2H), 3.84 (s, 3H).

**N-3,5-Ditrifluoromethylphenyl maleimide.** By a similar procedure as above, from 3-trifluoromethylaniline (13.1 g, 0.04 mol), acetic anhydride (38 mL), sodium acetate (2.1 g), the desired compound was recovered as a white crystalline solid upon recrystallization with hexane/ethyl acetate (8.34 g, 67.5%). $^1$H NMR $\delta$: 7.96 (s, 2H), 7.88 (s, 1H), 6.95 (s, 2H); $^{19}$F NMR $\delta$: 98.94.

**N-4-Trifluoromethylphenyl maleimide.** By a similar procedure as above, from 4-trifluoromethyl maleamic acid (5.18 g, 0.02 mol), acetic anhydride (19 mL), sodium acetate (1.01 g), the desired compound was recovered as a white/pinkish fine powder upon recrystallization with ethanol/water (4.42 g, 91.7%). $^1$H NMR $\delta$: 7.75 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 6.91 (s, 2H); $^{19}$F NMR $\delta$: 99.19.

**N-4-Nitrophenyl maleimide.** By a similar procedure as above, from 4-nitrophenyl maleamic acid (2.0 g, 8.5 mmol), acetic anhydride (8 mL), sodium acetate (430 mg), the desired compound was recovered as a fine crystalline beige solid upon recrystallization with ethanol/water (0.9 g, 49%). $^1$H NMR $\delta$: 8.34 (d, J = 9.2 Hz, 2H), 7.69 (d, J = 9.2 Hz, 2H), 6.94 (s, 2H).

**N-4-Bromophenyl maleimide.** By a similar procedure as above, from 4-bromophenyl maleamic acid (12.15 g, 45 mmol), acetic anhydride (52 mL), sodium acetate (2.27 g), the desired compound was recovered as fine yellow pale needles upon recrystallization with hexane/ethyl acetate (9.78 g, 86.2%). $^1$H NMR $\delta$: 7.60 (m, 2 H),
7.27 (m, 2 H), 6.87 (s, 2 H). IR 3090, 1722, 1592, 1492, 1444, 1400, 1386, 1148, 1066, 829, 708.

**N-3-Trifluoromethylphenyl maleimide.** By a similar procedure as above, from 3-trifluoromethyl maleamic acid (15.55 g, 0.06 mol), acetic anhydride (57 mL), sodium acetate (3.04 g) but after pouring the reaction mixture in iced water, no precipitation occurred, a yellow oil separated. It was extracted with Et₂O, neutralized with 10% aqueous K₂CO₃ and washed with brine. After drying with CaCl₂ and solvent removal, the resulting residue was put in the fridge overnight. A yellow pale solid was recovered (11.72 g, 81%). ¹H NMR δ: 7.68 (s, 1H), 7.62 (m, 3H), 6.90 (s, 2H); ¹⁹F NMR δ: 99.14.

**N-2-trifluoromethoxyphenyl maleimide.** A solution of N-2-trifluoromethoxyphenyl maleamic acid (3.03 g, 0.011 mol), acetic anhydride (10.4 mL, 0.11 mol), sodium acetate (560 mg, 0.007 mol) was heated at 90 °C for 1 hour. After cooling, the mixture was poured in 250 mL iced water. A yellow oil separated. It was extracted with ethyl acetate, washed with water until neutral and concentrated to give yellow oil. Two compounds were seen by TLC. The impurity was removed by passing the crude on a silica gel column using hexane / ethyl acetate (1/1) as eluant. Upon concentration, a pure pale yellow oil that solidified on standing was obtained (2.66 g, 94%). ¹H NMR δ: 7.50 (m, 1H), 7.42 (m, 2H), 7.32 (dd, J = 7.5, 2 Hz, 1H), 6.91 (s, 2H); ¹³C {¹H} NMR δ: 168.80, 145.47, 134.75, 130.80, 130.64, 127.60, 123.82, 121.63, 120.38 (q, J = 258 Hz); ¹⁹F NMR δ: 104.14.

**N-4-Hydroxyphenyl maleimide.** It was prepared by a similar procedure reported by Park et al.¹¹c In a 3 neck flask equipped with a mechanical stirrer and a thermometer,
4-aminophenol (5.45 g, 0.05 mol) was progressively added to a solution of maleic anhydride (0.055 mol, 5.4 g) in dry DMF (15 mL) under N2. The resulting mixture was stirred at RT for 2 hours. A mixture of P205 (0.01 mol, 2.84 g), concentrated H2SO4 (0.70 mL) in dry DMF (20 mL) was then added dropwise and the resulting solution was heated at 70 °C for 4 hours. After cooling, it was poured in 500 ml iced water and after 1 hour stirring, the orange precipitated was recovered by filtration, washed with a lot of water and dried under vacuum at 50 °C. Upon recrystallization with isopropanol, orange needles were obtained (4.40 g, 47%). 1H NMR (DMSO-d6) δ: 9.72 (s, 1H), 7.13 (s, 2H), 7.08 (d, J = 8.4 Hz, 2H), 6.83 (d, J = 8.4 Hz, 2H).

**endo-Tricyclo[4.2.2.02.5]deca-3,9-diene-7,8-dicarboxylandride** (M-1). A mixture of 1,3,5,7-cyclooctatetraene (3.12 g, 0.03 mol) and powdered maleic anhydride (2.94 g, 0.03 mol) was progressively heated to 165°C under N2. It was then kept at this temperature for 45 minutes. After cooling, the crude solid was washed with hexane and dried. Sublimation under reduced pressure (0.1 Torr) and heating (~ 120-140°C) lead to nice transparent crystals (5.0 g, 83%). mp: 170-171°C. 1H NMR (CDCl3) δ: 6.03 (m, 2H), 5.91 (s, 2H), 3.24 (br, 2H), 3.07 (db, J = 1.5 Hz, 2H), 2.81 (bs, 2H); 13C { 1H} NMR (DMSO-d6) δ: 173.83, 138.16, 128.95, 43.74, 42.68, 36.44.

**7,8-N-methylsuccinimide endo-tricyclo[4.2.2.02.5] deca-3,9-diene** (M-2). To 1,3,5,7-cyclooctatetraene (2.08 g, 0.02 mol) under argon was added N-methylmaleimide (2.11 g, 0.02 mol) and the resulting neat mixture was progressively heated with an oil bath. It was kept at 155-165 °C for 1h30’ as TLC indicated complete disappearance of the maleimide. The mixture solidified upon cooling. It was triturated with a small amount of
diethyl ether and the crude product was recovered by filtration and dried under vacuum.

Recrystallization from hexane / ethyl acetate yielded a white, floculent solid of M-2 (3.19 g, 74%): mp 175-176 °C; \(^1\)H NMR \(\delta\): 5.87 (m, 4H), 3.17 (br, 2H), 2.90 (s, 3H), 2.82 (br, 2H), 2.79 (s, 2H); \(^{13}\)C \({\{^{1}\text{H}}\} \) NMR \(\delta\): 179.05, 138.17, 128.41, 44.27, 43.56, 36.74, 24.72; IR 3032 (w), 2947, 2912, 1771, 1689, 1556 (w), 1434, 1374, 1280, 1241, 1134, 1001, 970, 850, 792, 762, 680, 643. Anal. Calcd for C\(_{13}\)H\(_{13}\)O\(_2\)N: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.62; H, 6.18; N, 6.47.

7,8-N-tert-butylsuccinimide endo-tricyclo[4.2.2.0\(2.5\)] deca-3,9-diene (M-3). By a procedure similar to M-2, in 3 ml of chlorobenzene, shiny white flakes of M-3 (0.70 g, 27%) were obtained: mp 201-202 °C; \(^1\)H NMR \(\delta\): 5.89 (m, 4H), 3.12 (br, 2H), 2.78 (br, 2H), 2.63 (m, 2H), 1.51 (s, 9H); \(^{13}\)C \({\{^{1}\text{H}}\} \) NMR \(\delta\): 180.14, 138.14, 128.38, 58.33, 44.34, 43.24, 37.16, 28.50; IR 3051 (w), 3021 (w), 2971, 2933, 1770 (w), 1690, 1458, 1365, 1355, 1340, 1259, 1161, 1001, 852, 812, 712, 683, 651. Anal. Calcd for C\(_{16}\)H\(_{19}\)O\(_2\)N: C, 74.68; H, 7.44; N, 5.44. Found: C, 74.39; H, 7.51; N, 5.41.

7,8-N-phenylsuccinimide endo-tricyclo[4.2.2.0\(2.5\)] deca-3,9-diene (M-4). By a procedure similar to M-2, M-4 (5.0 g, 90%) was obtained as a white powder: mp 241-242 °C; \(^1\)H NMR \(\delta\): 7.38 (m, 3H), 7.19 (d, \(J = 7.5\) Hz, 2H), 6.01 (m, 2H), 5.92 (s, 2H), 3.27 (br, 2H), 2.95 (s, 2H), 2.87 (br, 2H); \(^{13}\)C \({\{^{1}\text{H}}\} \) NMR \(\delta\): 178.04, 138.17, 132.10, 129.25, 128.74, 128.61, 126.70, 44.24, 43.53, 37.19. Anal. Calcd for C\(_{18}\)H\(_{15}\)O\(_2\)N: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.80; H, 5.57; N, 5.02.

7,8-N-2-fluorophenylsuccinimide endo-tricyclo[4.2.2.0\(2.5\)] deca-3,9-diene (M-5). By a procedure similar to M-2, in 0.5 ml chlorobenzene, M-5 (4.5 g, 75%) was
recovered as a white powder: mp 220-221 °C; \(^1\)H NMR \(\delta\): 7.38 (m, 1H), 6.03 (t, \(J = 3.6\) Hz, 2H), 5.93 (s, 2H), 3.28 (br, 2H), 3.01 (br, 2H), 2.88 (s, 2H); \(^{13}\)C \(^1\)H\} NMR \(\delta\): 177.27, 138.17, 131.06, 130.96, 129.41, 128.64, 128.48, 124.70, 116.97, 116.72, 44.17, 44.04, 43.92, 43.75, 37.10; \(^{19}\)F NMR \(\delta\): 42.65, 44.58; IR 3046, 2978, 2916, 2900, 1778, 1714, 1595, 1504, 1463, 1385, 1287, 1272, 1242, 1182, 818, 808, 793, 766, 742, 719, 676. Anal. Calcd for C\(_{18}\)H\(_{14}\)O\(_2\)NF: C, 73.21; H, 4.78; N, 4.74. Found: C, 73.00; H, 4.86; N, 4.86.

7,8-N-4-fluorophenylsuccinimide endo-tricyclo[4.2.2.0\(^2\)5\] deca-3,9-diene (M-6). By a procedure similar to M-2, in 5ml chlorobenzene, M-6 (4.4 g, 70%) was recovered as a white crystalline powder: mp 227-228 °C; \(^1\)H NMR \(\delta\): 7.18 (m, 4H), 6.00 (m, 2H), 5.92 (s, 2H), 3.27 (br, 2H), 2.95 (br, 2H), 2.88 (s, 2H); \(^{13}\)C \(^1\)H\} NMR \(\delta\): 177.98, 163.99, 138.17, 128.61, 128.48, 127.93, 116.42, 116.13, 44.21, 43.50, 37.16; \(^{19}\)F 49.84; IR 3048, 2941, 2912, 1772, 1704, 1601, 1507, 1396, 1291, 1234, 1218, 1192, 1150, 844, 820, 787, 713. Anal. Calcd for C\(_{18}\)H\(_{14}\)O\(_2\)NF: C, 73.21; H, 4.78; N, 4.74. Found: C, 73.26; H, 4.95; N, 4.88.

7,8-N-2,3,4,5,6-pentafluorophenylsuccinimide endo-tricyclo[4.2.2.0\(^2\)5\] deca-3,9-diene (M-7). By a procedure similar to M-2, in 2 ml chlorobenzene, M-7 (1.20 g, 70%) was recovered as a white powder: mp 218-219 °C; \(^1\)H NMR \(\delta\): 6.02 (m, 2H), 5.93 (s, 2H), 3.27 (br, 2H), 3.07 (s, 2H), 2.88 (s, 2H); \(^{13}\)C \(^1\)H\} NMR \(\delta\): 175.75, 143.68 (dm, \(J = 255\) Hz), 142.27 (dm, \(J = 257\) Hz), 138.20, 138.04 (dm, \(J = 248\) Hz), 128.61, 107.41 (td, \(J = 14.5, 4.9\) Hz), 44.30, 43.95, 37.10; \(^{19}\)F NMR \(\delta\): 20.75 (dt, \(J = 16.6, 5.4\) Hz, 1F), 18.92 (dt, \(J = 22, 5.6\) Hz, 1F), 10.75 (t, \(J = 22\) Hz, 1F), 1.02 (m, 2F); IR 3044, 2978,
7,8-N-2-trifluoromethylphenylsuccinimide endo-tricyclo[4.2.2.0^2.5] deca-3,9-diene (M-8). By a procedure similar to M-2, an atropisomeric mixture of M-8 (2.56g, 74%) was recovered after column chromatography purification (hexane/ethyl acetate): mp 171-172 °C; $^1$H NMR δ: 7.78 (d, $J = 7.5$ Hz, 2H), 7.61 (m, 2H), 7.17 (d, $J = 7.8$ Hz, 0.15H), 7.10 (d, $J = 7.8$ Hz, 0.85H), 6.08 (m, 1.8H), 6.02 (m, 0.2H), 5.93 (s, 2H), 3.29 (br, 2H), 3.05 (m, 1.8H), 2.99 (m, 0.2H), 2.88 (br, 2H); $^{13}$C {$^1$H} NMR δ: 177.79, 138.17, 133.36, 130.84, 130.74, 130.09, 129.06, 128.83, 128.41, 127.57 (q, $J = 4.8$ Hz), 128.25, 126.52 (q, $J = 259$ Hz), 44.46, 44.34, 44.14, 43.69, 36.94, 36.74; $^{19}$F NMR δ: 101.07 (s, 0.26F), 100.54 (s, 2.74F); IR 3041, 2944, 2908, 1780, 1719, 1607, 1588, 1502, 1457, 1381, 1319, 1274, 1179, 1163, 1129, 1111, 1060, 1033, 850, 793, 763, 744, 680. Anal. Calcd for C$_{19}$H$_{14}$O$_2$NF$_3$: C, 66.09; H, 4.09; N, 4.06. Found: C, 66.11; H, 4.12; N, 4.17.

7,8-N-3-trifluoromethylphenylsuccinimide endo-tricyclo[4.2.2.0^2.5] deca-3,9-diene (M-9). By a procedure similar to M-2, M-9 (4.1 g, 64%) was recovered as a floculous white powder upon recrystallization with ethyl acetate. $^1$H NMR δ: 7.58 (m, 2H), 7.52 (s, 1H), 7.43 (d, $J = 8.1$ Hz, 1H), 6.03 (m, 2H), 5.93 (s, 2H), 3.29 (s, 2H), 2.98 (d, $J = 1.5$ Hz, 2H), 2.89 (s, 2H); $^{13}$C {$^1$H} NMR δ: 177.55, 138.15, 132.64, 131.68 (q, $J = 32.9$ Hz), 129.99, 129.78, 128.65, 125.40 (q, $J = 3.8$ Hz), 123.66 (q, $J = 3.8$ Hz), 121.87, 44.15, 43.54, 37.18; $^{19}$F NMR δ: 99.17.
7,8-N-4-Trimethoxyphenylsuccinimide *endo*-Tricyclo[4.2.2.02.5]deca-3,9-diene (M-10). A mixture of COT (0.52 g, 4.9 mmol) and N-4-trifluoromethylphenyl maleimide (1.20 g, 5 mmol) with 1 ml chlorobenzene was progressively heated to 150ºC under nitrogen and kept at this temperature for 1.5 h. Upon cooling, the mixture solidified. The crude solid was recovered by filtration, washed with hexane and dried under vacuum. Recrystallization with hexane/ethyl acetate yielded long white needles of the Diels-Alder adduct. $^1$H NMR δ: 7.72 (d, $J = 8.4$ Hz, 2H), 7.39 (d, $J = 8.4$ Hz, 2H), 6.02 (m, 2H), 5.93 (s, 2H), 3.29 (br, 2H), 2.99 (t, $J = 1.2$ Hz, 2H), 2.90 (br, 2H). $^{13}$C {^1H} NMR δ: 177.55, 138.20, 135.22, 130.62 (d), 128.69, 126.95, 126.35 (q, $J = 3.8$ Hz), 123.87 (d), 44.20, 43.61, 37.24. $^{19}$F NMR δ: 99.09 (s). IR 3048, 2943, 2898, 1775, 1706, 1613, 1517, 1395, 1323, 1188, 1170, 1128, 1107, 1065, 847, 821, 792, 737, 718, 684. Anal. Calcd for C$_{19}$H$_{14}$O$_2$NF$_3$: C, ; H, ; N, . Found: C, ; H, ; N, .

7,8-N-2-trimethoxyphenylsuccinimide *endo*-tricyclo[4.2.2.02.5] deca-3,9-diene (M-11). By a procedure similar to M-2, M-11 (2.15 g, 80%) was recovered as a beige solid after silica gel chromatography purification ($R_f = 0.67$, hexane / ethyl acetate (2:1)). One single compound is observed on TLC but two isomers can be seen in solution. Atropisomeric mixture: mp 102-103 ºC; $^1$H NMR δ: 7.41 (m, 3H), 7.21 (m, 0.58H), 7.15 (m, 0.42H), 6.04 (m, 2H), 5.93 (s, 2H), 3.28 (br, 2H), 3.04 (s, 0.44H), 2.99 (s, 0.56H), 2.88 (br, 2H); $^{13}$C {^1H} NMR δ: 177.07, 145.12, 144.92, 138.17, 130.80, 130.09, 129.93, 128.67, 128.48, 127.48, 127.38, 124.83, 124.66, 121.43, 121.01, 120.37 (q, $J = 257$ Hz), 44.17, 43.62, 37.07, 36.90; $^{19}$F NMR δ: 104.88 (s, 1.74F), 104.41 (s, 1.26F); IR 3047, 2948, 2911, 1780, 1718, 1504, 1460, 1386, 1291, 1255, 1217, 1180, 791, 764, 748, 720,
7,8-N-3,5-ditrifluoromethylphenylsuccinimide \textit{endo}-tricyclo[4.2.2.0^{2,5}] dec-3,9-diene (M-12). By a procedure similar to M-2, M-12 (870 mg, 45%) was recovered as a white powder after silica gel column chromatography (hexane/ethyl acetate, 2/1). $^1$H NMR $\delta$: 7.88 (s, 1H), 7.77 (s, 2H), 6.04 (m, 2H), 5.94 (s, 2H), 3.30 (bs, 2H), 3.01 (s, 2H), 2.90 (s, 2H); $^{13}$C { $^1$H} NMR $\delta$: 177.11, 138.24, 133.55, 132.68 (q, $J = 4$ Hz), 128.8, 122.95 (q, $J = 271$ Hz), 122.24, 37.2, 34.2, 29; $^{19}$F NMR $\delta$: 98.92.

7,8-N-2-tert-butylphenylsuccinimide \textit{endo}-tricyclo[4.2.2.0^{2,5}] dec-3,9-diene (M-13). By a procedure similar to M-2, the two isomers of M-13 (0.154 g, 46%) were recovered as white powders. They were separated using silica gel column chromatography (hexane / ethyl acetate, 2/1).

\textbf{endo-exo isomer} (78%) $R_f = 0.68$; $^1$H NMR $\delta$: 7.54 (d, $J = 8.1$ Hz, 1H), 7.36 (t, $J = 7.5$ Hz, 1H), 7.24 (t, $J = 7.2$ Hz, 1H), 6.73 (d, $J = 7.2$ Hz, 1H), 6.08 (m, 2H), 5.92 (s, 2H), 3.30 (br, 2H), 2.98 (s, 2H), 2.87 (br, 2H); $^{13}$C { $^1$H} NMR $\delta$: 179.34, 148.03, 138.17, 131.03, 130.74, 129.83, 129.06, 128.70, 127.54, 44.30, 43.72, 36.94, 35.71, 31.77

\textbf{endo-endo isomer} (22%) $R_f = 0.45$; $^1$H NMR $\delta$: 7.52 (dd, $J = 8.1$, 1.5 Hz, 1H), 7.35 (td, $J = 7.5$, 1.5 Hz, 1H), 7.25 (td, $J = 7.8$, 1.5 Hz, 1H), 6.73 (dd, $J = 7.8$, 1.5 Hz, 1H), 6.04 (m, 2H), 5.92 (s, 2H), 3.30 (br, 2H), 2.97 (s, 2H), 2.88 (br, 2H)

IR 3037, 2959, 2914, 1771, 1703, 1491, 1445, 1381, 1291, 1239, 1184, 1073, 850, 793, 756, 700, 682.
Anal. Calcd for C_{22}H_{23}O_{2}N: C, 79.25; H, 6.95; N, 4.20. Found: C, 79.36; H, 6.99; N, 4.15.

**7,8-N-4-methoxyphenylsuccinimide endo-tricyclo[4.2.2.0^{2.5}] deca-3,9-diene (M-14).** By a procedure similar to M-2, in 7ml chlorobenzene, M-14 (4.50 g, 75%) was recovered as white shiny flakes: mp 213 °C; \(^1H\) NMR δ: 7.11 (d, J = 8.2 Hz, 2H), 6.95 (d, J = 8.3 Hz, 2H), 6.01 (br, 2H), 5.92 (s, 2H), 3.82 (s, 3H), 3.27 (br, 2H), 2.94 (s, 2H), 2.88 (s, 2H); \(^13C\) \({\{1H}\}\) NMR δ: 178.33, 159.66, 138.17, 128.61, 127.93, 124.73, 114.58, 55.64, 44.27, 43.46, 37.16; IR 3055, 2976, 2938, 2900, 1771, 1703, 1605, 1511, 1436, 1397, 1294, 1255, 1195, 1163, 1026, 844, 810, 787, 710, 683. Anal. Calcd for C_{19}H_{17}O_{3}N: C, 74.25; H, 5.57; N, 4.56. Found: C, 74.22; H, 5.65; N, 4.46.

**7,8-N-4-Nitrophenylsuccinimide endo-Tricyclo[4.2.2.0^{2.5}]deca-3,9-diene (M-15).** A mixture of COT (0.21 g, 2 mmol) and N-4-nitrophosphyl maleimide (0.64 g, 3 mmol) with 0.5 ml chlorobenzene was progressively heated to 150°C under nitrogen and kept at this temperature for 1.5 h. Upon cooling, the mixture solidified. The crude solid was recovered by filtration, washed with hexane and dried under vacuum. The desired compound (0.54 g, 84%) was recovered as a white powder after silica gel column chromatography (R\_f = 0.22, dichloromethane). \(^1H\) NMR δ: 8.31 (d, J = 8.8 Hz, 2H), 7.50 (d, J = 8.8 Hz, 2H), 6.02 (m, 2H), 5.93 (s, 2H), 3.30 (br, 2H), 3.01 (t, J = 1.2 Hz, 2H), 2.90 (br, 2H). \(^13C\) \({\{1H}\}\) NMR δ: 177.23, 147.11, 138.20, 137.64, 128.73, 127.17, 124.47, 44.12, 43.62, 37.27. IR 3119, 3048, 2939, 2905, 1774, 1707, 1610, 1592, 1528, 1493, 1384, 1346, 1291, 1232, 1185, 1164, 860, 823, 790, 750, 697.
7,8-N-4-Bromophenylsuccinimide *endo*-Tricyclo[4.2.2.0²5]deca-3,9-diene (M-16). A mixture of COT (1.0 g, 1 mmol) and N-4-bromophenyl maleimide (2.42 g, 0.95 mmol) was progressively heated to 160°C under nitrogen and kept at this temperature for 30 min. The mixture solidified progressively. After cooling, the crude solid was recovered by filtration, washed with hexane and dried under vacuum. The desired compound (2.13 g, 62%) was recovered as a fine white needles after recrystallization using hexane / ethyl acetate (R_f = 0.73, hexane / ethyl acetate (1/1)). ^1H NMR δ: 7.57 (m, 2H), 7.11 (m, 2H), 6.00 (m, 2H), 5.93 (s, 2H), 3.28 (br, 2H), 2.96 (t, J = 1.8 Hz, 2H), 2.88 (br, 2H). ^13C \{^1H\} NMR δ: 177.67, 138.17, 132.41, 131.07, 128.63, 128.22, 122.54, 44.20, 43.54, 37.18. IR 3041, 2952, 2902, 1775, 1710, 1490, 1399, 1288, 1232, 1183, 1069, 1012, 813, 750, 708.

7,8-N-4-Hydroxyphenylsuccinimide *endo*-Tricyclo[4.2.2.0²5]deca-3,9-diene (M-17). To 1,3,5,7-cyclooctatetraene (1.04 g, 0.01 mol) under N_2 was added N-4-hydroxyphenyl maleimide (1.89 g, 0.01 mol) and the resulting neat mixture was progressively heated with an oil bath. At 140 °C, the maleimide had not melted so 1.5 mL of chlorobenzene was added and the reaction mixture was heated at 170 °C for 1 hour during which, crystallization occurred in the flask. After cooling, the mixture was dried under vacuum and the resulting beige solid washed with hexane and dried under vacuum. Recrystallization with ethyl acetate yielded a white duvet-like solid (1.75g, 60%). This compound is not soluble in CHCl₃, partially soluble in acetone, soluble in THF and DMSO. ^1H NMR (DMSO-d₆) δ: 9.72 (s, 1H), 6.89 (d, J = 8.0 Hz, 2H), 6.80 (d, J = 8.0
Hz, 2H), 5.92 (s, 2H), 5.91 (s, 2H), 3.04 (s, 2H), 2.99 (s, 2H), 2.85 (s, 2H). $^{13}$C ($^{1}$H) NMR δ: 178.12, 157.27, 138.03, 128.20, 128.09, 123.42, 115.39, 43.60, 42.79, 36.59.
2.2. Polymerization studies

2.2.1. Catalyst activity comparison

In an attempt to identify a living system for the monomeric structure, the first polymerization studies were performed using the readily available well-defined molybdenum catalysts (Mo-I, Mo-II) and a Grubb's type catalyst (Ru-III). First polymerization trials were performed on the known Diels-Alder adduct from COT and maleic anhydride in dichloromethane. When using the Schrock's catalysts, best results have usually been reported with aromatic solvents like toluene or benzene. This was not possible in our case due to the very bad solubility of all functionalized structures in such solvents. With a typical catalyst concentration of 0.002 M and a monomer to catalyst ratio of 100, poly-I was isolated as a grey solid. With all catalysts, the reaction mixture became heterogeneous: polymer precipitation immediately occurred with the molybdenum catalysts whereas progressive precipitation over time was observed using Ru-III. These first results illustrate the characteristic higher activity of the Group VI catalysts with the cyclobutene ring as compared to the first generation Group VIII catalyst. It also confirms the already reported bad solubility of anhydride containing polymers in chlorinated aliphatic solvents.\textsuperscript{15} Yields were therefore limited by the unavoidable precipitation of the growing polymer chains (up to 60% after 24 h). The solubility of the resulting polymer was limited to DMSO and molecular weights were not determined. NMR data were consistent with the expected structure for poly-I, but no quantitative data on the stereochemistry could be calculated because of an unfortunate overlap between the peaks of the NMR solvent (DMSO-d\textsubscript{6}) and the 30-40 ppm region for
the allylic protons of the main chains. For $[\text{M-1}]/[\text{Ru-III}]$ ratios lower than 50, the oligomers were partially soluble in acetone. Poly-I prepared with $[\text{M-1}]/[\text{Ru-III}] = 100$ did not display any noteworthy features in the DSC analysis, which suggests a rigid polymer backbone and surprisingly good thermal stability. No specific decomposition pattern could be observed by thermogravimetric analysis as a continuous weight loss occurred between 300°C and 500°C ($T_{10\%}$ loss = 304°C).

Table 2.3. Catalyst activity comparison for the ROMP of M-4.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>[M-4] / [cat]</th>
<th>Time (h)</th>
<th>Isolated yield (%)</th>
<th>$M_w$ distribution (GPC)\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo-I</td>
<td>46</td>
<td>14</td>
<td>87</td>
<td>unimodal</td>
</tr>
<tr>
<td></td>
<td>93</td>
<td>15</td>
<td>100</td>
<td>polydisperse</td>
</tr>
<tr>
<td>Mo-II</td>
<td>40</td>
<td>14</td>
<td>88.5</td>
<td>tri-modal</td>
</tr>
<tr>
<td></td>
<td>94</td>
<td>15</td>
<td>100</td>
<td>1 polydisperse + 2 monodisperse peaks</td>
</tr>
<tr>
<td>Ru-III</td>
<td>93</td>
<td>5</td>
<td>71</td>
<td>(small high $M_n$ shoulder)</td>
</tr>
<tr>
<td></td>
<td>49</td>
<td>14</td>
<td>79</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Polymerization conditions: CH$_2$Cl$_2$, room temperature. \textsuperscript{b} GPC measured with CHCl$_3$ as the mobile phase, relative to narrow PDI polystyrene standards

The solubility problems encountered when dealing with the anhydride moiety prompted us to prepare the N-phenyl succinimide adduct M-4. In this case, no precipitation occurred during the polymerization of M-4 with the different catalysts (Table 2.3). The resulting polymer, a beige powder, is soluble in chloroform but insoluble
in acetone, methanol and hexane. The molybdenum catalysts lead to uncontrolled polymerizations. A tri-modal molecular weight distribution is observed with Mo-II whereas Mo-I leads to a polydisperse unimodal distribution (PDI = 1.4). This is reminiscent of the results obtained with catalyst Mo-I for the ROMP of 3,4-disubstituted cyclobutenes.\textsuperscript{15b} With Mo-II, however, a living polymerization of the 3,4-disubstituted cyclobutenes was observed, which is distinctly different from our results in this study.

The ruthenium catalyst Ru-III gave much better results in terms of controlled polymerization, which is consistent with its characteristic attenuated activity relative to the molybdenum catalysts. The molecular weight of poly-4 prepared with Ru-III had a narrow distribution (PDI = 1.1) and depended linearly on the monomer to catalyst ratio - both observations being consistent with a lack of chain transfer. The kinetic studies, however, of the polymerization showed that the monomer consumption did not strictly follow a first order rate law (indicating possible chain termination). Also, a narrow, high molecular peak (approximately 3x the M\textsubscript{n} of the main peak) was consistently observed. Polymerization studies indicated that this peak was present from the beginning of the polymerization and its relative proportion progressively increased up to 20%. This high molecular weigh fraction did not increase when the reaction mixture was allowed to continuing stirring for one day after complete monomer consumption. This latter result argues against possible coupling reactions between active polymer chains and the origin of this second monodisperse peak remains unknown.

The encouraging results achieved with Ru-III prompted us to study the ROMP of monomers containing the N-phenylsuccinimide moiety with various functional groups.
Using the same polymerization conditions as for M-4, polymers from monomers M-5 to M-13 were obtained in 80 to 90% yield after 5 hours with catalyst Ru-III. In most cases, the rate of polymerization was shown to be first order with respect to the monomer concentration, and the polymers displayed monodisperse molecular weight distributions (1.07 < PDI < 1.12). The lone exception was poly-6 for which a bi-modal molecular weight distribution, with a narrow high molecular weight peak, was observed. Ru-III seems to behave similarly vis-à-vis M-3 and M-6 as indicated by the presence of a small high molecular weight shoulder in the GPC spectra and a non first order rate law. No specific explanation can be given for this behavior: a controlled polymerization has been observed with other substituents at the para position of the aromatic ring and with the fluorine group present at the ortho position.

Incorporation of a nitro group in the monomer (M-15) had a deleterious effect on the solubility of the resulting polymer. Under typical conditions, rapid precipitation of the polymer as a white powder occurred during the polymerization. Following the polymerization by $^1$H NMR (CDCl$_3$, [M-15] = 0.2 M, 20 equiv) indicated that a first order rate law was followed up to the point at which precipitation occurred in the NMR tube (= 50% conversion). The low solubility of the polymer in chlorinated solvents is certainly a result of the polarity of the nitro group.

Intriguing results were obtained upon the study of the polymerization of M-16. This monomer had been prepared with the hope that the para-bromine group could be used as an initiator for the preparation of graft polymers with carbodiimide monomers for example. In typical conditions (CH$_2$Cl$_2$, [M-16] = 0.2 M, 100 eq.), the traditional dark
yellow color of the active polymerization turned to fluorescent orange after 4 h. After 24 h, precipitation had occurred from the turbid scent solution. The recovered brown-beige solid was insoluble in all common solvents, an indication of possible cross-linking. But at lower ratios (25 and 50 equiv) and monomer concentrations (0.05 and 0.1 M), no precipitation occurred during the polymerization (100% conversion). It was hard to remove catalyst traces from the isolated polymers and they maintained a brownish color. One single peak with tailing could be seen on the GPC spectrum with an increased PDI as \([\text{M-16}] / [\text{Ru-III}]\) increased (1.5 to 1.99). But the molecular weight seemed independent of the monomer to catalyst ratio and remained in the 5000-range.

<table>
<thead>
<tr>
<th>[M-16] / [Ru-III]</th>
<th>[M-16]</th>
<th>Predicted M&lt;sub&gt;n&lt;/sub&gt;</th>
<th>GPC M&lt;sub&gt;n&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.2 M</td>
<td>35600</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>50</td>
<td>0.1 M</td>
<td>17800</td>
<td>4950</td>
<td>1.99</td>
</tr>
<tr>
<td>25</td>
<td>0.05 M</td>
<td>8900</td>
<td>4820</td>
<td>1.5</td>
</tr>
</tbody>
</table>

<sup>a</sup> Polymerization conditions: CH<sub>2</sub>Cl<sub>2</sub>, room temperature, 18 hour reaction before quenching.  
<sup>b</sup> GPC measured with CHCl<sub>3</sub> as the mobile phase, relative to narrow PDI polystyrene standards

No quantitative structural data were available using \(^{13}\)C NMR for the N-phenylsuccinimide functionalized polymers because the allylic trans carbons usually overlapped with the aliphatic carbons \(\alpha\) to the carbonyls (around 44 ppm). Therefore, we decided to prepare N-alkyl succinimide functionalized polymers with the hope that a variation in the electronic effects of the substituent in the succinimide moiety would
allow differentiation between the allylic carbons of the polymer chain. Polymers from M-2 and M-3 were readily prepared in a controlled fashion with Ru-III. The allylic trans carbon of poly-2 distinctly appeared at 45.5 ppm, 5 ppm downfield from the carbons α to cis double bonds. Quantitative integration indicated a cis-double bond content in the polymer of 75%. As a point of comparison, a 58% cis-double bond configuration is observed for poly(bicyclo[3.2.0]heptene) prepared with Ru-I.\textsuperscript{16a} The high cis content contrasts with the usual high trans (> 80%) content for polynorbornenes prepared with Ru-III. Typical Ru-based catalytic systems have been shown to produce high-trans polymers but interestingly, the polymerization of chelating diolefins lead to dramatic increase in cis-content. For example, the ROMP of exo-DCP with RuCl\textsubscript{3} gives a high-trans polymer whereas the polymer from endo-DCP is highly cis.\textsuperscript{16b} Also, the inclusion of a small amount of endo-DCP in the ROMP of norbornene raises the cis-content from 5 to 95%. In our system, the unreactive olefin may interact by chelation with the metal center and therefore influence the way by which the catalyst associates with the cyclobutene ring (chelating assistance).

No attempts to study the polymer tacticity was made but multiple carbon resonances for most of the atoms in the repeat unit suggest an atactic structure.

With the exception of M-4, M-6 and M-16, well-defined monodisperse polymer samples over a wide range of molecular weights could be prepared with Ru-III. This catalyst exhibits a unique behavior with these potentially active cyclobutene monomers as illustrated by the fact that the polymerization of norbornene is not controlled at all under the same conditions. Furthermore, even though the potentially reactive [2.2.2]
strained ring is present within each repeat unit, they do not appear to be susceptible to attack by the active propagating species as evidenced by the overall absence of cross-linking or gelling phenomena. Also, an interesting feature of the polymer $^1$H NMR spectrum is the large downfield shift (0.2-0.6 ppm) of the remaining olefinic protons of the [2.2.2] ring and this downfield chemical shift depends on the nature of the substituents of the aromatic ring. The remarkable behavior of the ruthenium-based catalyst prompted us to study the activity of other well-defined ruthenium alkylidenes for the prepared cyclobutene derivatives (Table 2.5).

Table 2.5. Comparison of the well-defined ruthenium catalysts' activity.$^a$

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Catalyst</th>
<th>Yield (%)</th>
<th>GPC$^b$ $M_n \times 10^{-3}$</th>
<th>Predicted $M_n$</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-2</td>
<td>Ru-III</td>
<td>90</td>
<td>27</td>
<td>21500</td>
<td>1.07</td>
</tr>
<tr>
<td></td>
<td>Ru-VI</td>
<td>93</td>
<td>138</td>
<td>21500</td>
<td>1.49</td>
</tr>
<tr>
<td></td>
<td>Ru-III</td>
<td>77</td>
<td>29</td>
<td>36700</td>
<td>1.09</td>
</tr>
<tr>
<td></td>
<td>Ru-IV</td>
<td>83</td>
<td>12</td>
<td>23000</td>
<td>1.20</td>
</tr>
<tr>
<td>M-7</td>
<td>Ru-V</td>
<td>67</td>
<td>22</td>
<td>36700</td>
<td>1.57</td>
</tr>
<tr>
<td></td>
<td>Ru-VI</td>
<td>85</td>
<td>41</td>
<td>36700</td>
<td>1.66</td>
</tr>
</tbody>
</table>

$^a$ Polymerization conditions: CH$_2$Cl$_2$, room temperature, [cat] = 0.002 M, 5 hours reaction time before quenching. $^b$ GPC measured with CHCl$_3$ as the mobile phase, relative to narrow PDI polystyrene standards.

No polymer was recovered when using the first-generation Grubbs' catalyst Cl$_2$Ru(CHPh)(PPh$_3$)$_2$ (Ru-II). This result clearly supports the determinant role of the phosphine substituent in the tuning of the catalyst activity but is quite surprising as
norbornene (NBE) can be polymerized in a living fashion using Ru-II. As the ring strain energy of those cyclic structures is quite similar, the lack of activity must be related to the electronic character of the metal. Substitution of PPh₃ by PCy₃, a larger and more basic phosphine, is known to increase the metathesis activity: controlled polymerization of the cyclobutene derivatives but uncontrolled polymerization of norbornene in our case. Nevertheless, no polymer was recovered from the copolymerization of norbornene and M-2 ([NBE] = 0.6 M, [M-2] = 0.06 M, [Ru-III] = 0.006 M), suggesting that M-2 shuts down the activity of the catalyst. NMR analysis of a 1:1 mixture of M-2 and Ru-III indicated that the starting alkylidene proton, triplet at 19.57 ppm (J = 10.2 Hz), fully disappeared but a new triplet could be seen at 16.68 ppm (J = 17.2 Hz) along with 2 quartets at 17.44 and 17.22 ppm (J = 9.6 Hz). The coordination of Ru-III to M-2 may lead to the formation of dormant, inactive species.

The bis-ruthenium catalyst Ru-IV displayed a moderate activity but with increased molecular weight distributions. Polymerization trials with Ru-V and Ru-VI in which one PCy₃ ligand has been substituted by a N-heterocyclic carbene, resulted in less controlled polymerizations that produced polymers with higher PDIs and higher molecular weights than expected. Following of the polymerization behavior of M-2 by Ru-VI using ¹H NMR confirmed that propagation is much faster than initiation as indicated by an initiation efficiency of only 10% (20 eq. M-2). Those last results are not surprising: Ru-VI displays a high activity for the polymerization of low strained olefins and even tri-substituted cyclic olefin at the same level of Schrock's catalysts.¹⁶c
2.2.2. Characterization of a living system

The concept of living polymerization has been first outlined by Flory\textsuperscript{17}, Szwarc\textsuperscript{18} and Gold.\textsuperscript{19} A living polymerization can be defined as a chain growth process occurring in the absence of chain transfer and chain termination steps. Therefore, the immediate consequence is that the average molecular weight of the polymer can be described by the weight of monomer consumed divided by the number of moles of chain initiated. Upon complete conversion, a wide range of predictable monodisperse polymer samples can be obtained by varying the monomer to initiator ratio. As the chain ends do not die after complete monomer consumption, upon addition of another monomer, well-defined block copolymers can be prepared. Block copolymers are of particular interest for phase separation studies when each block displays different properties (e.g., hydrophobic, hydrophilic, etc.). Block copolymers can also have interesting properties in solution. They can aggregate in the form of micelles that can be used for the specific encapsulation of small drug molecules and be used as drug delivery systems. Dealing with a living system is not necessary the goal of every polymerization process as large molecular weight distributions can be useful for getting some specific properties such as lower shear viscosity and high gel strength in polymer melts. Also, in emulsion polymerization, latexes displaying adhesive properties usually have broad molecular weight distribution (PDI > 5).\textsuperscript{20}

From the initial polymerization studies monodisperse polymer samples of M-2 (PDI ≤ 1.1) were obtained with the Grubbs' ruthenium catalyst Ru-\textbf{III}. Therefore, the living behavior of this system was investigated with M-2 as a reference monomer.
To test for the presence of chain transfer, several polymer samples were prepared with different initiator / catalyst ratios. All polymerizations went to 100% completion. The measured molecular weights are slightly higher that the ones calculated from the monomer to initiator ratio (Table 2.6). This can be explained by the refractive index difference between the polystyrene standards used for the GPC calibration and the ROMP polymer. In all cases, monodisperse samples were obtained and a linear dependence was observed between the average molecular weight and \([\text{M-3}] / [\text{Ru-III}]\), indicating a lack of chain transfer (Figure 2.6).

Following the polymerization using \(^1\)H NMR indicated that the monomer consumption was a first order kinetic process, which indicates a lack of chain termination (Figure 2.6). The rate law for the polymerization can therefore be written under the form:

\[
\text{rate} = -\frac{d[\text{M-3}]}{dt} = k_{\text{obs}}[\text{M-3}]
\]

A first order rate law was also observed for monomers \textbf{M-3} to \textbf{M-14} (see 3.1), the only exception being \textbf{M-4} (Figure 2.8). A change in the slope is observed and the polymerization rapidly slows down. This phenomenon may be related to the constant presence of a high molecular weight shoulder on the GPC chromatogram.

The dependence of the polymerization vis-à-vis the catalyst concentration was also investigated. Keeping a monomer concentration of 0.2 M, several polymerization reactions with different monomer to catalyst ratios were followed using \(^1\)H NMR. The monomer consumption was shown to be a first order in all cases. The pseudo first order rate constant was found to be linearly dependent on the catalyst concentration.
Table 2.6. Molecular weight at various $[\text{M-2}] / [\text{Ru-III}]$ ratios.\textsuperscript{a}

<table>
<thead>
<tr>
<th>[M-2] / [Ru-III]</th>
<th>Predicted $M_n$</th>
<th>GPC $M_n^{b}$</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>50.7</td>
<td>10900</td>
<td>14700</td>
<td>1.07</td>
</tr>
<tr>
<td>100.6</td>
<td>21600</td>
<td>27200</td>
<td>1.07</td>
</tr>
<tr>
<td>146.8</td>
<td>31600</td>
<td>38900</td>
<td>1.09</td>
</tr>
<tr>
<td>192.2</td>
<td>41300</td>
<td>50400</td>
<td>1.09</td>
</tr>
<tr>
<td>254</td>
<td>54600</td>
<td>73500</td>
<td>1.09</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Polymerization conditions: CH$_2$Cl$_2$, room temperature, $[\text{Ru-III}] = 0.002$ M, 18 h reaction before quenching. \textsuperscript{b}GPC measured with CHCl$_3$ as the mobile phase, relative to narrow PDI polystyrene standards.

Figure 2.6. Molecular weight of poly-2 samples.
Figure 2.7. Plot of kinetic data for the polymerization of M-2 initiated by Ru-III.

Figure 2.8. Plot of kinetic data for the polymerization of M-4 initiated by Ru-III.
The polymerization rate law becomes

\[
\text{rate} = k_{\text{cat}}[\text{Ru-III}][\text{M-3}]
\]

For the system M-2 / Ru-III, we have: \(k_{\text{cat}} = 3.76 \times 10^{-2} \text{ s}^{-1}\text{M}^{-1}\) (Figure 2.9).

![Figure 2.9. Determination of the second order rate constant of polymerization for M-2 initiated by Ru-III at 25°C in CDCl₃.](image)

To our knowledge, no absolute rate constant has been reported for any polymerization performed with Ru-III. The polymerization of norbornene with the analog Cl₂Ru(CHPh)(PPh₃)₂ (Ru-II) is slower with \(k_{\text{cat}} = 1.28 \times 10^{-3} \text{ s}^{-1}\text{M}^{-1}\).²¹ Ru-II is known to be less active as compared to Ru-III with which the uncontrolled polymerization of norbornene is observed. The living polymerization of 3,4-diethylester cyclobutene proceeds at a faster rate with the Schrock's catalyst Mo-II \(k_{\text{cat}} = 1.40(6) \times 10^{-1} \text{ s}^{-1}\text{M}^{-1}\).¹⁵b Also, the polymerization of norbornene and functionalized norbornenes is two orders of magnitude faster.²²
The above kinetic studies along with the linear dependence of the molecular weight vis-à-vis the monomer to catalyst ratio, demonstrate that a living polymerization is achieved with catalyst \textbf{Ru-III}. This is a unique monomer / catalyst combination. The living character was also illustrated by the preparation of well-defined block copolymers in high yields (Table 2.7).

\begin{table}
\centering
\caption{Examples of well-defined block copolymers prepared with \textbf{Ru-III}.\textsuperscript{a}}
\begin{tabular}{cccc}
\hline
Block 1 & Block 2 & Predicted M\textsubscript{n} & GPC M\textsubscript{n}\textsuperscript{b} & PDI \\
\hline
M-2 & M-8 & 28100 & 26650 & 1.14 \\
M-8 & M-2 & 28100 & 27650 & 1.12 \\
\hline
\end{tabular}
\end{table}

\textsuperscript{a} Polymerization conditions: CH\textsubscript{2}Cl\textsubscript{2}, room temperature, \([\text{Ru-III}]_0 = 0.002 \text{ M}, \frac{[M-2]}{[\text{Ru-III}]} = \frac{[M-8]}{[\text{Ru-III}]} = 50, \text{ first block: 6h30 reaction, second block: 16h reaction.} \textsuperscript{b} GPC measured with CHCl\textsubscript{3} as the mobile phase, relative to narrow PDI polystyrene standards.

\subsection*{2.2.3. Experimental section}

\textit{General procedures and characterizations}

All polymerizations were carried out in a MBraun UNILab drybox under nitrogen atmosphere using dry and degassed solvents (MBraun solvent system).

Alternatively, manipulations involving air- and moisture-sensitive compounds were carried under an atmosphere of prepurified nitrogen using standard Schlenk techniques.

\textsuperscript{1}H NMR spectra were obtained at 300 MHz with GE NMR Omega spectrometer and at 300, 400 MHz with Varian-Mercury NMR spectrometers. Chemical shifts for \textsuperscript{1}H
NMR spectra are reported in $\delta$ (ppm), positive values indicating shifts downfield of tetramethylsilane and are referenced to selected residual proton peaks of the solvent as follows: CDCl$_3$, 7.27, singlet. Significant $^1$H NMR data are tabulated in order: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br: broad peak), coupling constant in Hertz, number of protons. $^{13}$C{$^1$H} proton decoupled NMR were measured at 75 MHz with a GE NMR Omega spectrometer and at 100 MHz on a Varian-Mercury spectrometer. Chemical shifts for $^{13}$C{$^1$H} NMR spectra are reported in $\delta$ (ppm), positive values indicating shifts downfield of tetramethylsilane, and are referenced to selected residual peaks of the solvents as followed: CDCl$_3$, 77.23. $^{19}$F NMR spectra were measured at 376.46 MHz using a Varian-Mercury spectrometer and $^{19}$F NMR spectra are referenced to C$_6$F$_6$ used as an external 0 ppm reference.

Molecular weight and molecular weight distribution were measured via gel permeation chromatography using a Jasco PU-1580 pump and a Jasco RI-1530 refractive index detector. The stationary phase consisted of two PL-Gel mixed C columns. Chloroform was used as the mobile phase. Molecular weights are relative to narrow molecular weight polystyrene standards (Pressure Chemical, Inc.).

**Reagents**

CH$_2$Cl$_2$ used for polymerization reactions was purified by passing through one column filled with activated A2 Alumina catalyst and one column filled with activated Q5 copper catalyst under nitrogen atmosphere (MBraun solvent system). CDCl$_3$ was dried over CaH$_2$, distilled under nitrogen and after three freeze-pump-thaw cycles was stored into the dry box and used no more than one month later. 1,2-dichloroethane used
as a reference in the $^1$H NMR kinetic experiments was dried over CaH$_2$, distilled under nitrogen and after three freeze-pump-thaw cycles stored in the dry box.

RuCl$_3$.nH$_2$O was purchased from Strem Chemicals, Inc. [Ru(p-cymene)Cl$_2$]$_2$ was purchased from Aldrich. Mo-I, Mo-II were purchased from Strem Chemicals, Inc. and stored in the freezer of the dry box at -35°C. Ru-II, was synthesized from Ru(PPh$_3$)$_3$Cl$_2$ according to published procedures. Mo-I, Mo-II were purchased from Strem Chemicals, Inc. and stored in the freezer of the dry box at -35°C. Ru-II, was synthesized from Ru(PPh$_3$)$_3$Cl$_2$ according to published procedures. Mo-I, Mo-II were purchased from Strem Chemicals, Inc. and stored in the freezer of the dry box at -35°C. Ru-II, was synthesized from Ru(PPh$_3$)$_3$Cl$_2$ according to published procedures.

$^{22}$ Ru-IV$^{23}$, Ru-V$^{25}$ were prepared according to the litterature and stored in the dry box. Ru-III$^{21,26}$ and Ru-VI$^{27}$ were initially purchased from Strem Chemicals, Inc. but were later one prepared according to the litterature.

**Experimental procedures**

**General polymerization procedure for the comparison of catalysts' activity.**

To the desired monomer (100 equiv) dissolved in CH$_2$Cl$_2$ was added a freshly prepared CH$_2$Cl$_2$ catalyst solution ([monomer] = 0.2 M, [catalyst] = 0.002 M). The reaction was stirred at room temperature for 5 hours. Polymerization reactions performed with the molybdenum catalysts were quenched by addition of benzaldehyde (100 equiv) whereas ethyl vinyl ether (100 equiv) was used to quench the polymerizations performed with ruthenium-based catalysts. After 1 h stirring, the polymer solution was added dropwise to methanol under vigorous stirring. The precipitated powder was recovered by filtration or centrifugation. It was reprecipitated into methanol from a CH$_2$Cl$_2$ solution and dried under vacuum for 24 h at 40°C.

**Determination of the relation between the polymer molecular weight and the $[M-2] / [Ru-III]$ ratio.** In 5 vials, 50 mg (0.23 mmol) of M-2 was exactly weighted. It was dissolved with CH$_2$Cl$_2$ so that $[M-2] = 0.2$ M after addition of the catalyst solution.
A stock solution of Ru-III was freshly prepared (10.1 mg, 1.32 mL CH₂Cl₂) and the desired amount was added via syringe to each monomer solution so that [M-2] / [Ru-III] = 50, 100, 150, 200, 250. After 18 h reaction at room temperature (23°C), each reaction was quenched by addition of ethyl vinyl ether (100 equiv). After 1 h stirring, the polymer solutions were added dropwise to 40 mL methanol. The precipitated white powders were recovered by centrifugation and dried under vacuum at 40°C.

**General procedure for the determination of the pseudo order rate constant (k_{obs}) using ¹H NMR.** The desired amount of monomer (20 equiv) was dissolved in CDCl₃. To this solution was added 1,2-dichloroethane (5 µL), used as a reference for integration. The solution was transferred in a NMR tube equipped with a teflon valve via a syringe. To this solution was added by syringe the desired amount of catalyst from a freshly prepared catalyst solution (CDCl₃). All the volumes of chloroform have been chosen so that the total volume is exactly 600 µL. As the catalyst solution is added, a timer is started. The NMR tube is taken out of the dry box, sealed with parafilm and ¹H NMR spectra are collected at various time intervals at 21-22°C (NMR room temperature). The evolution of the relative integration of the monomer alkene protons versus the reference is recorded with time. The evolution of the monomer concentration is usually followed during 2h30.

**Determination of the 2^{nd} order rate constant (k_{cat}) using ¹H NMR.** Several experiments using the above procedure were performed by keeping [M-2] constant at 0.2 M but the amount of Ru-III used was adjusted so that [Ru-III] = 0.00133, 0.002, 0.004, 0.01, 0.02 M. For each experiment, the evolution of [M-2] was followed during 2h30 and
each polymerization was first order in \([\text{M-2}]\). The plot of the determined \(k_{\text{obs}}\) versus \([\text{Ru-III}]\) gave the value of \(k_{\text{cat}}\) (slope).

**Preparation of block copolymers from M-2 and M-8 using Ru-III.** To M-2 (66.2 mg, 50 equiv) or M-8 (105.6 mg, 50 equiv) dissolved in 2.5 ml CH\(_2\)Cl\(_2\) was added a freshly prepared Ru-III catalyst solution (5.0 mg, 0.5 mL CH\(_2\)Cl\(_2\)). After stirring at RT for 6h30, M-8 (104.8 mg, 50 equiv) or M-2 (65.3 mg, 50 equiv) dissolved in CH\(_2\)Cl\(_2\) (0.5 mL) was added. The mixture were stirred for 16 h and then quenched with ethyl vinyl ether (50 µL). After stirring for 1 h, the polymers were precipitated by dropwise addition to 150 mL methanol. The precipitated solids were recovered by filtration and dry under vacuum at 40°C for 24 h. Both of them were white brittle solids (147.4 mg, 86% and 155 mg, 90%).

**Typical polymerization of M-2 using Ru-III.** To M-2 (262 mg, 200 equiv) dissolved in 2.5 mL of CH\(_2\)Cl\(_2\) was added a solution of Ru-III (5.4 mg, 0.5 mL of CH\(_2\)Cl\(_2\)) under vigorous stirring. The mixture progressively turned from purple/pinkish to dark yellow and was stirred for 5 h at room temperature. The polymerization was quenched by adding a few drops of ethyl vinyl ether and stirred for 30 min. It was taken out of the dry box, slightly concentrated, and added dropwise to methanol under vigorous stirring. The precipitated polymer was recovered by filtration and dried under vacuum. It was further purified by redissolution with CH\(_2\)Cl\(_2\) and subsequent precipitation with methanol. A brown pale flocculent solid was recovered (225 mg, 86%). \(^1\text{H} \text{NMR} \delta: 6.32 \text{ (br, 2H), 5.16} \text{ (br, 2H), 3.15, 3.10, 2.95, 2.88, 2.85, 2.69 (br, 9H).} \ ^{13}\text{C} \{^1\text{H}\} \text{NMR} \delta: 178.43, 132.12, 131.13, 130.84, 45.63, 44.37, 44.11, 40.52, 38.68, 38.20, 24.79.
Typical polymerization of M-7 using Ru-III. To M-7 (223 mg, 100 equiv) dissolved in 2.5 mL of CH$_2$Cl$_2$ was added a solution of Ru-III (5.0 mg, 0.5 mL of CH$_2$Cl$_2$) under vigorous stirring. The mixture progressively turned from purple/pinkish to dark yellow and was stirred for 5 h at room temperature. The polymerization was quenched by adding a few drops of ethyl vinyl ether and stirred for 30 min. It was taken out of the dry box, slightly concentrated, and added dropwise to methanol under vigorous stirring. The precipitated polymer was recovered by filtration and dried under vacuum. It was further purified by redissolution with CH$_2$Cl$_2$ and subsequent precipitation with methanol. A white powder was recovered (171 mg, 77%). $^1$H NMR $\delta$: 6.40 (br, 2H), 5.19 (br, 2H), 3.47, 3.33, 3.24, 3.01, 2.75 (br, 8H). $^{13}$C $\{$$^1$H$\}$ NMR $\delta$: 174.90, 143.55 (dm, J = 255 Hz), 142.67 (dm, J = 183.8 Hz), 137.95 (dm, J = 262 Hz), 132.26 (m), 131.09, 107.00, 44.92-44.69 (m), 40.23, 39.29-38.20 (m); $^{19}$F NMR $\delta$: 20.85 (br, 1F), 18.7, 17.9, 17.5, 16.95 (br, 1F), 10.87 (br, 1F), 0.65 (br, 2F).
2.3. Functionalization with fluorine groups

2.3.1. $^{19}$F NMR characterization of the fluorinated monomers

The $^{19}$F NMR spectrum of the first fluorinated polymer prepared from M-7 with catalyst Ru-III was intriguing as a pattern was observed for one of the ortho fluorine while the other peaks were quite broad. This broadening is a typical feature of polymer NMR spectra. In the $^{19}$F NMR spectrum of poly-7 prepared with a different catalyst (Ru-VI), the pattern changed (Figure 2.11). To get a better understanding of the origin of this phenomenon, a family of fluorinated N-phenyl succinimide functionalized monomers was prepared (Table 2.8). They differ by the bulkiness and the position of the fluorinated group on the aromatic ring.

Table 2.8. Investigated fluorinated monomers.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Group on the N-phenylsuccimide moiety</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-5</td>
<td>2-fluoro</td>
</tr>
<tr>
<td>M-6</td>
<td>4-fluoro</td>
</tr>
<tr>
<td>M-7</td>
<td>2,3,4,5,6-pentafluoro</td>
</tr>
<tr>
<td>M-8</td>
<td>2-trifluoromethyl</td>
</tr>
<tr>
<td>M-9</td>
<td>3-trifluoromethyl</td>
</tr>
<tr>
<td>M-10</td>
<td>4-trifluoromethyl</td>
</tr>
<tr>
<td>M-11</td>
<td>2-trifluoromethoxy</td>
</tr>
<tr>
<td>M-12</td>
<td>3,5-ditrifluoromethyl</td>
</tr>
</tbody>
</table>
In the $^{19}$F NMR spectra of the monomers having either meta or para substituents, only one signal was present, even for M-12 that possesses two bulky trifluoromethyl groups at the meta positions. Those substituents have no influence on the position of the phenyl ring vis-à-vis the diimide ring plane. Hence, the aromatic ring can rotate freely.

On the contrary, the incorporation of an ortho substituent slows down the rotation of the $N_{sp2}$-$C_{sp2}$ bond due to steric hindrance between the substituent and the carbonyl group of the succinimide moiety as already discussed (cf. 2.1.3). Therefore, two peaks were seen in the $^{19}$F NMR spectrum of M-5 (42.41, 44.35 ppm) in a 1:1 ratio, indicating that neither of the diimide faces is favored with the simple fluorine group. The same observation is valid for M-7: four peaks were seen in a 1:1:2:1 ratio as the ortho fluorines are not equivalent. As the size of the ortho substituent increases, the rotation process slows down and eventually, one conformation will be favored (lower energy) if it reduces the steric hindrance. Using molecular models, it clearly appears that the presence of the bulky substituent on the "endo" face of the diimide ring is greatly disfavored due to the steric interactions with the double bond of the [2.2.2] ring.

Two peaks were seen in the $^{19}$F NMR spectrum of M-11 at 104.88 and 104.41 ppm but in a 1.4:1 ratio, respectively, at room temperature. The face discrimination was more important with M-8: two signals at 101.07 and 100.54 ppm in a 1:10.5 ratio, respectively.
after equilibration of the major isomer (endo-exo) at room temperature. After annealing at 50°C for 24 h, this ratio equilibrated to 1:2.6. For M-11, one compound was seen on TLC whereas the two rotamers of M-8 could be differentiated. Attempts at their separation failed as isomerization occurred readily in solution at 25°C. On the other hand, when a tert-butyl group was introduced at the ortho position, the rotation was frozen and the two distinct rotamers could be separated and characterized independently (cf. 2.1.3). No isomerization was observed for this derivative at 50°C.

While the presence of rotamers was also seen on the $^1$H and $^{13}$C NMR spectra, $^{19}$F NMR proved to be very practical. This is because the fluorinated groups are very sensitive to the chemical environments and appear in distinct region of the spectrum, and this makes quantitative measurement possible.

### 2.3.2. Polymers prepared from fluorinated cyclobutene derivatives

Interesting and unexpected features were observed in the $^{19}$F NMR spectra of the new ROMP polymers prepared from these fluorinated monomers. For the polymer of the ortho fluorosubstituted M-5 monomer prepared with Ru-III, two broad peaks were present in a 1:1 ratio at 42.2 and 44.7 ppm (see the inserted spectrum). The latter showed some feature due to the overlap of two peaks (doublet-like). Variation of the NMR sample concentration did
not lead to any change in the spectrum, ruling the possible explanation that this doublet was the result of possible interactions between polymer chains. As the two main peaks are related to the presence of rotamers, the first possible explanation was that in one of the conformations, the fluorine atom was sensitive to the main chain stereochemistry. It appears that this can only occur in the "endo-endo" conformation. In this position, the fluorine group can interact through space with the double bond of the [2.2.2] ring that is itself sensitive to the stereochemistry present in the polymer backbone. If this explanation is correct, then features should also be present in the spectrum of poly-8. A broad singlet was seen at 100.5 ppm whereas overlapping peaks appeared around 101.0 ppm, the minor peak in the monomer spectrum (Figure 2.10).

Figure 2.10. $^{19}$F NMR spectra of poly-8 prepared with Ru-III (left) and Ru-VI (right).
These data support the previous explanation. Furthermore, the observed ratio was approximately 1.8 to 1; which is the apparent thermodynamic ratio as no change occurred upon annealing at 50°C for 24 h. Interestingly, the proportion of "endo-endo" conformation was higher in the polymer than in the starting monomer. This can result from additional steric constraints that are introduced by the polymer chain. It may also be possible that the interaction of the olefin of the [2.2.2] ring with the fluorinated group increased because it can no longer interact through orbital overlap with the cyclobutene as evidenced by the proton downfield chemical shift (≈ 0.3 ppm). Furthermore, in the $^1$H NMR the order of the signals for the ortho aromatic proton were reversed. In the minor conformation, the ortho proton appears at higher field and the chemical shift difference is significantly larger (6.95 vs 6.67 ppm). A change in the pattern of the lower field signal was observed when the polymer was prepared with the very active Ru-VI catalyst. As Ru-III and Ru-VI have a different structure in the propagation step, they are expected to generate a different polymer microstructure (cis/trans isomerism and/or tacticity). Therefore, those data seem to be representative of the sensitivity of the CF$_3$ vis-à-vis the polymer backbone microstructure.
Figure 2.11. $^{19}$F NMR spectra of poly-7 prepared with Ru-III (bottom) and Ru-VI (top).
The $^{19}$F NMR spectrum of poly-7 also proved to be very interesting. As significant broadening was present for each signal, a specific pattern was seen for one of the ortho fluorine groups (Figure 2.11). In this pattern, several peaks are overlapped ($\approx 4$). This observation permits to assign the signal corresponding to each rotamer: the endo-exo $o$-fluorine appears around 21 ppm whereas the endo-endo one is present in the 16-19 ppm region. We still observe a 1:1 ratio between the $o$-fluorine signals, which indicates that the polymer conformation has no influence on the rotation of the phenyl ring. Furthermore, no change in the pattern was observed upon concentration ($10 < c < 100$ mg/mL) and temperature (up to $50^\circ$C) changes. The bad solubility of the polymer in high boiling point NMR solvents (toluene, DMSO) limited the studied temperature range. The pattern did not change when poly-7 was prepared with Ru-IV.

As for poly-8, the pattern really changed when the polymer was prepared with Ru-VI. No information could be obtained on the polymer microstructure from quantitative $^{13}$C NMR experiments as peaks overlapped for the main chain olefinic carbons and in the aliphatic region.

Further evidence that the observed pattern in poly-7 is related to the polymer microstructure was obtained upon following of the polymerization using $^{19}$F NMR (Figure 2.12). Four sets of peaks progressively appear for one of the ortho fluorine groups as the polymerization proceeds. Apparently, the overall shape of the pattern does not change with time. Significant broadening is also observed for the signal of the other ortho fluorine group and interestingly for the meta groups. The broad peaks correspond to overlapping peaks. The meta groups may be sensitive themselves to the polymer
microstructure or the observed broadening may result from the proximity of the ortho fluorine groups.

The fact that the substituents at the meta positions could be themselves sensitive to the polymer microstructure was demonstrated by $^{19}$F NMR analysis of poly-12. First poly-9 was prepared that has only one meta position substituted by a CF$_3$ group. A relatively sharp peak was present in the $^{19}$F NMR spectrum, indicating a very weak sensitivity. But when both meta positions were substituted with the bulky CF$_3$ group, the single sharp signal observed for monomer M-12, was replaced by several overlapped but relatively sharp peaks in the polymer spectrum (Figure 2.13). Once again, when the polymer was prepared with Ru-VI, the overall shape of the pattern did not change but the relative ratio of the different peaks slightly changed.
Figure 2.12. Polymerization of M-7 with Ru-III followed by $^{19}$F NMR.$^a$

$^a$Conditions: CDCl$_3$, room temperature, [M-7] = 0.2 M, 20 equiv.
Figure 2.13. $^{19}\text{F}$ NMR spectra of poly-12 prepared with Ru-III and Ru-VI.
2.3.3. Copolymerization with Cis-cyclooctene

Only a few reports have appeared on the preparation of alternating copolymers from monomer mixtures using ring-opening metathesis polymerization. Alternating copolymers can display unusual and unexpected properties when various functionalized monomers are used. The alternating backbone is unique by itself and this should extend the scope of applications from multi-monomers mixture that are typically used for the preparation of random or block copolymers.

The first report on the preparation of alternating copolymers by ROMP was made in 1983.28 An enantiomeric mixture of 1-methylnorbornene was shown to polymerize in an alternating fashion using ReCl₅, steric hindrance in this heterogeneous system was cited as the driving force for the observed phenomenon. Alternating copolymers from cyclopentene and norbornene, two non-polar monomers, could also be prepared using RuCl₃, IrCl₃ or OsCl₃ in the presence of phenol as cocatalyst or solvent.29 The presence of the alcohol proved to be crucial and formation of a hydrogen-bonded solvent cage around the metal complex was proposed to explain the cross-affinity of the growing polymer chains relative to homopolymerization. Nevertheless, a maximum yield of 20% was obtained.

Another major report appeared in early 2002. Using the well-defined Ru-III catalyst, alternating copolymers could be prepared from cis-cycloctene and functionalized 7-oxanorbornene derivatives (Scheme 2.7).30 The observed catalyst behavior is unique and only applies to a specific combination mixture of polar and non-polar olefins. Best results were obtained with cis-cycloctene (COE) in combination with the exo-dicarboxy
anhydride (1) or the endo-N-ethyl succinimide functionalized 7-oxanorbornene (2) (alternating diads > 96%). The rate of copolymerization of a mixture of COE and 2 was intermediate between the fast rate of the homopolymerization of COE and the slow homopolymerization rate of 2. But surprisingly, the copolymerization of a mixture of COE and 1 was reported to be much faster than both homopolymerizations.

**Scheme 2.7.** Alternating ROMP copolymers from non-polar and polar olefins.

As in our new family of monomers, similar functional groups had been introduced and to compare our system to the reported one, the copolymerization of M-7 and cis-cyclooctene using Ru-III was investigated. M-7 was also chosen so that $^{19}$F NMR studies could be performed.

Monomer mixtures of different compositions could be polymerized using Ru-III. Typically upon addition of the light pink catalyst solution to the colorless solution of monomers, the mixture rapidly turned dark yellow, which is a characteristic color observed for the homopolymerization of M-7. After a period that appeared to depend on
the initial feed, the mixture turned reddish as observed for the homopolymerization of COE performed with Ru-III. The first trial was made from an equivalent mixture of both monomers (100 eq each) with a 24 h reaction time. Estimated using $^1$H NMR, the polymer composition was slightly different from the feed (67% content in M-7) and main chain double bond peaks were very similar to those observed on the NMR spectra of the homopolymers, therefore, the resulting polymer obviously did not have an alternating structure. Also, polymers with different mixture compositions were prepared. In the $^1$H NMR spectra, peaks from both polymers were present and the relative integration was relatively closed to the initial feed. From the color change observation, it appeared that block copolymers might have been produced.

<table>
<thead>
<tr>
<th>Initial M-7 / COE feed $^b$</th>
<th>Polymer composition $^c$</th>
<th>GPC $M_n$ $^d$</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>90 / 10</td>
<td>94 / 6</td>
<td>6300</td>
<td>2.4</td>
</tr>
<tr>
<td>75 / 25</td>
<td>88 / 12</td>
<td>7000</td>
<td>1.91</td>
</tr>
<tr>
<td>60 / 40</td>
<td>76 / 24</td>
<td>9000</td>
<td>2</td>
</tr>
<tr>
<td>40 / 60</td>
<td>47 / 53</td>
<td>11000</td>
<td>2.6</td>
</tr>
<tr>
<td>20 / 80</td>
<td>30 / 70</td>
<td>13000</td>
<td>1.7</td>
</tr>
<tr>
<td>10 / 90</td>
<td>10.5 / 89.5</td>
<td>51000</td>
<td>2.2</td>
</tr>
</tbody>
</table>

$^a$ Polymerization conditions: CH$_2$Cl$_2$, room temperature, 24 h, [M-7] / [Ru-III] = 100, [M-7] = 0.2 M.  
$^b$ Molar ratio %.  
$^c$ from $^1$H NMR by integration of the overlapped main chain olefinic protons relative to the alkene protons of the [2.2.2] ring of poly-7.  
$^d$ Relative to monodisperse polystyrene standards, using CHCl$_3$ as eluant.

Table 2.9. Analysis of copolymers produced from different M-7 / COE mixtures.$^a$

GPC analysis indicated that unimodal polydisperse (PDI > 1.7) molecular weight distributions were obtained (Table 2.9). But, measured molecular weights were relatively
small as compared to the calculated ones, indicating the presence of chain transfer reactions. Also, as the feed was richer in M-7, the molecular weight dropped dramatically and M-7 could be regarded as a chain transfer reagent: the homopolymerization of COE was not controlled and the resulting polymer was barely soluble in chloroform. Kinetic studies indicated that the polymerization of COE with Ru-III was complete within minutes whereas hours were required for the living polymerization of M-7.

**Figure 2.14.** The $^1$H NMR spectrum of an on-going copolymerization of M-7 and COE.

The $^{19}$F NMR analysis of the prepared copolymers was surprising: changes in the pattern of the ortho and meta fluorine groups could be observed. Also, the patterns' evolution was dependent on the copolymer composition (Figure 2.15).
To get a better idea of the copolymer microstructure, the copolymerization was followed using $^1$H NMR. Conveniently, the monomer and polymer peaks were distinct enough to allow quantitative measurements (Figure 2.14).

Figure 2.15. Dependence of the $^{19}$F NMR spectrum on the copolymer composition

$^a$ Copolymer content in cis-cycloctene (mol %, from $^1$H NMR): 89.5 (A), 70 (B), 45 (C), 37 (D), 23 (E), 12 (F), 6 (G).

As expected from the observed color change, the following of the copolymerization using $^1$H NMR indicated that M-7 was the first consumed monomer
whereas the **COE** concentration remained relatively constant in the mixture (Figure 2.16). When the polymerization of **M-7** was complete, **COE** was then incorporated in the polymer chains within a few minutes. In contrast, the polymerization of **M-7** had taken several hours. This selectivity in the copolymerization can be explained by the higher strain present in the cyclobutene ring as compared to the **COE** eight-member ring. Nevertheless, a straight line was not obtained when plotting the logarithm of \([\text{M-7}]\) versus time. The disappearance of **M-7** in the presence of **COE** was no longer a first order kinetic process, indicating the possible presence of chain termination reaction but the polymerizations of both monomers were complete.

![Kinetic data plots of the copolymerization of a M-7 / COE mixture using Ru-III.](image)

**Figure 2.16.** Kinetic data plots of the copolymerization of a **M-7** / **COE** mixture using **Ru-III**.
Could the presence of COE have an influence on the initiation stage? To test this possibility and further estimate the influence of COE on the kinetics of polymerization, the following experiment was conducted. The homopolymerization of M-7 (20 equiv) using Ru-III was followed by $^1$H NMR. After 10 min, initiation was complete as indicated by the disappearance of the initial catalyst proton carbene signal. After 30 min, 60 equiv of cis-cycloctene were added via syringe and the $^1$H NMR experiment continued. Once again, COE was not consumed until the point that M-7 had completely disappeared. In the presence of COE, the kinetics of polymerization of M-7 changed and it was no longer a first order process (Figure 2.17). A rate increase was observed.

![Figure 2.17. Logarithm plot of the disappearance of M-7 versus time.](image-url)
Those data indicate that the presence of cis-cyclooctene certainly modifies the catalyst reactive site during the propagation stage. The influence of olefinic additive on polymerizations performed with ill-defined catalyst has already been reported. In our system, the dissociation of one phosphine ligand has been proposed in the polymerization mechanism.\textsuperscript{31} This generates one coordination site for the olefin monomer but the phosphine dissociation process is an equilibrium as indicated by the rate dependence on phosphine concentration. This dependence has not been evaluated in our system but it is fair to assume that polymerization proceeds with the same mechanism. Among the metal substrates used for ROMP, the affinity of ruthenium for olefins is known to be one of the highest. Therefore, COE could compete and disturb the equilibrium of the phosphine dissociation leading to an uncontrolled polymerization. One could also think that a slight incorporation of COE in the polymer could influence the polymerization through weak coordination of olefins in the backbone to the propagating species. But as already reported, this would have slowed down the propagation and the opposite happens in our case.

Spectator additives (e.g., solvents) can also have an influence on the generated microstructure as they weakly interact with the propagating species.\textsuperscript{32} This can explain the dependence of the $^{19}$F NMR spectrum of the copolymer on the composition of the initial monomer mixture. This influence on the polymer microstructure was also demonstrated by the following experiment. The polymerization of M-7 was initiated with Ru-III. The solution was separated in several fractions and to each fraction, COE was
added at different times. The $^{19}$F NMR spectra of the recovered copolymers had a different aspect (Figure 2.18).

![Figure 2.18. $^{19}$F NMR spectra of copolymers with COE added at different times.\textsuperscript{a,b}

\textsuperscript{a}Polymerization conditions: CH$_2$Cl$_2$, [M-7] / [Ru-III] = 20, [M-7] = 0.2 M, 60 eq COE added. \textsuperscript{b} Time of COE addition: $t=0$ (A), $t = 30$ min (B), $t = 1$ h (C), $t = 2$ h (D), $t = 3$ h (E); no COE addition (F).

Addition of COE after a 3 h reaction time (93% conversion) had no effect on the $^{19}$F NMR spectrum that was similar to the homopolymer one. This also indicates that the observed differences in the NMR spectra are not related to the presence of the
cyclooctene block and the formation of a possible polymeric superstructure can be ruled out.

**Figure 2.19.** $^{19}$F NMR spectra of a M-7/COE copolymer (20% M-7) in C$_6$D$_6$ (top) and in CDCl$_3$ (bottom).

All those experiments confirm that the presence of cis-cyclooctene modifies the kinetics of the polymerization of the ento-tricyclo[4.2.2.0$^{2,5}$]deca-3,9-diene structure
with catalyst Ru-III. The form of the reactive site during propagation is different as indicated by the loss of control and different polymer microstructure generated. The incorporation of cis-cyclooctene leaded to a slight improvement of the solubility with high COE content. Apart from chloroform, benzene was the only good solvent for NMR. On the $^{19}$F NMR spectrum taken from a C$_6$D$_6$ solution, the overall pattern does not change except that more overlapping is present (Figure 2.19).

2.3.4. Conclusions

The functionalization of the monomer with fluorine groups has lead to interesting and unexpected observations. The ortho and meta fluorinated substituents of the N-phenyl succinimide moiety can be regarded as sensitive reporters vis-à-vis the polymer microstructure. Unfortunately, limited solubility of the polymers and overlapping peaks in the $^{13}$C NMR spectra prevented us from precisely relating the $^{19}$F NMR pattern with the fine polymer microstructure.

2.3.5. Experimental section

*General procedures and characterizations*

All polymerizations were carried out in a MBraun UNILab drybox under nitrogen atmosphere using dry and degassed solvents (MBraun solvent system).

$^1$H NMR spectra were obtained at 300, 400 MHz with Varian-Mercury NMR spectrometers. Chemical shifts for $^1$H NMR spectra are reported in $\delta$ (ppm), positive values indicating shifts downfield of tetramethysilane and are referenced to selected
residual proton peaks of the solvent as follows: CDCl$_3$, 7.27, singlet; $^{19}$F NMR spectra were measured at 282.34 MHz using a Varian-Geminy NMR spectrometer or at 376.46 MHz using a Varian-Mercury NMR spectrometer in CDCl$_3$. $^{19}$F NMR spectra are referenced to C$_6$F$_6$ used as an external 0 ppm reference.

Molecular weight and molecular weight distribution were measured via gel permeation chromatography using a Jasco PU-1580 pump and a Jasco RI-1530 refractive index detector. The stationary phase consisted of two PL-Gel mixed C columns. Chloroform was used as the mobile phase. Molecular weights are relative to narrow molecular weight polystyrene standards (Pressure Chemical, Inc.).

**Reagents**

CH$_2$Cl$_2$ used for polymerization reactions was purified by passing through one column filled with activated A2 Alumina catalyst and one column filled with activated Q5 copper catalyst under nitrogen atmosphere (MBraun solvent system). CDCl$_3$ was dried over CaH$_2$, distilled under nitrogen and after three freeze-pump-thaw cycles was stored into the dry box and used no more than one month later. 1,2-dichloroethane used as a reference in the $^1$H NMR kinetic experiments was dried over CaH$_2$, distilled under nitrogen and after three freeze-pump-thaw cycles stored in the dry box.

**Experimental procedures**

General polymerization procedure of the fluorinated monomers with the ruthenium-based catalysts. To the desired monomer (100 equiv) dissolved in CH$_2$Cl$_2$ was added a freshly prepared CH$_2$Cl$_2$ catalyst solution ([monomer] = 0.2 M, [catalyst] = 0.002 M). The reaction was stirred at room temperature until complete conversion was
obtained as indicated by the $^1$H NMR analysis of a quenched aliquot. The polymerization was quenched with ethyl vinyl ether (100 equiv). After 1 h stirring, the polymer solution was added dropwise to methanol under vigorous stirring. The precipitated powder was recovered by filtration or centrifugation. It was reprecipitated into methanol from a CH$_2$Cl$_2$ solution and dried under vacuum for 24 h at 40°C.

**Preparation of copolymers from M-7 and cis-cyclooctene with Ru-III.** A stock solution of M-7 and a stock solution of cis-cyclooctene were prepared in CH$_2$Cl$_2$. The desired amount of each solution was added in a vial via syringe. More CH$_2$Cl$_2$ was added so to get a final concentration in M-7 of 0.2 M. To the monomer mixture, the desired amount of catalyst from a stock solution was added via syringe and the reaction mixture was vigorously stirred for 24 h. All reactions were performed with [M-7] / [Ru-III] = 100 and [M-7] = 0.2 M. The polymerization was quenched by addition of ethyl vinyl ether (100 eq). After 1 h stirring, the mixture was added dropwise to methanol and the resulting powder was recovered by centrifugation. It was reprecipitated into methanol from a CH$_2$Cl$_2$ solution and dried under vacuum for 24 h at 40°C before analysis.

**Determination of the kinetics of the copolymerization using $^1$H NMR.** 44.6 mg (0.121 mmol, 20 equiv) of M-7 were dissolved with exactly 500 µL CDCl$_3$. To this solution were added 16 µL (0.123 mmol, 20 equiv) of cis-cyclooctene and 1,2-dichloroethane (3 µL). The mixture was transferred to a NMR tube equipped with a Teflon valve using a pipette. To this mixture was added a freshly prepared solution of Ru-III (5.0 mg, 0.006 mmol, 100 µL CDCl$_3$) and a timer was started. The NMR tube was shaken, taken out of the dry box and sealed with parafilm. The evolution of the alkene
proton signals for both monomers (6.02 and 5.93 ppm for M-7, 5.75-5.55 ppm for cis-cyclooctene) compared to the 1,2-dichloroethane signal (3.78 ppm) was followed using $^1$H NMR at 21-22°C.

**Influence of cis-cyclooctene addition on the on-going homopolymerization of M-7 with Ru-III.** To a solution of M-7 (251.1 mg, 0.0684 mmol, 20 equiv) in CH$_2$Cl$_2$ (2.8 mL) was added a solution of Ru-III (28.6 mg, 0.0034 mmol, 610 µL CH$_2$Cl$_2$) and a timer was started. The solution rapidly turned dark yellow. At different times, a 680 µL aliquot (0.0137 mmol M-7, 0.68 µmol Ru-III) was transferred with a syringe in another vial and cis-cyclooctene was added (53 µL, 0.041 mmol, 60.3 equiv) under vigorous stirring. All aliquots progressively turned reddish after some time. After 8 h, each aliquot was quenched with ethyl vinyl ether (50 µL). After stirring for 1 h, the polymerization mixture was added dropwise to 75 mL methanol. The precipitated powder was recovered by centrifugation, dried under vacuum at 40°C for 24 h before $^{19}$F NMR analysis.

**Influence of cis-cyclooctene addition on the on-going homopolymerization of M-7 with Ru-III followed by $^1$H NMR.** The homopolymerization of M-7 (46.5 mg, 0.127 mmol, 20 equiv) in CDCl$_3$ (600 µL) with Ru-III (5.0 mg, 0.006 mmol) and 1,2-dichloroethane (3 µL) as a reference is closely followed using $^1$H NMR in a NMR tube equipped with a sealed rubber septum. Initiation was complete in less that 10 min. After 32 min (29% conversion of M-7), cis-cyclooctene (47 µL, 60 eq) was added with a syringe and NMR data acquisition continued until complete disappearance of both monomers.
2.4. References and notes


   
   
   
   
   
   
   (15) (a) Sanders, R.S. *Macromolecules* **1995**, 28, 4347
   
   (b) Perrott, M. PhD. Thesis, University of California Berkeley, 1996
   
   
   
   (c) Trnka, T.M.; Grubbs, R.H. *Acc. Chem. Res.* **2001**, 34, 18
   
   
   
   
   
   (20) Personal experience with latexes preparation
   
   


Scholl, M.; Ding, S.; Lee, C.W.; Grubbs, R.H. *Org. Lett.* **1999**, *1*, 953


3.1. Variation of the electronic character of the substituents

A slight variation in the yields of polymerizations performed for a fixed time (5 h) with monomers having different substituents on the succimide moiety using Ru-III prompted us to study the influence of the substituents on the kinetics of the polymerizations. As mentioned, with the lone exceptions of M-4 and M-6, the monomer consumption was a first order kinetic process, which indicated a lack of chain termination in all cases. The pseudo first order rate constants were determined using $^1$H NMR in CDCl$_3$ at 21-22 °C (NMR room temperature). Those rates ($k_{\text{obs}}$) varied from $1.82 \times 10^{-4}$ s$^{-1}$ for M-7 to $4.08 \times 10^{-4}$ s$^{-1}$ for M-2, thus a relative polymerization rate of 1 to 2.24 (Table 3.1).

**Table 3.1.** Relative polymerization rates of various succinimide functionalized monomers.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Succinimide substituent</th>
<th>Relative polymerization rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-7</td>
<td>2,3,4,5,6-pentafluorophenyl</td>
<td>1</td>
</tr>
<tr>
<td>M-12</td>
<td>3,5-ditrifluoromethylphenyl</td>
<td>1</td>
</tr>
<tr>
<td>M-11</td>
<td>2-trifluoromethoxyphenyl</td>
<td>1.16</td>
</tr>
<tr>
<td>M-5</td>
<td>2-fluorophenyl</td>
<td>1.29</td>
</tr>
<tr>
<td>M-15</td>
<td>4-nitrophenyl</td>
<td>1.30</td>
</tr>
<tr>
<td>M-10</td>
<td>4-trifluoromethylphenyl</td>
<td>1.42</td>
</tr>
<tr>
<td>M-14</td>
<td>4-methoxyphenyl</td>
<td>1.60</td>
</tr>
<tr>
<td>M-8</td>
<td>2-trifluoromethylphenyl</td>
<td>1.61</td>
</tr>
<tr>
<td>M-3</td>
<td>tert-butyl</td>
<td>2.02</td>
</tr>
<tr>
<td>M-2</td>
<td>methyl</td>
<td>2.24</td>
</tr>
</tbody>
</table>
The fact that the polymerization rate could vary upon the substituent of the diimide moiety was quite surprising. To help put this in perspective under the conditions used (20 equiv, [monomer] = 0.2 M), with M-2, a conversion of 90% is achieved in 1 h 20 min, whereas 3 h 30 min are necessary to reach the same conversion with M-7. These variations are not expected as the succinimide group is not located next to the cyclobutene coordination site. Nevertheless, the polymerization rates can be correlated to electronic effects: as the electronic donating ability of the succinimide moiety increases, polymerization proceeds faster. The order of reactivity of M-15, M-10 and M-14 parallels the \( \sigma_p \) values for the present substituents.\(^{22} \) No specific explanation can be given for the influence of the ortho substituents.

Similar kinetic experiments were also performed with monomers bearing different functional groups at the 7,8-positions.

**Scheme 3.1.** Synthesis of O-benzyl and N-benzyl functionalized monomers.

An increase in polymerization rate was observed with those monomers that do not contain the diimide moiety. A relative rate of 2.29 was measured for M-19 whereas M-20
with the presence of a tertiary amine could be polymerized much faster as compared to M-7 (relative rate = 3.32). Those data confirmed the observed trend with the succinimide functionalized monomers. Nevertheless, a specific phenomenon was observed in the polymerization of M-19 with Ru-III. As observed with the other monomers, the monomer solution of M-19 progressively turned dark yellow upon addition of the Ru-III catalyst solution. But after approximately 1 h, the color had changed to emerald green and this color persisted until quenching. Upon quenching with ethyl vinyl ether, the traditional color change to orange was not observed. The green color was observed with all polymerizations and copolymerizations performed with M-19. Furthermore, the molecular weight distribution was not as monodisperse (1.2 < PDI < 1.5). The ether groups may coordinate by chelation to the propagating species. This specificity of ether groups with Grubbs' type catalysts has already been reported. A nearest neighbor chelation effect was observed in the polymerization of 3-substituted cyclobutenes with ether substituents close to the cyclobutene ring.\(^1\) In this case, the ether substituent could coordinate to the propagating metal center present on the same monomer unit, resulting in the stabilization of the active (mono)phosphine species (Figure 3.1).

\[ X = \text{OCH}_2\text{Ph}, \text{OC(Ph)}_3, \text{OC(O)Ph} \]

**Figure 3.1.** Neighboring chelation effect in the ROMP of 3-substituted cyclobutenes.\(^1\)
Consequently, the propagation was shown to be faster as compared to other 3-substituted cyclobutenes and relatively high PDIs were observed (PDI > 1.3). Nevertheless, chelation of an ether atom to the Ru metal center has also been used to prepare recyclable catalysts and in this case, a lower metathesis activity is observed at room temperature as compared to Ru-III (Figure 1.5). In our case, the ether substituents of a monomer unit can not interact with the propagating species on the same unit. As the initiation is fast (< 15 min) and as the color change appears after some time (∼1 h), one can rule out the possible chelation of ether groups from unincorporated monomer. A more plausible explanation is the coordination of monomer units already polymerized within a polymer chain (intramolecular coordination) or between polymer chains (intermolecular coordination). The presence of chelation probably leads to a slower propagation rate, as one would expect the polymerization of M-19 to be faster than the polymerization of M-3. Nevertheless, no color difference was observed with M-20 containing a more basic tertiary amine. Also, molecular weights of the resulting polymer could not be determined due to its high affinity with the GPC columns.

The chemical shift variations of the alkene protons of the [2.2.2] cyclic structure observed in the different polymers seem to be indicative of the influence of the substituents at the 7,8-positions on the whole structure. For the polymers containing the succinimide moiety, those protons are located between 6.32 and 6.45 ppm and no definitive trend can be made due to peak broadening. On the other hand, those protons appear at 6.06 ppm for poly-19 and 6.11 ppm for poly-20. The observed differences are particularly useful to estimate the monomer content of block copolymers (Figure 3.2).
Figure 3.2. $^1$H NMR spectrum of a block copolymer (M-7, M-19) prepared with Ru-III.
3.2. Functionalization of the monomer structure with polyaryl ether dendrons

3.2.1. Motivations

In the early 1990s, Percec and co-workers initiated a research program involving tapered or conical building blocks of the following type:\(^3\)

\[
\begin{align*}
\text{X} & \text{O} \\
& \text{O(CH}_2\text{)}_n\text{CH}_3
\end{align*}
\]

Early experiments indicated that those compounds behaved like thermotropic mesogens. The tapered building blocks could self-assemble in supramolecular cylinders which self-organized in a 2-D columnar hexagonal \textit{p6mm} lattice whereas conical building blocks self-assembled in spherical objects which self-organized in a 3-D \textit{Pm3n} lattice.\(^4\) Those building blocks were designed so that self-assembly could occur through an \textit{endo-exo} type molecular recognition: the \textit{endo} molecular recognition involves the X fragment (X = COOH, CO\textsubscript{2}CH\textsubscript{3}, monomeric structure) whereas the large polyaryl ether fragment provides the \textit{exo}-molecular recognition.\(^5\) \textit{Endo-exo} molecular recognition, preorganization and self-organization have been shown to be the basic criteria for the spontaneous formation of supramolecular structures via self-assembly from their component.\(^6\) This system was inspired by some self-assembly processes observed in nature in complexes of nucleic acids with proteins including rodlike (Tobacco Mosaic Virus for example) and icosahedral viruses.\(^7\)
Various alkyl chain lengths were studied but the dodecyl chain proved to be the most convenient one due to the good availability of the starting material and good stability of the supramolecular structure over accessible and long temperature range. The shapes adopted by the building blocks were dependent on the number of benzyloxy substituents but also on the number of alkyloxy ether groups on the periphery (Table 3.2).8

Table 3.2. Structures of polyaryl ether dendritic building blocks.a,8

<table>
<thead>
<tr>
<th>Type</th>
<th>Benzyloxy substituent (s) on the inner aromatic ring</th>
<th>Alkyloxy ether group (s) at the periphery</th>
<th>Observed structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1 4 hexagonal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>2 3,4 cubic</td>
<td>4 3,4,5</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>3 3,4,5 crystalline</td>
<td>3 4</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>1 4 hexagonal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>3 3,4,5 hexagonal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>2 3,4,5 hexagonal</td>
<td>3 4,5</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>3 3,4,5 cubic</td>
<td>3 4,5</td>
<td></td>
</tr>
</tbody>
</table>

a X = COOH

To evaluate the influence of the self-assembly process on a polymeric backbone, styrene and methacrylate monomers were functionalized with those dendritic compounds and polymerized via radical polymerization.9 In those sytems, the polymerizable fragments are responsible for the endo-molecular recognition. Those monomeric units were chosen as they lead to flexible polymeric backbones that usually adopt a random-coil conformation. Upon functionalization with the flat monodendrons, the polymeric
backbones adopted a helical conformation due to the self-assembly of the tapered side-chains. On the other hand the incorporation of conical monodendrons (type E) lead to unexpected results. The shape adopted by the polymeric backbone was dependent on the degree of polymerization (DP): at low DP (DP < 20 (PS), DP < 25 (PS)), the formation of a cubic phase was observed whereas at higher DPs, a columnar hexagonal phase was characterized by X-ray diffraction (XRD). This process was explained by the fact that initially, the polymer adopts a random coil conformation whereas the organization is dictated by the spherical self-assembly of the dendrons. But at this stage, the polymeric backbones are concentrated in the core of the sphere. When a precise DP is achieved, the different sphere fragments are no longer complementary (the complementarity is also favored by the polydisperse molecular weight distribution). So to minimize its free energy, the polymer adopts a different shape that turns to be cylindrical and the dendritic side chains self-assemble in a hexagonal fashion.

![Structure of 7-Oxanorbornene functionalized with "zero-generation" dendrons.](image)

**Figure 3.3.** 7-Oxanorbornene functionalized with "zero-generation" dendrons.

To evaluate the influence of the polymeric backbone on the self-assembly process, those dendrons were incorporated on monomers that could be polymerized by
ROMP. The 7-oxanorbornene structure was first functionalized with a "zero-generation" dendron (Figure 3.3). First polymerization studies were performed with RuCl$_3$·3H$_2$O and Ru-I.$^{10}$ Only the ill-defined catalytic system gave polymers in good yield and high molecular weight. It had been speculated that the poly(7-oxanorbornene) backbone could itself adopt a helical conformation.$^{11}$ In this case, the assembly of the tapered side chains into a tubular structure induced the backbone to adopt a 3/1 helical conformation. The advent of the well-defined catalyst Ru-III was of great interest due to its good tolerance towards functional groups and the functionalized 7-oxanorbornenenes could be polymerized in a living fashion.$^{12}$ Poly(7-oxanorbornene)s with 2 type D (Table 3.2) dendrons per unit were prepared with various DPs and the dependence of the supramolecular columnar phase on the DP was studied. As the polymerization was living, kinetic studies of the polymerization with various monomer to catalyst ratios could be performed. Later, the 7-oxanorbornene structure was functionalized with two similar first generation dendrons (B, F, G).$^{7}$ Kinetic experiments demonstrated that the propagation rate constant was dependent on the shape of the propagating macromolecules. With monomers bearing dendrons B or G, two rate constants were observed. The change of rate corresponded to the change of the polymer shape from spherical to cylindrical. Therefore, kinetics could be used to detect the change of shape of macromolecules during their synthesis, a major discovery.

The polymerization of those 7-oxanorbornenes was also recently investigated with the last generation Grubbs' catalyst Ru-VI.$^{13}$ First of all, a secondary methathesis reaction was observed, leading to the decrease of the molecular weight with time. Only in
the presence of the bulky dendron G was the secondary metathesis reaction not present and monodisperse samples with a stable molecular weight could be prepared but the conversion was low and a plateau was observed (52% after 24 h). While the presence of those bulky side chains really slew down the usual high activity of Ru-VI, the propagation rate was much faster than initiation and polydisperse samples were obtained. A self-inhibition phenomenon through chelation of the ether groups was proposed for the dramatic decrease in polymerization rates for all dendritic monomers. The dendritic coat formed by the side groups could also explain the slow propagation rates.

As monomers based on the endo-tricyclo[4.2.2.0²,5]deca-3,9-diene structure could be polymerized in a living fashion with Ru-III and willing to investigate the influence of steric hindrance on catalysts' activity, we functionalized the studied monomer structure with the polyaryl ether dendrons developed by Percec and co-workers.
Figure 3.4. Dendritic monomers used in this study (R = (CH$_2$)$_{11}$CH$_3$).
3.2.2. Monomer synthesis

The convergent synthesis of the polyaryl ether dendrons has been well-documented. First of all, the outer sphere of the dendron must be prepared. The starting materials are methyl hydroxybenzoates, the number of hydroxy groups determining the number of alkoxy chains. The following sequence is followed: etherification of the alkoxy groups (CH₃(CH₂)₁₁Br, K₂CO₃), reduction of the methyl benzoate ester to the benzyl alcohol (LiAlH₄), transformation of the benzyl alcohol to the benzyl chloride by nucleophilic substitution (SOCl₂). The generated piece is then coupled with the desired methyl hydroxybenzoate to generate a first generation dendron by nucleophilic substitution. The methyl benzoate ester group is then reduced to generate a dendron functionalized with a carboxylic acid moiety by saponification (KOH) (Scheme 3.2).

Scheme 3.2. Synthetic route to polyaryl ether dendrons.

A family of acid functionalized dendrons was prepared using the above synthetic route (Figure 3.5). Repeated difficulties were met in the coupling of various zero-generation benzyl chloride dendrons with methyl 3,4,5-trihydroxy benzoate. The resulting compound was difficult to isolate by column chromatography and the
subsequent saponification was not successful. Therefore, no studies were made with a tri-benzyloxy substituted inner core.

**Figure 3.5.** Dendritic compounds used for the functionalization of the monomer unit.

For the functionalization of the 7-oxanorbornene structure with the first generation dendrons, the benzyl alcohol derivatives were reacted with the cyclic anhydride present on the 7-oxanorbornene moiety. At first a mixed ester-acid intermediate was formed through the base-catalyzed opening of the anhydride, then by a mild acid-catalyzed esterification, a second dendron unit was connected (Scheme 3.3).

**Scheme 3.3.** Procedure used for the functionalization of the 7-oxanorbornene moiety.
Nevertheless, several days were required for completion of the above procedure. We chose to introduce those dendrons through a one-step mild esterification reaction with the acid functionalized derivatives (Scheme 3.4).\textsuperscript{14}

**Scheme 3.4.** Functionalization of the *endo*-tricyclo[4.2.2.0\(^{2,5}\)]deca-3,9-diene structure with two polyaryl ether dendrons.

Using this route, monomers that differed by the bulkiness of the dendritic side-chains were prepared (Table 3.3).

**Table 3.3.** Dendritic monomers prepared by a one-step coupling.

<table>
<thead>
<tr>
<th>Dendritic precursor compound</th>
<th>Monomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>DM-1</td>
</tr>
<tr>
<td>II</td>
<td>DM-2</td>
</tr>
<tr>
<td>III</td>
<td>DM-3</td>
</tr>
<tr>
<td>IV</td>
<td>DM-4</td>
</tr>
<tr>
<td>V</td>
<td>DM-5</td>
</tr>
</tbody>
</table>

This route also permitted the preparation of an unsymmetrical monomer carrying different dendritic groups through the isolation of the first monofunctionalized intermediate (Scheme 3.5).
Scheme 3.5. Preparation of a dendritic monomer carrying two different dendrons.

For comparison purposes, Percec's coupling sequence was used for the preparation of DM-1B from M-1 and the alcohol derivative of I. The main difference in our approach is that the ester connecting groups are conjugated with the dendritic side chains.

All the above monomers are carrying two dendritic side chains. To get more information on the possible influence of steric hindrance, two monomers carrying only one dendritic side-chain were prepared (Scheme 3.6). In one of them (DM-7), a zero-generation dendron was directly connected to the succimide substituent whereas in the other one (DM-8), a 11-carbon spacer was introduced between the succinimide moiety and the dendritic group.
Scheme 3.6. Synthetic route to monomers carrying one dendritic side-chain.

The dendritic monomers were all recovered as white fine powders after purification by column chromatography followed by recrystallization with acetone. The yield of the catalyzed esterification varied upon the bulkiness of the dendrons and the alcohol substrate (Table 3.4). Even in the presence of a slight excess of the carboxylic acid, some monodendron functionalized monomer could usually be recovered. Steric hindrance seems to disfavor the addition of a second dendritic unit. Also the formation of N-acyl urea by-products was observed.

Table 3.4. Yields of the esterification for the coupling of the dendritic side-chains.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Yield for the incorporation of the dendritic side-chain(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DM-1</td>
<td>64%</td>
</tr>
<tr>
<td>DM-2</td>
<td>40%</td>
</tr>
<tr>
<td>DM-3</td>
<td>75%</td>
</tr>
<tr>
<td>DM-4</td>
<td>42%</td>
</tr>
<tr>
<td>DM-5</td>
<td>36%</td>
</tr>
<tr>
<td>DM-7</td>
<td>37%</td>
</tr>
<tr>
<td>DM-8</td>
<td>51%</td>
</tr>
</tbody>
</table>
The DSC thermal analysis of the dendritic monomers indicated the presence of liquid crystalline transitions in some cases (Table 3.5). Even if no XRD analysis were performed, the observed transitions certainly correspond to the formation of the same liquid crystalline phase observed for the dendritic precursors as it was reported for the 7-oxanorbornenes functionalized with dendritic side chains.\textsuperscript{7,10,12}

Table 3.5. DSC analysis of the dendritic monomers and precursors.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Endotherm (s) on 2nd heating (°C)\textsuperscript{b}</th>
<th>Exotherm (s) on 2nd cooling (°C)\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>58.5 (T_m)</td>
<td>30.6 (T_c)</td>
</tr>
<tr>
<td>DM-1</td>
<td>14.1, 21.1, 35.4</td>
<td>-0.2</td>
</tr>
<tr>
<td>DM-1B</td>
<td>11.5</td>
<td>2.9</td>
</tr>
<tr>
<td>III\textsuperscript{a}</td>
<td>k -8 $\phi_h$ 125 i</td>
<td>i 114 $\phi_h$ 110 $\phi_h$ -15 k</td>
</tr>
<tr>
<td>DM-3</td>
<td>11.5, 113.3</td>
<td>92.5, 85, 6.5</td>
</tr>
<tr>
<td>IV\textsuperscript{a}</td>
<td>86 k 108 Cub 118 i</td>
<td>i 114 Cub 67 k</td>
</tr>
<tr>
<td>DM-4</td>
<td>-2.5, 56, 107</td>
<td>101.7, 46.6, 13</td>
</tr>
<tr>
<td>V\textsuperscript{a}</td>
<td>k -7 Cub 91 i</td>
<td>i 84 Cub -12 k</td>
</tr>
<tr>
<td>DM-5</td>
<td>-11.5, 57</td>
<td>42, -11</td>
</tr>
<tr>
<td>DM-6</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>DM-7</td>
<td>100 (T_m)</td>
<td>86.5 (T_c)</td>
</tr>
<tr>
<td>DM-8</td>
<td>7.6, 43.3, 50.3</td>
<td>32, 25.3, -2.1</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Litterature data, k: crystal phase, $\phi_h$: LC hexagonal phase, Cub: cubic lattice, i: isotropic liquid; \textsuperscript{b} Heating rate: 10 °C/min, -50 to 200 °C, N\textsubscript{2} atmosphere, T\textsubscript{m}: melting temperature, T\textsubscript{c}: crystallisation temperature

Nevertheless while only a melting point is observed for the precursor I, several LC transitions are seen on the DSC spectrum of DM-1. Optical polarized microscope images of DM-1 indicated the formation of a liquid crystalline phase on cooling from the isotropic liquid. Interestingly, the way that the dendritic group is connected to the monomer unit seems to be important as indicated by the different DSC data obtained for
DM-1 and DM-1B. Only a melting transition and the associated crystallization were observed for M-1B, M-7 and M-8. For the latter ones, this may indicate that the endo-recognition group is too large as compared to the exo-recognition group (dendron).

3.2.3. Kinetic studies of the polymerization

The polymerization of the dendritic monomers with Ru-III and Ru-VI was investigated using gel permeation chromatography (GPC). The conversion could be easily estimated by the relative integration of the polymer versus the monomer peak. In all experiments with Ru-VI, the apparent formation of low molecular weight (= trimers) in small proportion (< 20%) was observed in the early stage of the polymerization. But those rapidly disappeared as the propagation continued and therefore, they were added to the monomer peak area in every case for the establishment of the conversion. Similar conditions were used for all experiments (unless indicated): CH₂Cl₂, room temperature, [catalyst] = 0.001 M, [monomer] / [catalyst] = 50. Such a high ratio was chosen in the event that a possible change in the kinetics could be observed with the degree of polymerization, as it happened with the functionalized PS and PMA at DP > 20.⁵

The first experiments were conducted with the zero-generation DM-1. With both catalysts, monodisperse samples (PDI < 1.2) were obtained at different times of the reaction. In both cases, a first order monomer consumption was observed. After 24 h, a conversion of 96.3% had been reached with Ru-VI whereas the polymerization was much slower with Ru-III (77% after 24 h) (Figure3.5). The control observed with Ru-VI was quite surprising as with M-7 for example, the polymerization was complete in a
matter of minutes in a non-controlled fashion: high molecular weight with relatively high PDIs (1.5-2.0) as a result of a fast propagation compared to the initiation stage. The presence of dendritic side-chains seems to significantly slow down the propagation.

Table 3.6. Kinetic data of the polymerization of DM-1 with Ru-III and Ru-VI.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>2.25</th>
<th>7</th>
<th>22</th>
<th>31</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion with Ru-III</td>
<td>39.7 %</td>
<td>50.6 %</td>
<td>77 %</td>
<td>82.3 %</td>
</tr>
<tr>
<td>$M_n$</td>
<td>5350</td>
<td>8000</td>
<td>9600</td>
<td>11000</td>
</tr>
<tr>
<td>Conversion with Ru-VI</td>
<td>35.9 %</td>
<td>74.2 %</td>
<td>96.3 %</td>
<td>97.7 %</td>
</tr>
<tr>
<td>$M_n$</td>
<td>10200</td>
<td>15260</td>
<td>18400</td>
<td>18500</td>
</tr>
</tbody>
</table>

$^{a}$DM-1 ($M_w = 1506$); polymerization conditions: [catalyst] = 0.002 M, [DM-1]/[catalyst] = 20

The surprising control obtained with Ru-VI was not observed in the polymerization of DM-7 and DM-8 in which only one dendritic side chain is present (Figure 3.6).

Figure 3.6. Kinetic plots for the polymerization of DM-7 with Ru-III (---) and Ru-VI (—).
The polymerization was complete in 3 h with a broader molecular weight distribution (1.3 < PDI < 1.45). On the contrary, the polymerization with Ru-III was controlled and was following the same kinetics as the polymerization of DM-1 with Ru-VI.

The introduction of a spacer that kept the bulky dendron away from both the propagating specie and the polymer backbone leaded to an increase in the polymerization rate with Ru-III (Figure 3.7).

![Figure 3.7. Kinetic plots of the polymerization of DM-7 (—) and DM-8 (---) with Ru-III.](image)

Those first experiments indicated that the presence of two dendritic side chains per monomer unit were necessary to observe a controlled polymerization with Ru-VI and with reasonable rates. In the presence of dendritic side-chains, the activity of Ru-III had dramatically decreased. Therefore, the polymerization of the higher generation dendritic monomers was only investigated with Ru-VI. But was the observed phenomenon a
consequence of steric hindrance and/or a consequence of self-organization of the growing polymer chains due to the presence of the dendritic side-chains?

Valuable information was obtained upon the polymerization of DM-1B with Ru-VI. The rate of polymerization was very similar to the one measured with DM-1. If a self-organization of the polymer chain had been involved, this result may have been different, as DM1-B does not display any liquid crystalline properties whereas DM-1 does. Nevertheless, the presence of a liquid crystalline phase with the starting monomer is not necessary to get a liquid crystalline polymer, as it was observed with the 7-oxanorbornene analog of DM-1. But in this case, the resulting backbone could adopt a helical conformation whereas in our case the backbone is very rigid. Also, no liquid crystalline transitions were observed on the DSC spectra of the isolated polymers (Table 3.7).

Figure 3.8. Kinetic plots of the polymerization of DM-1 (---), DM-6 (••••) and DM-4 (---) with Ru-VI.
The influence of steric hindrance was evident when comparing the kinetics of polymerization of DM-1, DM-4 and DM-6 (Figure 3.8). First of all, the polymerization rate of the more bulky monomer DM-4 was much slower as compared to DM-1: 50% conversion in ≈10 h versus ≈5 h for DM-1. Also, the kinetic of the polymerization of the "mixed" monomer DM-6 was very similar to the one of DM-4, indicating that the biggest dendritic side chain was dictating the polymerization rate.

As the number of alkyl chains on the periphery increases, one would expect a decrease in the polymerization rate as the propagating species is less accessible and also the monomer that wants to get incorporated is more bulky. This effect is evident when comparing the kinetics of polymerization of DM-3, DM-4 and DM-5 (Figure 3.9)

![Figure 3.9. Kinetic plots of the polymerization of DM-3 (—), DM-4 (···) and DM-5 (---) with Ru-VI.](image-url)
The incorporation of more alkoxy chains resulted in a significant decrease in the rate of polymerization. While the polymerization of DM-3 was almost complete in less than 12 h, the polymerization of DM-5 reached a plateau at less than 50% conversion after several days. At this point, stirring is no longer possible due to the viscosity of the solution. While diffusion certainly influences the propagation at some point, in the early stage of the polymerization (up to 10 hours), the polymerization still follows a first order kinetic with a constant pseudo-order rate.

The morphology of the resulting polymers was not investigated in details. The thermal properties of the recovered polymers from the GPC studies (conversion > 99%) were evaluated using DSC in the -50/200°C temperature range (Table 3.7).

### Table 3.7. Thermal transitions of the polymers functionalized with dendritic side-chains.\(^a\)

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Catalyst used</th>
<th>Endotherms(^b)</th>
<th>Exotherms(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DM1</td>
<td></td>
<td>-9°C</td>
<td>-15°C</td>
</tr>
<tr>
<td>DM1B</td>
<td>Ru-VI</td>
<td>9.3°C</td>
<td>-1.4°C</td>
</tr>
<tr>
<td>DM-3</td>
<td></td>
<td>-6.1, 173.5°C (T&lt;sub&gt;g&lt;/sub&gt;)</td>
<td>173.8, 9.7</td>
</tr>
<tr>
<td>DM-4</td>
<td></td>
<td>-3.5</td>
<td>-10</td>
</tr>
<tr>
<td>DM-7</td>
<td>Ru-III</td>
<td>23.5 (T&lt;sub&gt;g&lt;/sub&gt;)</td>
<td>none</td>
</tr>
<tr>
<td>DM-8</td>
<td></td>
<td>-9.1</td>
<td>-15.2</td>
</tr>
</tbody>
</table>

\(^a\) 10°C/min, N\(_2\) atmosphere; \(^b\) 2\(^{nd}\) heating; \(^c\) 2\(^{nd}\) cooling

No specific correlations can be made with the measured transitions and the ones observed with the mesogenic precursors. In most cases, apparent broad T<sub>m</sub> and T<sub>c</sub> transitions are observed and they are probably induced by the long alkyl side-chains. Contrary to the polymers prepared from the functionalized 7-oxanorbornenes, the liquid crystalline
properties associated with the dendritic side-chains are not observed on those new ROMP polymers.

3.2.4. Conclusions

The functionalization of the monomer with polyaryl ether side-chains but also the way that those dendrons were connected to the endo-tricyclo[4.2.2.0²,₅]deca-3,9-diene structure had a remarkable influence on the activity of catalysts Ru-III and Ru-VI. It was found that the incorporation of two dendritic side-chains per monomer unit leaded to significant decrease in the rates of polymerization and a controlled polymerization was obtained with Ru-VI. This control behavior is explained by the decrease of the propagation rate due to the bulkiness of the dendritic functional groups. Also, as the dendritic coat became larger, the polymerization rates dropped dramatically. The variations in the polymerization rate do not appear to be the consequence of the formation of a supramolecular structure. Those results are particularly interesting as they demonstrate that the fine-tuning of the catalyst activity can be obtained by a specific monomer design, a rarely exploited idea.

3.3. Thermal properties

For all polymer functionalized with a "simple" succinimide moiety (M-X, X= 2-9,14) and for poly-I, no T_g was observed from -50 to 300 °C (decomposition temperature). Thermogravimetric analysis indicated that the T_d (temperature at 10% weight loss) varied from 304 to 344 °C, the anhydride being less stable than the
succinimide moiety. The decomposition occurred regularly from 300 to 450 °C and no precise pattern could be identified. These data are consistent with the expected rigidity of the polymer chains and indicate surprisingly good thermal stability of these polymers. This last observation runs counter to our expectation that the retro-pericyclic reaction yielding conjugated polymers will occur through ejection of the dienophile molecule.

We wanted to determine if noticeable changes would be observed in the thermal properties upon hydrogenation of the unsaturated centers. p-Toluenesulfonyl hydrazide is commonly used for the chemical hydrogenation of ROMP polymer backbones. Upon heating to 110°C, this reagent decomposes, generating diimide (H-N=N-H), which is known to transfer hydrogen to olefins in a pericyclic process that yields dinitrogen and a hydrogenated olefin. Using a large excess of this diimide precursor, the main chain of poly-2 could be fully hydrogenated while the olefin of the [2.2.2] structure was hydrogenated to approximately 85% as evidenced by 1H NMR. The resulting saturated polymer was no longer a powder, but a beige shiny solid. Consistent with the loss of a semi-rigid backbone, a T_g was now observed at 285 °C. Also, the T_d was increased by almost 100 °C to 423 °C and the weight loss occurred steadily over a short-range from 400 to 470 °C. This remarkable improvement of the thermal stability is related to the preparation of a saturated polymer backbone lacking allylic hydrogens that is less sensitive to radical decomposition.

The attempted hydrogenation of monomers functionalized with fluorinated N-phenyl succinimide side chains was not so successful. Two main reasons can account for these results: the ROMP polymer has a bad solubility in the reaction media (xylene) and
the hydrogenation reagent is sensitive to steric hindrance, an already reported observation.\textsuperscript{21} Analysis of the partially hydrogenated polymer indicated that the main chain unsaturation was easier to reduce than the olefin of the [2.2.2] structure. Thermogravimetric analysis of partially hydrogenated polymers indicated again an improvement of the thermal stability. For example, the T\textsubscript{d} of poly-8 with a 72\% hydrogenated backbone (hydrogenation of the side olefin: 40\%) was shifted by 36°C from 327°C to 363°C.

3.4. Experimental section

\textit{General procedures and characterizations}

All polymerizations were carried out in a MBraun UNILab drybox under nitrogen atmosphere using dry and degassed solvents (MBraun solvent system).

All manipulations involving air- and moisture-sensitive compounds were carried under an atmosphere of prepurified nitrogen using standard Schlenk techniques.

\textsuperscript{1}H NMR spectra were obtained at 300 MHz with GE NMR Omega spectrometer and at 300, 400 MHz with Varian-Mercury NMR spectrometers. Chemical shifts for \textsuperscript{1}H NMR spectra are reported in δ (ppm), positive values indicating shifts downfield of tetramethylsilane and are referenced to selected residual proton peaks of the solvent as follows: CDCl\textsubscript{3}, 7.27, singlet. Significant \textsuperscript{1}H NMR data are tabulated in order: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, bs = broad signal, m = multiplet), coupling constant in Hertz, number of protons. \textsuperscript{13}C{\textsuperscript{1}H} proton decoupled NMR were measured at 75 MHz with a GE NMR Omega spectrometer and at 100 MHz
on a Varian-Mercury spectrometer. Chemical shifts for $^{13}$C{\H} NMR spectra are reported in $\delta$ (ppm), positive values indicating shifts downfield of tetramethylsilane, and are referenced to selected residual peaks of the solvents as followed: CDCl$_3$, 77.23, triplet.

Infrared spectra were obtained using a Jasco FT/IR-410 spectrometer as thin films on NaCl disks or neat samples between NaCl disks and are uncalibrated. IR data are reported in units of wavenumber (cm$^{-1}$) for characteristic peaks.

Before sample analysis, solvents were removed with a rotary evaporator and under Schlenk line vacuum (approximately 0.05 Torr). Column chromatography was carried out with Selecto Scientific 63-200 mesh silica gel.

Molecular weight and molecular weight distribution were measured via gel permeation chromatography using a Jasco PU-1580 pump and a Jasco RI-1530 refractive index detector. The stationary phase consisted of two PL-Gel mixed C columns. Chloroform was used as the mobile phase. Molecular weights are relative to narrow molecular weight polystyrene standards (Pressure Chemical, Inc.).

Thermal analyses were performed using Hi-Res TGA 2950 and DSC 2920 TA instruments using a nitrogen purge and heating/cooling rates of 10 °C/min.

Elemental analyses were performed by Atlantic Microlab, Inc.

**Reagents**

CH$_2$Cl$_2$ used for polymerization reactions and reactions with air and moisture sensitive materials was purified by passing through one column filled with activated A2 Alumina catalyst and one column filled with activated Q5 copper catalyst under nitrogen.
atmosphere (MBraun solvent system). CDCl$_3$ was dried over CaH$_2$, distilled under nitrogen and after three freeze-pump-thaw cycles was stored into the dry box and used no more than one month later. 1,2-dichloroethane used as a reference in the $^1$H NMR kinetic experiments was dried over CaH$_2$, distilled under nitrogen and after three freeze-pump-thaw cycles stored in the dry box. THF was distilled from a Na/K stille. Thionyl chloride was dried with CaH$_2$ and was stored in the fridge after distillation under N$_2$. DPTS was prepared according to literature.$^{15}$

**Experimental procedures and characterizations**

**endo-Tricyclo[4.2.2.0$^{2,5}$]deca-3,9-diene-7,8-dimethanol.**

endo-Tricyclo[4.2.2.0$^{2,5}$]deca-3,9-diene-7,8-dicarboxyanhydride (M-1) (3.04 g, 15 mmol) in 35 mL dry THF was added dropwise to a cold THF suspension (30 mL) of LiAlH$_4$ (2.30 g, 60 mmol). The mixture was then refluxed for 24 hours under nitrogen. After cooling, it was immersed in an ice bath and quenched by successive addition of 2.3 mL H$_2$O, 2.3 mL 15% aqueous NaOH and 6.9 mL H$_2$O. It was then stirred for 1 hour. The Li-complex was then removed by filtration and washed with THF. Concentration of the filtrate leaded to the first portion of the desired product (1.50 g). A second portion (1.205 g) was recovered upon overnight soxlet extraction of the filtered Li-complex with THF (200 mL). From both fractions, the pure desired compound was obtained as a white powder (2.705 g, 94%). $^1$H NMR (CDCl$_3$) δ: 5.88 (m, 2H), 5.82 (s, 2H), 3.73 (bt, J = 7.8 Hz, 2H), 3.59-3.56 (br, 4H), 2.75 (s, 2H), 2.48 (bs, 2H), 2.14 (d, J = 7.8 Hz, 2H). $^{13}$C {$^1$H} NMR (CDCl$_3$) δ: 137.58, 129.05, 65.57, 45.68, 44.73, 39.49. IR 3206 (br), 3046, 3031, 2934, 2903, 1470, 1380, 1221, 1044, 875, 816, 762, 712.
**endo-Tricyclo[4.2.2.0\textsuperscript{2.5}]deca-3,9-diene-7,8-dimethylbenzylalcohol (M-19).** To a mixture of pur NaH powder (260 mg, 11 mmol) and *endo*-Tricyclo[4.2.2.0\textsuperscript{2.5}]deca-3,9-diene-7,8-dimethanol (576 mg, 3 mmol) immersed in an iced bath was added 20 mL of anhydrous DMF under N\textsubscript{2}. Immediate gas bubbles could be seen and the mixture was stirred for 15 minutes. Benzyl bromide (0.74 mL, 6.2 mmol) was then added drop wise with a syringe. The mixture was stirred for 2 hours at 0\textdegree C and then at RT for 16 hours. Few drops of MeOH were added and the mixture was stirred for 1 hour. The solvents were removed under vacuum and the residue was dissolved in ethyl acetate. The solution was washed with water, brine, dried with MgSO\textsubscript{4} and upon concentration a white solid was obtained. Purification by silica gel chromatography (hexane / ethyl acetate, 3/1) and further recrystallization with hexane to remove traces of benzyl bromide leaded to a white crystalline solid (1.03 g, 92%). \textsuperscript{1}H NMR $\delta$: 7.32 (m, 8H), 5.91 (m, 2H), 5.86 (s, 2H), 4.45 (m, 4H), 3.49 (dd, $J = 8.8$, 5 Hz, 2H), 3.21 (t, $J = 8.8$ Hz, 2H), 2.78 (s, 2H), 2.72 (s, 2H), 2.15 (br, 2H). \textsuperscript{13}C \textsuperscript{1}H NMR $\delta$: 138.74, 137.93, 129.51, 128.50, 127.73, 127.63, 73.08, 71.40, 45.65, 40.88, 37.90.

**7,8-N-4-Benzylsuccinimide endo-Tricyclo[4.2.2.0\textsuperscript{2.5}]deca-3,9-diene (M-18).** A mixture of COT (2.08 g, 2 mmol) and N- benzyl maleimide (3.74 g, 2 mmol) was progressively heated to 160\textdegree C under nitrogen and kept at this temperature for 1 h. Upon cooling, the mixture solidified. The beige solid was washed with hexane and dried under vacuum. Recrystallization with hexane / ethyl acetate led to fine white needles (4.6 g, 79%). \textsuperscript{1}H NMR $\delta$: 7.29 (m, 5H), 5.87 (s, 2H), 5.79 (m, 2H), 4.57 (s, 2H), 3.15 (m, 2),
2.78 (m, 4H). $^{13}$C \{$^1$H\} NMR $\delta$: 178.59, 138.11, 136, 128.67, 128.57, 128.41, 127.83, 44.27, 43.50, 42.33, 36.81.

**M-20.** To a cold (ice bath) suspension of LiAlH$_4$ (2.6 g, 68.5 mmol) in purified THF (80 ml) under N$_2$, was added dropwise a THF solution (40 ml) of 7,8-N-4-Benzylsuccinimide $\text{endo}$-Tricyclo[4.2.2.0$^{2.5}$]deca-3,9-diene (4.0 g, 14 mmol). After complete addition, the mixture was progressively heated to 65 °C for 8 h (reaction followed by TLC). After cooling down, few ml of ethyl acetate were added and the Li complex quenched by successive addition of 2.6 ml H$_2$O, 2.6 ml 15% aqueous NaOH and 7.8 ml H$_2$O. After stirring for 2 h., the white Li complex was removed by filtration, washed with THF and the filtrate dried with MgSO$_4$. The desired compound (3.0 g, 85%) was recovered as white flakes after silica gel column chromatography (hexane / ethyl acetate). $^1$H NMR $\delta$: 7.27 (m, 5H), 5.91 (m, 2H), 5.87 (m, 2H), 3.53 (s, 2H), 3.0 (t, $J = 7.2$ Hz, 2H), 2.70 (s, 2H), 2.53 (m, 2H), 2.41 (m, 2H), 2.05 (t, $J = 7.2$ Hz, 2H); $^{13}$C \{$^1$H\} NMR $\delta$: 139.39, 138.15, 130.79, 129.10, 128.36, 127.06, 60.83, 59.57, 46.16, 43.68, 37.77.

**Kinetic studies experiments using Ru-III.** In a Teflon-valve NMR tube, 100 µL of a freshly prepared stock solution of Ru-III in CDCl$_3$ was added to a solution of the desired monomer (20 equiv, 500 µL of CDCl$_3$) and 1,2-dichloroethane (5 µL) used as an internal reference. The used quantities were always chosen to have [monomer] = 0.2 M and [monomer] / [Ru-III] = 20. The chronometer was started and the monomer disappearance was followed by $^1$H NMR for a total time of 2½ hours at 22.5°C. Evolution
of the cyclobutene signal or the cyclobutene and side olefin signals with respect to the reference was recorded over time.

**Preparation of block copolymers (M-7 / M-19, 1:1).** To 50.9 mg (0.14 mmol, 50 eq) of M-7 dissolved in CH$_2$Cl$_2$ (580 µL) was added 115 µL of a Ru-III stock solution (5.0 mg in 250 µL of CH$_2$Cl$_2$). After 8 hours, analysis of an aliquot by $^1$H NMR indicated that the conversion was complete. To the dark yellow solution was then added a CH$_2$Cl$_2$ solution (200 µL) of M-19 (50.9 mg, 0.137 mmol, 50 eq). The solution progressively turned green. The conversion was complete after stirring for 12 hours. After quenching with ethyl vinyl ether (100 µL), the mixture was stirred for 1 h. A white powder was recovered after two precipitations from a CH$_2$Cl$_2$ solution into methanol. The polymer content in M-18 was easily established by the relative integration of the methylene groups (4.40-4.25) of the benzyl moieties. $^1$H NMR δ: 7.24 (br, 10H), 6.6-6.25 (br, 2H), 6.25-5.9 (2H), 5.6-4.7 (br, 4H), 4.36, 4.30 (br, 4H), 4.0-2.0 (max 3.40, 3.33, 3.24, 3.03, 2.78, 2.50, 2.28, 16H).

**Synthesis of the polyaryl ether dendrons**

**Methyl 3,4-dihydroxybenzoate.** A mixture of 3,4-dihydroxybenzoic acid (15.41 g, 0.1 mol), concentrated H$_2$SO$_4$ (1.1 mL) and anhydrous methanol (60 mL) was refluxed under N$_2$ with a Dean-Stark trap containing activated molecular sieves for 24 hours (reaction complete from IR). The orange solution was concentrated to one-half, diluted with brine (100 mL) and extracted with Et$_2$O (150 mL, 2 x 50 mL). The ethereal phase was washed with 10% aq, NaHCO$_3$ (3 x 50 mL), brine (2 x 50 mL) and dried with
Na₂SO₄. Upon concentration, a yellow pale powder (14.36 g, 85.5 %) pure from ¹H NMR was obtained. ¹H NMR (CDCl₃) δ: 7.62 (s, 1H), 7.58 (d, J = 8.4 Hz, 1H), 6.91 (d, J = 8.4 Hz, 1H), 5.6 (sh, 2H), 3.89 (s, 3H). IR 3450-3200 (sh), 1692, 1183.

Etherification of the phenolic compounds

**Methyl 4-dodecyloxybenzoate.** In a 500 mL 3 neck-flask equipped with a mechanical stirrer and a condenser, 4-hydroxybenzoate (25 g, 0.164 mol) was dissolved in acetone (240 mL) and the solution was purged with nitrogen for 20 minutes. K₂CO₃ (69.76 g, 0.498 mol) and 18-crown-6 (0.35 g, 1.34 mmol) were then added. After 10 minutes, 1-bromododecane (38.7 g, 0.155 mol) was added drop wise and the solution progressively heated to reflux. The reaction was monitored by ¹H NMR of aliquots. After 48 hours, it was cooled down, filtered and concentrated. The residue was taken up in Et₂O (350 mL), washed with dilute HCl, water and dried with MgSO₄. Upon concentration, shiny flakes were obtained and further recrystallization with hexane lead to the shiny white flakes (47.15 g, 94.6 %). ¹H NMR (CDCl₃) δ: 7.98 (d, J = 9 Hz, 2H), 6.91 (d, J = 9 Hz, 2H), 4.0 (t, J = 6.6 Hz, 2H), 3.89 (s, 3H), 1.80 (m, 2H), 1.46 (m, 2H), 1.27 (m, 16H), 0.89 (t, J = 6.6 Hz, 3H).

**Methyl 3,4-Bis(n-dodecan-1-yloxy)benzoate.** Using the literature procedure, starting from methyl 3,4-dihydroxybenzoate (6.72 g, 0.04 mol), K₂CO₃ (37.6 g, 0.268 mol), 1-bromododecane (19.91 g, 0.08 mol) in DMF (150 mL), 17.23 g (85.5 %) of a white powder was obtained after two recrystallizations (CH₂Cl₂ / acetone). ¹H NMR (CDCl₃) δ: 7.64 (d, J = 8.4 Hz, 1H), 7.54 (s, 1H), 6.87 (d, J = 8.4 Hz, 1H), 4.05 (m, 4H),
3.89 (s, 3H), 1.84 (m, 4H), 1.47 (m, 4H), 1.27 (m, 32H), 0.89 (t, J = 6.8 Hz, 6H). IR 2919, 2849, 1710.

**Methyl 3,4,5-Tris(n-dodecan-1-yloxy)benzoate.** By the same procedure as above, from 3,4,5-trihydroxybenzoate (5.52g, 0.03 mol), K₂CO₃ (42.05 g, 0.3 mol), 1-bromododecane (22.40 g, 0.09 mol) in DMF (150 mL), 19.15 g (92.8 %) of a white powder was obtained after two recrystallizations with acetone. \(^1\)H NMR (CDCl₃) δ: 7.27 (s, 2H), 4.02 (m, 6H), 3.89 (s, 3H), 1.77 (m, 6H), 1.50 (m, 6H), 1.27 (m, 48H), 0.89 (t, J = 6.7 Hz, 9H).

**Reduction of the methyl benzoate to the benzyl alcohol**

**4-Dodecyloxybenzyl alcohol.** As reported,\(^{16}\) from methyl 4-dodecyloxybenzoate (32.05 g, 0.1 mol), LiAlH₄ (3.8 g, 0.1 mol) in THF (315 mL), 26.18 g (89.5%) of a white solid was obtained. \(^1\)H NMR (CDCl₃) δ: 7.27 (d, J = 9 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 4.61 (s, 2H), 3.95 (t, J = 6.4 Hz, 2H), 1.77 (m, 2H), 1.45 (m, 2H), 1.26 (m, 16H), 0.88 (t, J = 6.7 Hz, 3H).

**3,4-Bis(n-dodecan-1-yloxy)benzyl alcohol.** Using the literature procedure,\(^8\) starting from methyl 3,4-Bis(n-dodecan-1-yloxy)benzoate (15 g, 29.76 mmol), LiAlH₄ (1.19 g, 29.76 mmol) in Et₂O (210 mL), a white solid (13.24 g, 93.6%) was obtained after recrystallization using acetone. \(^1\)H NMR (CDCl₃) δ:6.93 (s, 1H), 6.86 (s, 2H), 4.61 (s, 2H), 4.00 (m, 4H), 1.82 (m, 4H), 1.46 (m, 4H), 1.27 (m, 32H), 0.89 (t, J = 6.8 Hz, 6H). IR 3330 (sh), 1137.

**3,4,5-Tris(n-dodecan-1-yloxy)benzyl alcohol.** Using the literature procedure,\(^{17}\) starting from methyl 3,4,5-Tris(n-dodecan-1-yloxy)benzoate (12.0 g, 17.41 mmol),
LiAlH₄ (680 mg, 17.6 mmol) in Et₂O (220 mL), 10.35 g (90%) of a white solid was obtained after recrystallization with acetone. \(^1\)H NMR (CDCl₃) \(\delta\): 6.57 (s, 2H), 4.60 (s, 2H), 3.96 (m, 6H), 1.80 (m, 4H), 1.75 (m, 2H), 1.47 (m, 6H), 1.27 (m, 48H), 0.89 (t, \(J = 7\) Hz).

**Conversion of the benzyl alcohol to the benzyl chloride**

4-Dodecylbenzyl chloride Using the literature procedure,\(^1\) to a solution of 4-dodecyloxybenzyl alcohol (17.12 mmol, 5 g) in dry CH₂Cl₂ (80 mL) immersed in an ice-bath was added distilled thionyl chloride (20.55 mmol, 1.5 mL) under N₂. The reaction was followed using TLC. After complete conversion, excess SOCl₂ and CH₂Cl₂ were removed under vacuum and the recovered white powder used immediately in the next step. It can also be dissolved again in CH₂Cl₂, washed with water, 5% aqueous NaHCO₃ and water to neutral pH. After drying with MgSO₄, a clean white powder is obtained.

3,4-Bis(n-dodecan-1-yloxy)benzyl chloride. It was prepared according to the above procedure using 3,4-Bis(n-dodecan-1-yloxy)benzyl alcohol (16.8 mmol, 8.0 g), SOCl₂ (20 mmol, 1.5 mL) in CH₂Cl₂ (80 mL) and used immediately in the next step.

3,4,5-Tris(n-dodecan-1-yloxy)benzyl chloride. It was prepared according to the above procedure using 3,4,5-Tris(n-dodecan-1-yloxy)benzyl alcohol (5 mmol, 3.23 g), SOCl₂ (6.3 mmol, 0.5 mL) in CH₂Cl₂ (25 mL) and used immediately in the next step.

**Nucleophilic substitution reaction to get the first generation dendrons**

Methyl 3,5-Bis[(4-(n-dodecan-1-yloxy)benzyl)oxy]benzoate. Using the literature procedure,\(^8\) starting from methyl 3,5-dihydroxybenzoate (1.34 g, 7.95 mmol), K₂CO₃ (10.03 g, 71.55 mmol), 4-dodecylbenzyl chloride (5.0 g, 16.1 mmol) in 40 mL
DMF, 4.16 g (74%) of a white powder was obtained after recrystallization with acetone.

$^1$H NMR (CDCl$_3$) δ: 7.32 (d, J = 8.4 Hz, 4H), 7.28 (d, J = 2 Hz), 6.90 (d, J = 8.8 Hz, 4H), 6.77 (t, J = 2 Hz, 1H), 4.98 (s, 4H), 3.95 (t, J = 6.8 Hz, 4H), 3.90 (s, 3H), 1.78 (m, 4H), 1.43 (m, 4H), 1.27 (m, 32H), 0.88 (t, J = 6.8 Hz, 6H). IR 1714.

**Methyl 3,4-Bis[(3,4-Bis(n-dodecan-1-yloxy)benzyl)oxy]benzoate.** Using the literature procedure, starting from methyl 3,4-dihydroxybenzoate (447 mg, 2.67 mmol), K$_2$CO$_3$ (3.37 g, 24 mmol), 3,4-Bis(n-dodecan-1-yloxy)benzyl chloride (4.0 g, 8 mmol) in 40 mL DMF, 2.45 g (85%) of a white powder was obtained after recrystallization with acetone / CH$_2$Cl$_2$. $^1$H NMR (CDCl$_3$) δ: 7.65 (m, 1H), 7.62 (d, J = 2.4 Hz, 1H), 6.95 (m, 5H), 6.84 (dd, J = 8, 2 Hz, 2H), 5.12 (s, 2H), 5.09 (s, 2H), 3.95 (m, 8H), 3.88 (s, 3H), 1.80 (m, 8H), 1.45 (m, 8H), 1.27 (s, 64H), 0.89 (t, J = 6.8 Hz, 12H). IR 1716.

**Methyl 3,4,5-Tris[(3,4-Bis(n-dodecan-1-yloxy)benzyl)oxy]benzoate.** Using the literature procedure, starting from methyl 3,4,5-trihydroxybenzoate (497 mg, 2.70 mmol), K$_2$CO$_3$ (3.40 g, 24.3 mmol), 3,4-Bis(n-dodecan-1-yloxy)benzyl chloride (4.0 g, 8 mmol) in 50 mL DMF, 2.62 g (62%) of a white / pale brown powder was obtained after two recrystallizations with acetone. $^1$H NMR (CDCl$_3$) δ: 7.38 (s, 2H), 7.0-6.8 (m, 8H), 6.72 (d, J = 8 Hz, 1H), 5.04 (s, 4H), 5.02 (s, 2H), 3.95 (m, 10H), 3.89 (s, 3H), 3.75 (t, J = 6.4 Hz, 2H), 1.75 (m, 12H), 1.44 (m, 12H), 1.27 (m, 96H), 0.89 (t, J = 6.6 Hz, 18H). IR 1720.

**Methyl 3,4-Bis[(4-(n-dodecan-1-yloxy)benzyl)oxy]benzoate.** Using the literature procedure, starting from methyl 3,4-dihydroxybenzoate (1.33 g, 7.95 mmol), K$_2$CO$_3$ (10.03 g, 71.6 mmol), 4-(n-dodecan-1-yloxy)benzyl chloride (5.0 g, 16.1 mmol)
in 40 mL DMF, an impure off-white powder was obtained after recrystallization with acetone. Silica gel chromatography (CH$_2$Cl$_2$) lead to the desired pure compound (3.20 g, 56%). $^1$H NMR (CDCl$_3$) δ: 7.63 (m, 2H), 7.36 (d, J = 8.8 Hz, 2H), 7.32 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.4 Hz, 1H), 6.89 (m, 4H), 5.13 (s, 2H), 5.10 (s, 2H), 3.96 (t, J = 6.6 Hz), 3.88 (s, 3H), 1.79 (m, 4H), 1.46 (m, 4H), 1.27 (m, 32H), 0.89 (t, J = 6.8 Hz, 6H). IR 1717.

**Methyl 3,4-Bis[(3,4,5-Tris(n-dodecan-1-yloxy)benzyl)oxy]benzoate.** Using the literature procedure,$^8$ starting from methyl 3,4-dihydroxybenzoate (311 mg, 1.85 mmol), K$_2$CO$_3$ (2.3 g, 16.7 mmol), 3,4,5-Tris(n-dodecan-1-yloxy)benzyl chloride (2.5 g, 3.76 mmol) in 30 mL DMF, 2.03 g (75.6%) of a white powder was obtained after recrystallization with acetone. $^1$H NMR (CDCl$_3$) δ: 7.66 (s, 1H), 7.63 (d, J = 2 Hz, 1H), 6.94 (d, J = 8 Hz, 1H), 6.66 (s, 2H), 6.62 (s, 2H), 5.1 (s, 2H), 5.08 (s, 2H), 3.92 (m, 12H), 3.88 (s, 3H), 1.75 (m, 12H), 1.44 (m, 12H), 1.27 (m, 96H), 0.89 (t, J = 6.8 Hz, 18H). IR 1716.

**Saponification of the methyl benzoate ester$^{3,18,8}$**

**3,4,5-Tris(n-dodecan-1-yloxy)benzoic acid.** By a procedure already reported, from methyl 3,4,5-Tris(n-dodecan-1-yloxy)benzoate (13.76 g, 0.02 mol), KOH (7.85 g, 0.14 mol) in 95% EtOH (200 mL), 10.54 g (78%) of a white powder was obtained after two recrystallizations with acetone. $^1$H NMR (CDCl$_3$) δ: 7.33 (s, 2H), 4.03 (m, 6H), 1.83 (m, 4H), 1.75 (m, 2H), 1.48 (m, 6H), 1.27 (m, 48H), 0.89 (t, J = 6.8 Hz, 9H). IR 3500-2500 (broad shoulder), 1684.
3,5-Bis[(4-(n-dodecan-1-yloxy)benzyl)oxy]benzoic acid. Using the literature procedure, starting from methyl 3,5-bis[(4-(n-dodecyl-1- oxy)benzyl)oxy]benzoate (2.15 g, 3 mmol), KOH (1.2 g, 0.021 mol) and 95% EtOH (25 mL), 1.93 g (91.5 %) of a white powder was obtained after recrystallization with acetone. $^1$H NMR (CDCl$_3$) $\delta$: 7.36 (m, 4H), 7.34 (m, 2H), 6.92 (d, $J = 8.4$ Hz, 4H), 6.84 (t, $J = 2.4$ Hz, 1H), 5.01 (s, 4H), 3.97 (t, $J = 6.8$ Hz, 4H), 1.79 (m, 4H), 1.45 (m, 4H), 1.28 (m, 32H), 0.89 (t, $J = 6.8$ Hz, 6H). IR 3400-2400 (broad shoulder), 1692.

3,4-Bis[(3,4-Bis(n-dodecan-1-yloxy)benzyl)oxy]benzoic acid. Using the literature procedure, starting from methyl 3,4-bis[(3,4-bis-(n-dodecan-1-yloxy)benzyl)oxy]benzoate (1.5 g, 1.38 mmol), KOH (540 mg, 9.69 mmol) and 95% EtOH (20 mL), 907 mg (61.4 %) of a white powder was obtained after recrystallization with CH$_2$Cl$_2$ / acetone. $^1$H NMR (CDCl$_3$) $\delta$: 7.72 (br, 1H), 7.71 (bs, 1H), 6.95 (m, 5H), 6.84 (d, $J = 8$ Hz, 2H), 5.13 (s, 2H), 5.09 (s, 2H), 3.95 (m, 8H), 1.80 (m, 8H), 1.45 (m, 8H), 1.27 (m, 64H), 0.89 (t, $J = 6.8$ Hz, 12H). IR 3300-2400 (broad shoulder), 1677.

3,4-Bis[(3,4,5-Tris(n-dodecan-1-yloxy)benzyl)oxy]benzoic acid. Using the literature procedure, starting from methyl 3,4-Bis[(3,4,5-Tris(n-dodecan-1-yloxy)benzyl)oxy]benzoate (1.5 g, 1.03 mmol), KOH (406 mg, 7.2 mmol) and 95% EtOH (20 mL), 1.15 g (78 %) of a white powder was obtained after recrystallization with acetone. A minor impurity ($R_f = 0.9$) was removed using silica gel column chromatography (hexane / ethyl acetate (3/1), $R_f = 0.4$). $^1$H NMR (CDCl$_3$) $\delta$: 7.75-7.72 (m, 3H), 6.97 (d, $J = 8.2$ Hz, 1H), 6.67 (s, 2H), 6.63 (s, 2H), 5.12 (s, 2H), 5.09 (s, 2H),
3.93 (m, 12H), 1.76 (m, 12H), 1.52-1.2 (m, 108H), 0.89 (t, J = 6.4 Hz, 18H). IR 3400-
2400 (broad shoulder), 1687.

7,8-N-4-(11-hydroxy-undecyl-1-oxy)phenylsuccinimide  \textit{endo-}

Tricyclo[4.2.2.0^{2,5}]deca-3,9-diene.  7,8-N-4-Hydroxyphenylsuccinimide  \textit{endo-}

Tricyclo[4.2.2.0^{2,5}]deca-3,9-diene (M-17) (490 mg, 1.67 mmol) was dissolved with acetone (26 mL) and the solution was degazed with N₂ for 15 minutes. K₂CO₃ (820 mg, 5.85 mmol) and 18-crown-6 (12 mg) were then added and the mixture degazed again. 11-
bromo-1-undecanol (504 mg, 2.0 mmol) was added and the mixture was heated to reflux. The reaction was monitored using \(^1\)H NMR (CDCl\(_3\) / DMSO-d\(_6\) and CDCl\(_3\)) by following the disappearance of the aromatic phenol (\(\delta = 6.80\) ppm, doublet) and appearance of the aromatic phenol ether (\(\delta = 7.08\) ppm, doublet). After 64 hours, the starting phenol derivative had been completely consumed. After cooling, the reaction mixture was filtered. It was dissolved with CH\(_2\)Cl\(_2\), washed with 0.5 N HCl and water until neutral pH. After drying with MgSO\(_4\) and concentration, a white solid was obtained (680 mg). The excess of 11-bromo-1-undecanol was removed by washing the crude powder with hexane. After drying, a pure fine white powder was obtained (572 mg, 74%). \(^1\)H NMR \(\delta\) 7.08 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 6.01 (m, 2H), 5.92 (s, 2H), 3.95 (t, J = 6.4 Hz, 2H), 3.64 (t, J = 6.4 Hz, 2H), 3.27 (s, 2H), 2.94 (t, 2H), 2.87 (s, 2H), 1.77 (m, 2H), 1.57 (m, 2H), 1.44 (m, 2H), 1.30 (m, 12H); \(^{13}\)C \({}^1\)H\} NMR \(\delta\) 178.36, 159.17, 138.09, 128.51, 127.83, 127.78, 115.03, 68.29, 63.03, 44.21, 43.39, 37.09, 32.85, 29.65, 29.59, 29.57, 29.50, 29.39, 29.21, 26.05, 25.84. IR 3382 (br), 3050, 3019, 2924, 2851,
Calcd for C_{29}H_{37}NO_{4}: C, 75.13; H, 8.04; N, 3.02. Found: C, 74.44; H, 8.13; N, 2.99.

**Monomers carrying one dendritic side-chain**

7,8-N-[4-[3,4,5-Tris(n-dodecyl-1-oxy)-benzoic acid]-phenyl ester]succinimide-endo-Tricyclo[4.2.2.0^{2.5}]deca-3,9-diene (DM-7). To a mixture of 7,8-N-4-Hydroxyphenylsuccinimide endo-Tricyclo[4.2.2.0^{2.5}]deca-3,9-diene (146.5 mg, 0.5 mmol), 3,4,5-Tris(n-dodecan-1-yloxy)benzoic acid (337 mg, 0.5 mmol) and DPTS (7.2 mg, 0.02 mmol) in dry THF (8 mL) was added DCC (160 mg, 0.775 mmol). The mixture was stirred at RT for 8 hours and then refluxed for 13 hours to get complete consumption of the acid derivative. After cooling and filtration, it was concentrated and dried. Upon recrystallization with acetone, a white powder was obtained (355 mg, 75%). TLC indicated the presence of two compounds that were separated by silica gel chromatography using hexane / ethyl acetate (2/1) as eluant. The desired compound (175 mg, 37%) was the second fraction with R_f = 0.63. For the first fraction (R_f = 0.83, 169 mg), IR, ^1H NMR and ^13C NMR analyses indicated the presence of the desired compound and an other compound that was not identified. (IR new bands at 3320, 1635 cm^{-1}, ^1H NMR new peaks at 6.75 (s), 5.98 (s), 3.96 (m), 3.48 (m), 2.03 (m) ppm, ^13C NMR new peaks at 171.27, 154.70, 153.33, 140.55, 131.77, 105.53...). mp: 100°C; ^1H NMR δ: 7.39 (s, 2H), 7.29 (bs, 4H), 6.02 (m, 2H), 5.94 (s, 2H), 4.05 (m, 6H), 3.29 (bs, 2H), 2.98 (s, 2H), 2.89 (s, 2H), 1.79 (m, 6H), 1.49 (m, 6H), 1.27 (m, 48H), 0.89 (t, J = 8.6 Hz, 9H). ^13C \{^1H\} NMR δ: 177.89, 164.75, 153.14, 150.88, 143.24, 138.18, 129.53, 128.64, 127.73, 123.79, 122.58, 108.73, 73.75, 69.43, 44.27, 43.54, 37.22, 32.13, 32.10, 30.52, 29.92,
7,8-N-4-[3,4,5-tris(n-dodecyl-1-oxy)-benzoic acid]-11-undecyl ester -1-oxy|phenylsuccinimide endo-Tricyclo[4.2.2.02.5]deca-3,9-diene (DM-8). To a mixture of 7,8-N-4-(11-hydroxy-undecyl-1-oxy)phenylsuccinimide endo-Tricyclo[4.2.2.02.5]deca-3,9-diene (250 mg, 0.85 mmol), 3,4,5-Tris(n-dodecan-1-yloxy)benzoic acid (547.5 mg, 0.85 mmol), DPTS (55 mg, 0.17 mmol) in dry CH2Cl2 (8 mL) was added DCC (230 mg, 1.05 mmol). The reaction mixture was stirred at RT. After 24 hours, no acid was present on TLC. The mixture was filtered and concentrated. The desired compound (410 mg, 51%) was isolated as fine white powder by silica gel column chromatography (hexane / ethyl acetate, 3/1, Rf = 0.56). It was further recrystallized using acetone. 1H NMR δ: 7.25 (s, 2H), 7.08 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 6.00 (t, J = 3.2 Hz, 2H), 5.92 (s, 2H), 4.29 (t, J = 6.8 Hz, 2H), 4.02 (t, J = 6.4 Hz, 6H), 3.95 (t, J = 6.4 Hz, 2H), 3.27 (s, 2H), 2.94 (s, 2H), 2.87 (s, 2H), 1.79 (m, 10H), 1.48-1.27 (m, 68H), 0.89 (t, J = 6.8 Hz, 9H). 13C {1H} NMR δ: 178.34, 166.69, 159.24, 152.95, 142.41, 138.17, 128.58, 127.84, 125.24, 124.45, 115.09, 108.10, 73.65, 69.30, 68.34, 65.33, 44.30, 43.47, 32.12, 32.10, 30.50, 29.90, 29.89, 29.84, 29.82, 29.75, 29.71, 29.59, 29.55, 29.53, 29.47, 29.31, 28.92, 26.27, 26.23, 26.19, 26.17, 22.87, 14.31. IR 3045, 2922, 2852, 1770, 1703, 1586, 1514, 1466, 1429, 1398, 1334, 1297, 1250, 1215, 1114, 999, 843, 820, 790, 764, 718. Anal. Calcd for C72H113NO8: C, 77.17; H, 10.16; N, 1.25. Found: C, 77.08; H, 10.29; N, 1.30.
endo-7-[3,4,5-Tris(n-dodecyl-1-oxy)-benzoic acid methyl ester]-endo-8-methanol-tricyclo[4.2.2.02.5]deca-3,9-diene. A mixture of endo-Tricyclo[4.2.2.02.5]deca-3,9-diene-7,8-dimethanol (100 mg, 0.52 mmol), 3,4,5-Tris(n-dodecan-1-yloxy)benzoic acid (318 mg, 0.47 mmol), DPTS (30 mg, 0.1 mmol), DCC (120 mg, 0.58 mmol) in CH₂Cl₂ (3 mL) was stirred under nitrogen at RT for 24 hours. The solution was then filtered to remove the precipitated urea and concentrated. Silica gel column chromatography (hexane / ethyl acetate (3/1), Rf = 0.45) leads to the desired compound (168 mg, 42 %). ¹H NMR δ: 7.24 (s, 2H), 6.02-6.01 (m, 2H), 5.86 (m, 2H), 4.35 (dd, J = 10.4, 6.4 Hz, 1H), 4.20 (dd, J = 8, 10.4 Hz, 1H), 4.01 (t, J = 6.8 Hz, 6H), 3.74 (dd, J = 10.4, 6.4 Hz, 1H), 3.53 (dd, J = 10.4, 8 Hz, 1H), 2.75 (br, 3H), 2.70 (br, 1H), 2.29 (m, 1H), 2.08 (m, 1H), 1.85-1.70 (m, 6H), 1.50-1.42 (m, 6H), 1.40-1.03 (m, 54H), 0.88 (t, J = 6.8 Hz). ¹³C {¹H} NMR δ: 166.50, 153.04, 142.75, 137.97, 137.84, 129.77, 129.47, 125, 108.30, 73.72, 69.44, 66.26, 64.04, 45.71, 45.53, 43.92, 40.31, 38.40, 37.82, 32.13, 30.53, 29.95, 29.93, 29.90, 29.84, 29.77, 29.62, 29.59, 29.57, 29.53, 26.30, 26.26, 22.89, 14.31. IR 3650-3150 (br), 3112, 3040, 2924, 2854, 1715, 1587, 1500, 1466, 1430, 1382, 1335, 1215, 1115, 1046, 995, 864, 805, 764, 712. Anal. Calcd for C₅₅H₉₂O₆: C, 77.78; H, 10.92. Found: C, 77.61; H, 11.00.

Monomers carrying two dendritic side-chains

endo,endo-7,8-Bis[3,4,5-tris(n-dodecyl-1-oxy)-benzoic acid methyl ester]tricyclo[4.2.2.02.5]deca-3,9-diene (DM-1). A mixture of endo-tricyclo[4.2.2.02.5]deca-3,9-diene-7,8-dimethanol (134.4 mg, 0.7 mmol), 3,4,5-Tris(n-dodecan-1-yloxy)benzoic acid (1.038 g, 1.54 mmol), DMAP (34 mg, 0.28 mmol), p-
TsOH (52 mg, 0.28 mmol) and DCC (360 mg, 1.75 mmol) in dry CH₂Cl₂ (14 mL) was stirred at RT under N₂ for 48 h. The solution was then filtered and the solvent remove. The desired compound was recovered as a white powder (666 mg, 64%) after silica gel column chromatography (hexane / ethyl acetate (3/1)) followed by recrystallization with acetone. ¹H NMR δ: 7.26 (s, 4H), 6.05 (m, 2H), 5.86 (s, 2H), 4.39 (dd, J = 10.4, 5.2 Hz, 2H), 4.28 (dd, J = 11.2, 7.2 Hz, 2H), 4.01 (m, 12H), 2.76 (s, 2H), 2.73 (br, 2H), 2.33 (br, 2H), 1.85-1.71 (m, 12H), 1.55-1.40 (m, 12H), 1.40-1.18 (br, 96H), 0.87 (t, J = 6.8 Hz, 18H). ¹³C {¹H} NMR δ: 166.39, 153.06, 142.66, 138.05, 137.88, 129.69, 129.58, 129.46, 124.99, 108.34, 108.15, 73.86, 73.72, 73.58, 69.54, 69.40, 69.27, 66.11, 45.52, 45.40, 40.40, 40.32, 40.24, 38.28, 38.16, 32.16, 30.56, 29.94, 29.89, 29.81, 29.67, 29.60, 29.57, 26.35, 26.29, 22.92, 17.40, 14.28. IR 3041, 2924, 2853, 1716, 1587, 1500, 1466, 1430, 1385, 1334, 1211, 1115, 998, 862, 765, 720. Anal. Calcd for C₉₈H₁₆₈O₁₀: C, 78.14; H, 11.24. Found: C, 77.97; H, 11.33.

**endo,endo-7,8-Bis[[[3,4,5-Tris(n-dodecyl-1-oxy)benzyl]oxy]carbonyl]-tricyclo[4.2.2.0²⁵]deca-3,9-diene (DM-1B).** A mixture of *endo*-Tricyclo[4.2.2.0²⁵]deca-3,9-diene-7,8-dicarboxyanhydride (*M*-1) (229 mg, 1.134 mmol), 3,4,5-Tri(*n*-Dodecan-1-yloxy)benzyl alcohol (1.5 g, 2.27 mmol) and DMAP (25 mg, 0.2 mmol) in CH₂Cl₂ (7 mL) was stirred at RT under nitrogen. After 48 hours, DPTS (76 mg, 0.24 mmol) and DCC (350 mg, 1.5 mmol) were added. After 24 hours, no starting alcohol could be seen by TLC. The mixture was then filtrated and concentrated. Silica gel column chromatography (dichloromethane, Rₜ = 0.79) lead to the desired compound. A white powder was obtained upon recrystallization with acetone (0.95 g, 56%). ¹H NMR δ: 6.48
(s, 4H), 6.06 (m, 2H), 5.84 (s, 2H), 4.97 (d, J = 12 Hz, 2H), 4.71 (d, J = 12 Hz, 2H), 3.93 (m, 12H), 2.97 (s, 2H), 2.95 (bs, 2H), 2.73 (bs, 2H), 1.75 (m, 12H), 1.46 (m, 12H), 1.27 (br, 96H), 0.89 (t, J = 6.6 Hz, 18H). $^{13}$C $^{1}$H NMR δ: 172.90, 153.34, 138.23, 127.98, 131.03, 128.48, 106.99, 73.60, 69.31, 66.89, 46.99, 44.63, 37.78, 32.15, 30.58, 29.99, 29.95, 29.90, 29.87, 29.70, 29.66, 29.60, 26.37, 22.91, 14.33. IR 3040, 2923, 2853, 1742, 1590, 1505, 1466, 1439, 1378, 1333, 1233, 1168, 1116, 1005, 816, 789, 755, 721. Anal. Calcd for C$_{99}$H$_{172}$O$_{10}$: C, 78.10; H, 11.39. Found: C, 78.00; H, 11.42.

**endo-7-[3,4,5-Tris(n-dodecyl-1-oxy)-benzoic acid methyl ester]-endo-8-[3,4-Bis((3,4-(n-dodecyl-1-oxy)benzyl)oxy)-benzoic acid methyl ester]-tricyclo[4.2.2.0$^{2,5}$]deca-3,9-diene (DM-6).** A mixture of endo-7-[[[3,4,5-tris(n-dodecyl-1-oxy)benzyl]oxy]methyl]-endo-8-methanol-tricyclo[4.2.2.0$^{2,5}$]deca-3,9-diene (149 mg, 0.176 mmol), 3,4-bis[(3,4-bis(n-dodecyl-1-oxy)benzyl)oxy]benzoic acid (189 mg, 0.177 mmol), DPTS (15 mg, 0.05 mmol) and DCC (55 mg, 0.267 mmol) in dry CH$_2$Cl$_2$ (4 mL) was gently heated to 40°C under N$_2$ until no acid was present on TLC. The cooled solution was then filtered and the solvent removed. The desired compound was isolated by silica gel chromatography (hexane / ethyl acetate (3/1), R$_f$ = 0.95) as a waxy solid. Upon recrystallization with acetone, a white powder was obtained (202 mg, 61%). $^{1}$H NMR δ: 7.65 (m, 3H), 7.02-6.92 (m, 6H), 6.84 (dd, J = 8, 2.8 Hz, 2H), 6.05 (m, 2H), 5.88 (s, 1H), 5.87 (s, 1H), 5.11 (s, 2H), 5.10 (s, 2H), 4.40 (m, 2H), 4.24 (m, 2H), 3.97 (m, 16H), 2.77 (bs, 4H), 2.33 (bs, 2H), 1.80 (m, 14H), 1.46 (m, 14H), 1.27 (br, 146H). $^{13}$C $^{1}$H NMR δ: 166.44, 166.22, 153.25, 153.06, 149.48, 149.46, 149.18, 149.12, 148.61, 142.65, 138, 137.93, 129.67, 129.62, 129.50, 129.26, 124.99, 121.12, 123.27, 120.38,
endo,endo-7,8-Bis[3,5-bis(4-((n-dodecyl-1-oxy)benzyl)oxy)-benzoic acid methyl ester]-tricyclo[4.2.2.0\(^2\).5\]deca-3,9-diene (DM-2). A mixture of endo-tricyclo[4.2.2.0\(^2\).5\]deca-3,9-diene-7,8-dimethanol (65 mg, 0.34 mmol), 3,5-bis[(4-(n-dodecyl-1-oxy)benzyl)oxy]benzoic acid (400 mg, 0.62 mmol), DMAP (16 mg, 0.11 mmol), p-TsOH (22 mg, 0.11 mmol) and DCC (176 mg, 0.86 mmol) in dry CH\(_2\)Cl\(_2\) (15 mL) was stirred at RT under N\(_2\) until no acid was present on TLC. The solution was then filtered and the solvent removed. Two compounds were isolated by silica gel chromatography (hexane / ethyl acetate (3/1): the mono-substituted product (116 mg, R\(_f\) = 0.36) and the desired disubstituted product (R\(_f\) = 0.87). The desired compound was recovered as white powder after a second column using CH\(_2\)Cl\(_2\) as eluant (181 mg, 40%).

\(^1\)H NMR \(\delta\): 7.34 (d, J = 8.8 Hz, 8H), 7.29 (d, J = 2.4 Hz, 4H), 6.90 (dt, J = 8.4, 2.2 Hz, 8H), 6.78 (t, J = 2.2 Hz, 2H), 6.05 (br, 2H), 5.88 (s, 2H), 4.98 (s, 8H), 4.44 (dd, J = 11.2, 5.4 Hz, 2H), 4.22 (dd, J = 10.8, 8 Hz, 2H), 3.94 (t, J = 6.6 Hz, 8H), 2.77 (s, 4H), 2.33 (br, 2H), 1.78 (m, 8H), 1.55-1.40 (m, 8H), 1.40-1.20 (br, 68H), 0.89 (t, J = 7 Hz, 12H). \(^{13}\)C \(^{1}\)H NMR \(\delta\): 166.28, 160.04, 159.35, 137.99, 132.24, 139.61, 128.45, 114.79, 108.46, 107.41, 70.34, 68.23, 66.13, 45.37, 40.12, 38.04, 32.13, 29.88, 29.85, 29.83, 29.81, 29.63,
Characterization of the mono-substituted derivative

$^1$H NMR δ: 7.33 (d, J = 8.8 Hz, 4H), 7.25 (s, 2H), 6.91 (dt, J = 8.8, 2.2 Hz, 4H), 6.78 (t, J = 2.2 Hz, 1H), 6.00 (br, 2H), 5.86 (m, 2H), 4.98 (s, 4H), 4.38 (dd, J = 10.8, 6.4 Hz, 1H), 4.12 (dd, J = 11.2, 8.8 Hz, 1H), 3.96 (t, J = 6.8 Hz, 4H), 3.72 (dd, J = 10.8, 6.4 Hz, 1H), 3.50 (br t, 1H), 2.73 (br, 4H), 2.26 (m, 1H), 2.06 (m, 1H), 1.78 (m, 4H), 1.48-1.40 (m, 4H), 1.39-1.2 (br, 34 H), 0.88 (t, J = 7 Hz, 6H). IR 3650-3150 (br), 3110, 3039, 2924, 2853, 1718, 1595, 1514, 1466, 1447, 1376, 1346, 1299, 1248, 1158, 1111, 1048, 825, 767, 712.

**endo,endo-7,8-Bis[3,4-bis((3,4-dodecyl-1-oxy)benzyl)oxy]-benzoic acid methyl ester-tricyclo[4.2.2.0^{2.5}]deca-3,9-diene (DM-4).** A mixture of endo-tricyclo[4.2.2.0^{2.5}]deca-3,9-diene-7,8-dimethanol (42.8 mg, 0.22 mmol), 3,4-bis[(3,4-bis(n-dodecyl-1-oxy)benzyl)oxy]benzoic acid (500 mg, 0.47 mmol), DMAP (11 mg, 0.09 mmol), p-TsOH (17 mg, 0.09 mmol) and DCC (111 mg, 0.53 mmol) in dry CH$_2$Cl$_2$ (12 mL) was stirred at RT under N$_2$ until no acid was present on TLC (24 h). The solution was then filtered and the solvent removed. The desired compound was isolated as a white powder after silica gel chromatography using CH$_2$Cl$_2$ as eluant (215 mg, 42%).$^1$H NMR δ: 7.67-7.63 (m, 4H), 7.01 (d, J = 2 Hz, 2H), 6.97-6.91 (m, 8H), 6.83 (dd, J = 8, 2.8 Hz, 4H), 6.04 (br, 2H), 5.88 (s, 2H), 5.11 (s, 4H), 5.10 (s, 4H), 4.41 (dd, J = 10.4, 4.4 Hz, 2H), 4.21 (m, 2H), 3.99-3.91 (m, 16H), 2.77 (s, 4H), 2.32 (br, 2H), 1.79 (m, 16H), 1.44 (br, 16H), 1.27 (br, 128H), 0.89 (t, J = 6.4 Hz, 24H). $^{13}$C {${^1}$H} NMR δ: 166.26, 153.23, 146.7, 144.6, 137.7, 134.8, 129.9, 124.8, 115.8, 111.0, 105.1, 82.4, 76.6, 72.0, 67.6.
149.49, 149.45, 149.18, 149.12, 148.62, 137.96, 129.63, 129.59, 129.26, 124.12, 123.29,
120.40, 120.12, 115.75, 113.79, 113.75, 113.51, 113.23, 71.44, 71.13, 69.49, 69.40,
69.33, 65.76, 45.43, 40.23, 38.06, 32.14, 29.95, 29.90, 29.89, 29.74, 29.71, 29.68, 29.60,
29.55, 26.33, 26.30, 26.28, 22.90, 14.33. IR 3038, 2922, 2853, 1709, 1596, 1517, 1467,
C₁₅₂H₂₄₈O₆: C, 78.30; H, 10.72. Found: C, 78.15; H, 10.76.

endo,endo-7,8-Bis[3,4-Bis((4-(n-dodecyl-1-oxy)benzyl)oxy)benzoic acid methyl ester]-tricyclo[4.2.2.0²⁵]deca-3,9-diene (DM-3). A mixture of endo-
tricyclo[4.2.2.0²⁵]deca-3,9-diene-7,8-dimethanol (125 mg, 0.65 mmol), 3,4-bis[(4-(n-
dodecyl-1-oxy)benzyl)oxy]benzoic acid (1.01 g, 1.42 mmol), DMAP (34 mg, 0.28
mmol), p-TsOH (50 mg, 0.26 mmol) and DCC (400 mg, 1.94 mmol) in dry CH₂Cl₂ (45
mL) was stirred at RT under N₂ until no alcohol was present on TLC (24 h). The solution
was then filtered and the solvent removed. The desired compound was isolated as a white
gel after silica gel chromatography using CH₂Cl₂ as eluant. A white powder obtained
after recrystallization with acetone (760 mg, 75%). ¹H NMR δ: 7.63 (m, 4H), 7.36 (d, J =
8.8 Hz, 4H), 7.33 (d, J = 8.8 Hz, 4H), 6.92 (d, J = 8.4 Hz, 2H), 6.88 (m, 8H), 6.04 (t, J =
3.6 Hz, 2H), 5.88 (s, 2H), 5.13 (s, 4H), 5.11 (s, 4H), 4.39 (dd, J = 10.5, 5.2 Hz, 2H), 4.20
(dd, J = 10.4, 7.6 Hz, 2H), 3.94 (m, 8H), 2.76-2.75 (br, 4H), 2.31 (br, 2H), 1.77 (m, 8H),
1.45 (br, 8H), 1.27 (br, 64H), 0.89 (t, J = 6.8 Hz, 12H). ¹³C {¹H} NMR δ: 166.25, 159.21,
159.16, 153.24, 148.61, 137.96, 129.58, 129.34, 129.06, 128.94, 128.55, 124.09, 123.23,
115.88, 114.72, 114.64, 113.62, 71.26, 70.93, 68.23, 68.20, 65.77, 45.44, 40.24, 38.09,
32.13, 29.88, 29.84, 29.81, 29.65, 29.62, 29.56, 29.50, 29.49, 26.26, 22.90, 14.34. IR
endo,endo-7,8-Bis[3,4-Bis((3,4,5-Tris(n-dodecyl-1-oxy)benzyl)oxy)benzoic acid methyl ester]-tricyclo[4.2.2.0^2.5]deca-3,9-diene (DM-5). A mixture of endo-tricyclo[4.2.2.0^2.5]deca-3,9-diene-7,8-dimethanol (27 mg, 0.14 mmol), 3,4-bis[(3,4,5-tris(n-dodecyl-1-oxy)benzyl)oxy]benzoic acid (1.01 g, 1.42 mmol), DMAP (34 mg, 0.28 mmol), p-TsOH (50 mg, 0.26 mmol) and DCC (400 mg, 1.94 mmol) in dry CH₂Cl₂ (45 mL) was stirred at RT under N₂ for 48 h. The solution was then filtered and the solvent removed. The desired compound was isolated as a white gel (148 mg, 36%) after silica gel chromatography using CH₂Cl₂ as eluant (Rf = 0.9). \(^1\)H NMR δ: 7.66 (m, 4H), 6.94 (d, J = 8.4 Hz, 2H), 6.66 (s, 4H), 6.62 (s, 4H), 6.04 (br, 2H), 5.87 (s, 2H), 5.09 (s, 4H), 5.08 (s, 4H), 4.41 (bddd, 2H), 4.20 (bddd, 2H), 3.91 (m, 24H), 2.76 (bs, 4H, 2.32 (br, 2H), 1.75 (m, 24H), 1.43 (m, 24H), 1.26 (br, 192H), 0.88 (t, J = 6.8 Hz, 36H). \(^13\)C \(^{1}\)H NMR δ: 166.22, 153.53, 153.45, 153.26, 148.63, 138.11, 138.07, 137.97, 131.96, 131.68, 129.61, 124.27, 123.46, 115.87, 113.58, 106.1, 105.75, 73.59, 71.81, 71.47, 69.30, 69.26, 65.74, 45.41, 40.20, 38.01, 32.16, 30.61, 30.0, 29.96, 29.91, 29.73, 29.71, 29.67, 29.65, 29.61, 26.39, 22.92, 14.34. IR 2923, 2853, 1709, 1593, 1509, 1466, 1439, 1379, 1336, 1269, 1207, 1117, 997, 808, 763, 721. Anal. Calcd for C₂₀₀H₃₄₄O₂₀: C, 78.27; H, 11.30. Found: C, 77.83; H, 11.31.

Kinetic studies using GPC. To a solution of monomer (50 mg, 50 equiv, CH₂Cl₂) was added with a syringe the desired catalyst amount from a freshly prepared
stock solution (CH$_2$Cl$_2$) under vigorous stirring. Reaction conditions were adjusted so that [catalyst] = 0.001 M, and [monomer] / [catalyst] = 50. At different times, an aliquot (25 µL) was quenched with two drops of ethyl vinyl ether and precipitated upon addition of a few drops of methanol. After drying under vacuum, the monomer conversion was determined using GPC.

**Hydrogenation of poly-2.** 2 g (10-fold excess) of $p$-toluenesulfonhydrazide was added to 95 mg of poly-2 ($D_p = 200$) in xylene (10 mL). The mixture was heated to 120°C for 6 h under vigorous stirring. It was then poured in methanol, and a yellow pale solid was recovered by filtration. It was centrifuged several times in acetone to remove traces of the byproduct. After drying under vacuum, a shiny yellow pale solid (60 mg) was recovered. $^1$H NMR $\delta$: 5.68 (br, 0.29H), 3.02, 2.96, 2.90 (br, 5H), 2.17, 2.12, 1.88, 1.65, 1.45, 1.36, 1.17 (br, 10H). $^{13}$C {$^1$H} NMR $\delta$: 180.18, 131.50 (m), 45.60-44.75 (m), 39.45-39.30 (m), 38.70-38.20 (m), 29.30-29.00 (m), 27.30-27.20 (m), 27.00-26.30 (m), 24.85, 16.75-15.75 (m).

3.5. **References**

(1) Maughton, B.R.; Grubbs, R.H. *Macromolecules* 1997, 30, 3459


166


(7) Percec, V.; Holerca, M.N. *Biomacromolecules* 2000, 1, 6


CHAPTER IV.

INVESTIGATIONS ON THE PREPARATION OF GRAFT COPOLYMERS BY
ROMP-ATRP CATALYSIS

4.1. Introduction

Free radical polymerization is the most important industrial process for preparing high molecular weight polymers. The main problem of conventional free-radical methods is the lack of control associated with the uncontrolled generation of radicals and subsequent chain transfer and termination processes. Therefore, for a long time, only very limited control over molecular weight was possible and polydisperse samples were obtained. While much attention has been paid to the successful development of ionic living systems in the last decades, those systems can rarely be used in industry due to the stringent reaction conditions. Also, with the objective of developing living systems that could be readily used on the industrial scale, a renewed interest over the last ten years has appeared in the area of free-radical polymerization.

Different techniques have been recently developed and have allowed the preparation of monodisperse samples from monomers such as styrene, acrylates, acrylonitrile and the generation of polymers with controlled architecture in a living fashion. They are all based on a common strategy: suppressing the bimolecular termination reactions by converting the growing radicals, reversibly and temporally, into dormant species. Therefore, the radical concentration in the reaction media decreases and the rate of termination that is second order in radical concentration will significantly slow
One of these techniques, first introduced by both Sawamoto and Matyjaszewski in 1995, is atom transfer radical polymerization (ATRP), a catalytic step growth polymerization technique. The general mechanism of ATRP is outlined in Scheme 4.1.

**Scheme 4.1.** General ATRP mechanism.2

The initiating system consists of an alkyl halide and a transition metal species such as a copper(I) complex in the presence of coordinative bidentate ligands (2,2'-bipyridine for example). ATRP lies on the iteration of the Kharash reaction, in which a transition metal catalyst acts as a carrier of the halogen atom in a reversible redox process. Therefore, due the reversibility of this process, an exchange equilibrium is observed between the dormant and active polymer chains. If the concentration of growing radicals is low and the redox reaction is fast as compared to the bimolecular coupling of the radicals, then the termination reactions are minimized, which results in a living process. Also, if $k_{\text{deact}}$ is comparable or higher than $k_p$ then narrow molecular weight distributions should be obtained. Studies have shown that initiator efficiency is of prime importance for successful polymerization control: tertiary alkyl halides, especially alkyl bromide in combination with a copper(I) chloride catalyst is the preferred system.1,2
While the ATRP concept was introduced with copper based catalysts, pioneering work by Sawamoto had been also done with Ru$^{II}$ metal species.$^4$ The living radical polymerization of methyl methacrylate (MMA) was possible with a tertiary initiating system consisting of CCl$_4$, RuCl$_2$(PPh$_3$)$_3$ and methylaluminium bis-(2,6-di-tert-butylphenoxide) [MeAl(ODBP)$_2$]. The Ru(II) complex had been shown to promote the Kharash reaction between carbon tetrachloride and monosubstituted alkenes.$^5$ Upon addition of an aluminum alkoxide compound that may coordinate the ester group of the CCl$_4$-MMA adduct and activate the C-Cl bond for homolytic cleavage, iteration of the Kharash reaction occurred, leading to PMMA (Scheme 4.2). Interestingly, the reversible activation of the C-Cl bond with the Ru(II)-MeAl(ODP)$_2$ system was a key feature to observe the controlled polymerization of MMA in the same fashion as the traditional copper-based ATRP system.$^6$

**Scheme 4.2.** Proposed mechanism for the polymerization of MMA with the ternary system CCl$_4$, RuCl$_2$(PPh$_3$)$_3$, MeAl(ODBP)$_2$.}$^4$
Studies have been made with a variety of alkyl-halides and aluminium alkoxides in association with the Ru(II) complex.\textsuperscript{7} They indicated that the Lewis acid additive had no effect on the rate of the halogen-exchange reaction but was affective in the acceleration of the polymerization, which leaded to narrower molecular weight distributions.\textsuperscript{8}

While a Lewis acid activator is necessary in the ruthenium-based system developed by Sawamoto, Demonceau and co-workers recently reported the living radical polymerization of MMA with no activator by Ru(II) complexes of the type \([\text{RuCl}_2(\text{p-cymene})(\text{PR}_3)]\) in the presence of a tertiary alkyl bromide initiator.\textsuperscript{9} Those complexes were generated in-situ from the ruthenium dimer \([\{\text{RuCl}_2(\text{p-cymene})\}_2]\) and the desired \(\text{PR}_3\) phosphine in the ratio \(\text{Ru:PR}_3 = 2:1\). The best control over the polymerization was obtained with the sterically demanding and more basic phosphanes such as \(\text{PCy}_3\). While the mechanism of the polymerization was not investigated in details, a correlation was found between the arene ligand lability and the catalyst activity. The activity dependence on the phosphine properties were similar to the trend observed for the activity of the Grubbs' type ruthenium carbenes and surprisingly, \textbf{Ru-III} was shown to promote the polymerization of MMA with a higher activity than the \(\text{p-cymene-based catalysts}\) but to the detriment of molecular weigh control and dispersity (PDI \(\approx 1.3\)). Nevertheless, monodisperse (PDI < 1.2) polymer samples from various acrylates could be prepared in moderate to high yields with the \(\text{p-cymene-based ruthenium catalysts}\). The exact mechanism that was shown to be radical in nature and involving arene dissociation has not been determined.
As well-defined ruthenium carbene catalysts have been shown to promote both ROMP and ATRP, Grubbs and co-workers combined both polymerization techniques in a one-pot reaction. The alkylidene moiety of a ruthenium carbene complex was functionalized with a tertiary alkyl bromide that could act as a radical polymerization initiator. With this, the ROMP of 1,5-cyclooctadiene (COD) was possible but also the control radical polymerization of MMA could be performed. For the first time, ATRP could be performed with a single complex that carried both the radical initiator and the transition metal complex. Therefore, this catalyst could initiate in tandem the ROMP of 1,5-cyclooctadiene and the radical polymerization of MMA at 65°C (Scheme 4.3).

**Scheme 4.3.** Tandem ROMP and ATRP with a single modified Ru-carbene catalyst.

Well-defined block copolymers containing polybutadiene and PMMA fragments could be prepared in one-pot in toluene at 65°C (60% yield, reaction for 18 h). Kinetic studies indicated that ROMP was much faster than ATRP. Nevertheless, the ROMP activity could be decreased by addition of PCy₃, a known technique to reduce the catalyst activity when the polymerization mechanism involves phosphine dissociation. Also, as the copolymerization rates were comparable to the homopolymerization rates, this indicated that both polymerizations were proceeding simultaneously. Also, copolymers with PE and PMMA fragments could be prepared by a subsequent hydrogenation step.
The fact that a Grubbs' type catalyst could promote both ATRP and ROMP appeared very interesting to us. We had shown that the living ROMP of the endo-tricyclo[4.2.2.0²⁵]deca-3,9-diene structure was obtained with Ru-III but this catalyst also had been reported to promote the ATRP of MMA. Therefore, it appeared possible that by the specific functionalization of the ROMP monomer structure with an alkylbromide group that would act as an ATRP initiator, graft copolymers with a ROMP main chain and PMMA side fragments could be prepared in one-pot with a single catalyst.

4.2. Results

4.2.1. Monomer design

Efficient initiation for the ATRP of MMA has been extensively reported with 2-bromo-2-methyl propionate. This in part results from the chemical similarity of this compound with MMA and secondly, from the presence of a tertiary bromide that leads to a fast exchange reaction, a necessary condition for the preparation of polymers with low polydispersities.¹

Scheme 4.4. Synthesis of monomers functionalized with an ATRP initiator.
The radical initiator was first introduced on the monomer structure by the mild esterification of 2-bromo-2-methyl propionic acid and M-17 catalyzed by DMAP in the presence of DCC. In the resulting compound (M-21), the functional group was relatively close to the ROMP cyclic structure. Therefore, it was also placed further away by the use of a 11-carbon spacer (Scheme 4.4).

4.2.2. Polymerization studies

![Diagram of polymerization structure]

**Figure 4.1.** $^1$H NMR spectrum of poly-22 (20-mer) prepared with Ru-III.

First of all, 20-mers of M-21 and M-22 were prepared with Ru-III. Monodisperse samples (PDI = 1.12) were obtained in quantitative yields. Interestingly, in the $^1$H NMR
spectrum of poly-22, well-defined signals could be identified for the functionalized alkyl side-chain (Figure 4.1).

Also, whereas no transition was observed by the DSC analysis of poly-22, a low T_g (37°C) was present for poly-21. This is a unique characteristic among all the functional polymers with functionalized N-phenyl succinimide moieties: in no other case has a T_g been observed. This proved to be important for the characterization of graft copolymers with a backbone formed from M-21.

We investigated the polymerization of mixtures of the functionalized monomers M-21 or M-22 and MMA with Ru-III in toluene at 65°C under a nitrogen atmosphere. In all experiments, upon addition of the catalyst solution to the monomer mixture, the solution turned the same yellow color as is observed for the ROMP of the functionalized monomers. With time, the color progressively became orange-reddish and the viscosity increased dramatically

Unfortunately, the use of M-21 proved to be unpractical as its solubility in toluene was limited to 0.04 M. A better solubility was observed in MMA but the neat copolymerizatin led to a bimodal, polydisperse molecular weight distribution, possibly resulting from the coupling between polymer chains. In several experiments with the same initiator concentration, [I], as in entry 1 but with varying [I]:[MMA] ratios, an unexplained bimodal molecular weight distribution was still obtained (Table 4.1).

While the relative molecular weights measured by GPC do not really have meaning because the conformation of a graft polymer has a substantial influence on its
hydrodynamic volume, in all cases (entries 1, 2, 4-7), no trace of the homo-ROMP polymer was present.

Table 4.1. Graft copolymerization results.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Initiator (I)</th>
<th>[I]</th>
<th>Yield</th>
<th>GPC data</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>M-21</td>
<td>0.04 M</td>
<td>70 %</td>
<td>M_n = 53600 PDI = 2.62</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Neat (13.6 mg / 1 mL MMA)</td>
<td>66 %</td>
<td>2 high M_n overlapped peaks</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.01 M</td>
<td>only the ROMP polymer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.20 M</td>
<td>bimodal M_w distribution</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>M-22</td>
<td>0.15 M</td>
<td>53 %</td>
<td>M_n = 34000 PDI = 1.89</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.1 M</td>
<td>30 %</td>
<td>M_n = 27800 PDI = 1.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.05 M</td>
<td>31 %</td>
<td>M_n = 23800 PDI = 1.67</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a Conditions: toluene, 65°C, 24 h, [Ru-III]:[I]:[MMA] = 1:20:800 (entries 1-6), 1:20:100 (entry 7); *b Based on the weight of recovered polymer; *c CHCl_3 as eluant, relative to monodisperse polystyrene standards.*

For highly concentrated polymerization runs, bimodal polydisperse, molecular weight distributions, and high molecular weights were obtained. The best results were obtained with M-22. One peak with a smooth Gaussian shape was observed by GPC and it appeared that grafting of PMMA on the ROMP-backbone had occurred. After 24 hours, the conversion of MMA was not complete as indicated by the low yields. The incorporation of MMA units appeared to be very slow. With a smaller [I]: [MMA] ratio (entry 4), almost complete conversion was obtained and ^1^H NMR confirmed the incorporation of apparently 4.4 MMA units per ROMP unit (88%). Nevertheless, in the ^1^H NMR spectra of the isolated polymers (entries 3-5, 7), many unexpected peaks were observed (Figure 4.2).
As reported by Sawamoto, the protons of the methoxy propagating unit are found at 3.76 ppm. The methyl protons connected at the extremities of the PMMA fragments must be present in the 1.2-1.6 ppm region of the spectrum. Unfortunately due to significant overlapping with the ROMP polymer backbone signals, the PMMA content was not determined. The sharp peak at 1.93 ppm does not correspond to the monomer methyl protons $\beta$ to the bromine group as the peak intensity is very high as compared to the one observed for the ROMP backbone. The small triplet observed at 4.17 ppm could not be assigned to the protons $\alpha$ to the propionate group observed in the ROMP homopolymer (Figure 4.1) because a similar triplet was present in the $^1$H NMR spectrum of a copolymer prepared from M-21 and its origin remains unexplained.

Surprisingly, the $^1$H NMR of the copolymer measured in toluene-d$_8$ was very different than the one measured in CDCl$_3$ (Figure 4.3). First of all, the copolymer is not as readily soluble in toluene as it is in chloroform. Significant change in the chemical shifts of the protons of the PMMA fragments can be observed: the methylene and methyl protons are shifted downfield whereas the methoxy protons are shielded. Also, the unassigned peaks in the 1.2-1.6 ppm region in chloroform can no longer be distinguished and the small signal for the alkyl protons of the cyclic ROMP monomer structure around 3.2-2.8 ppm can no longer be seen. The signals corresponding to the protons present on the cyclic structure and the alkene protons, i.e., the ROMP polymer backbone were also hardly visible on the $^1$H NMR spectrum in chloroform and NMR integration was not consistent. Those observations indicate that the copolymer may adopt a micelle-like morphology in solution, the ROMP backbone being segregated in the core.
Figure 4.2. The $^1$H NMR spectrum (in CDCl$_3$) of a copolymer (poly-22)-graft-PMMA (entry 3).
Figure 4.3. $^1$H NMR spectrum of a graft copolymer measured in toluene-$d_8$ (top) and in CDCl$_3$ (bottom).
To better characterize this tandem system, the copolymerization was performed in toluene-\textsubscript{d$_8$} at 65°C and followed by $^1$H NMR. This kinetic study indicated that within one hour, the ROMP monomer had been polymerized whereas the ATRP of MMA had barely started. The MMA polymerization was followed over 48 h using naphthalene as an internal reference (Figure 4.4).

![Figure 4.4](image)

**Figure 4.4.** Logarithm plot of the kinetic data of the ATRP of MMA during a copolymerization with M-22 and Ru-III.

While the polymerization is relatively slow in the reaction conditions used ([M-22] = 0.05 M, Ru-III:M-22:MMA = 1:10:400), the MMA consumption is a first order kinetic process and this indicates the absence of chain termination, the usually major problem of radical polymerizations. Those data support that the ATRP of MMA with M-22 as initiator and Ru-III as promotor is well-controlled.
The $^1$H NMR pattern of the PMMA methyl protons (h) and quantitative $^{13}$C NMR analysis indicated that syndiotactic rich PMMA blocks had been synthesized (Figure 4.5).

**Figure 4.5.** The $^1$H and $^{13}$C NMR spectra of a (poly-21)-*graft*-PMMA copolymer (right side) (the left side spectra are reprinted from reference 12).
In the DSC spectra of the copolymers, the \( T_g \) of the PMMA blocks was present at 124°C, confirming that syndiotactic blocks had been prepared.\(^{13}\) Also, no other transition was seen for the (poly-22)-graft-PMMA copolymers up to 150°C. On the contrary, the \( T_g \) of the poly-21 backbone could be seen at the lower value of 30°C, suggested that the PMMA fragments may behave as a plasticizer. As the glass transition temperatures of both blocks are seen, phase segregation certainly occurs.

The propagation stage may be slowed down due to the increasing crowdiness around the ROMP polymer backbone. To avoid this problem, the copolymerization was performed in two steps: first a random copolymer was prepared with various M-22 and M-3 contents using Ru-III in toluene. M-3 was chosen because it is fairly soluble in toluene and the \(^1\)H NMR of the resulting polymer was simple. After complete copolymerization, MMA was added and the mixture was heated at 65°C. As less ATRP initiator was present in the ROMP backbone, the backbone periphery was expected to be less crowded. The same color change was observed with time. PMMA fragments were generated as indicated by the \(^1\)H NMR spectra and the GPC data (Table 4.2).

**Table 4.2. Analyses of poly(M-22-co-M-3)-graft-PMMA.\(^a\)**

<table>
<thead>
<tr>
<th>Entry</th>
<th>ROMP copolymer composition (M-3 / M-22)(^c)</th>
<th>GPC analysis of the ROMP copolymer (aliquot)(^b)</th>
<th>Yield</th>
<th>GPC data</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>1.2 / 1</td>
<td>no aliquot taken</td>
<td>66 %</td>
<td>( M_n = 65000 )  ( \text{PDI} = 1.69 )</td>
</tr>
<tr>
<td>9</td>
<td>3.1 / 1</td>
<td>( M_n = 26000 ) ( \text{PDI} = 1.12 )</td>
<td>68 %</td>
<td>( M_n = 81000 )  ( \text{PDI} = 1.62 )</td>
</tr>
</tbody>
</table>

\(^a\) Reaction conditions: see experimental part; \(^b\) Using CHCl\(_3\) as eluant, relative to monodisperse polystyrene standards. \(^c\) Determined by \(^1\)H NMR
Once again, a Gaussian type monomodal molecular weight distribution was obtained with no trace of the ROMP copolymer precursor. As the ROMP copolymer was prepared in 16 h, it is interesting to see that the ruthenium catalyst was still able to promote the ATRP of MMA after such a long time in solution. Furthermore, initiation for ROMP is complete and this indicates that the active ROMP propagating species can promote ATRP.

On DSC analysis, the $T_g$ of the PMMA blocks was present at 122.5 °C when the content of the ROMP copolymer in ATRP initiator was $\approx 50\%$ (entry 8). At a lower content (entry 9), no $T_g$ was observed, indicating that phase separation was not occurring anymore.

**4.2.3. Conclusions**

Graft copolymers based on a ROMP polymer skeleton and with PMMA branches could be prepared in a one-pot procedure using the Grubbs' ruthenium carbene $\text{Ru-III}$ and monomers based on the *endo*-tricyclo[4.2.2.0^2,5]deca-3,9-diene structure functionalized with a tertiary alkyl bromide, present as an ATRP initiator. $\text{Ru-III}$ has been shown to promote the living polymerization of the ROMP structure and as the absence of chain termination has been observed for the polymerization MMA, it also seems to promote the controlled ATRP of MMA. Those results are very promising as to my knowledge, no catalyst has been reported to promote two different kinds of polymerization, both of them in a living fashion and in a one-pot reaction.
**1H NMR analysis** indicated that the prepared polymer architecture might adopt a specific morphology in solution. DSC analysis confirmed the presence of phase segregation between the different polymer backbones.

As this technique can certainly be extended to norbornene and 7-oxanorbornene type monomers with the appropriate well-defined ruthenium catalysts and to other ATRP monomers, this opens a new route to unknown polymer architectures that could result in unexpected properties.

### 4.3. Experimental section

**General procedures and characterizations**

All manipulations involving air- and moisture-sensitive compounds were carried under an atmosphere of prepurified nitrogen using standard Schlenk techniques.

**1H NMR** spectra were obtained at 300 MHz with GE NMR Omega spectrometer and at 300, 400 MHz with Varian-Mercury NMR spectrometers. Chemical shifts for **1H** NMR spectra are reported in δ (ppm), positive values indicating shifts downfield of tetramethylsilane and are referenced to selected residual proton peaks of the solvent as follows: CDCl₃, 7.27, singlet; toluene-d₈, 7.00, singlet. Significant **1H** NMR data are tabulated in order: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, bs = broad singlet, m = multiplet), coupling constant in Hertz, number of protons.

**13C {1H} proton decoupled** NMR were measured at 75 MHz with a GE NMR Omega spectrometer and at 100 MHz on a Varian-Mercury spectrometer. Chemical shifts for
$^{13}$C{\textsuperscript{1}H} NMR spectra are reported in δ (ppm), positive values indicating shifts downfield of tetramethylsilane, and are referenced to selected residual peaks of the solvents as

Infrared spectra were obtained using a Jasco FT/IR-410 spectrometer as thin films on NaCl disks or neat samples between NaCl disks and are uncalibrated. IR data are reported in units of wavenumber (cm$^{-1}$) for characteristic peaks.

Before sample analysis, solvents were removed with a rotary evaporator and under Schlenk line vacuum (approximately 0.05 Torr). Column chromatography was carried out with Selecto Scientific 63-200 mesh silica gel.

Molecular weight and molecular weight distribution were measured via gel permeation chromatography using a Jasco PU-1580 pump and a Jasco RI-1530 refractive index detector. The stationary phase consisted of two PL-Gel mixed C columns. Chloroform was used as the mobile phase. Molecular weights are relative to narrow molecular weight polystyrene standards (Pressure Chemical, Inc.).

Thermal analyses were performed using Hi-Res TGA 2950 and DSC 2920 TA instruments using a nitrogen purge and heating/cooling rates of 10 °C/min.

Elemental analyses were performed by Atlantic Microlab, Inc.

**Reagents**

Toluene, CH$_2$Cl$_2$ used for polymerization reactions and reactions with air and moisture sensitive materials were purified by passing through one column filled with activated A2 Alumina catalyst and one column filled with activated Q5 copper catalyst under nitrogen atmosphere (MBraun solvent system). CDCl$_3$ was dried over CaH$_2$, distilled under nitrogen and after three freeze-pump-thaw cycles was stored into the dry
box and used no more than one month later. Toluene-d$_8$ was dried over CaH$_2$, distilled trap-to-trap after three freeze-pump-thaw cycles and was stored into the dry box. Naphthalene used as a reference in the $^1$H NMR kinetic experiments was purified by sublimation and stored in the dry box. DPTS was prepared according to the literature.$^{14}$ MMA was dried over CaH$_2$ and stored in the fridge under nitrogen after three freeze-pump-thaw cycles. A small amount was transferred to a Schlenk tube by trap-to-trap distillation, put in the dry box and used immediately.

**Experimental procedures and characterizations**

7,8-N-(4-(2-bromo-2-methyl-propionic acid)-phenyl ester)-succinimide endo-Tricyclo[4.2.2.0$^{2.5}$]deca-3,9-diene (M-21). To 7,8-N-4-Hydroxyphenylsuccinimide endo-Tricyclo[4.2.2.0$^{2.5}$]deca-3,9-diene (1 mmol, 293.1 mg), 2 bromo-2 methyl propionic acid (1.04 mmol, 173.6 mg) and DPTS (0.2 mmol, 64 mg) dissolved in dry THF (16 mL) was added DCC (1.25 mmol, 258 mg) and the mixture was stirred at RT for 24 hours. The solution was then filtered and concentrated. The desired compound (200 mg, 46%) was recovered as a white crystalline solid after silica gel column chromatography (hexane / ethyl acetate, 1/1). $^1$H NMR (CDCl$_3$) $\delta$: 7.28 (d, J = 8.8 Hz, 2H), 7.22 (d, J = 8.8 Hz, 2H), 6.02 (m, 2H), 5.93 (s, 2H), 3.28 (bs, 2H), 2.97 (s, 2H), 2.89 (s, 2H), 2.07 (s, 6H); $^{13}$C $\{^1$H$\}$ NMR $\delta$: 177.83, 169.96, 150.53, 138.18, 129.84, 128.64, 127.79, 121.86, 55.39, 44.23, 43.52, 37.18, 30.73. IR 3041, 2955, 2901, 1754, 1698, 1506, 1400, 1290, 1264, 1235, 1188, 1158, 1136, 1103, 878, 789, 732, 684. Anal. Calcd for C$_{22}$H$_{20}$O$_4$NBr: C, 59.74; H, 4.56; N, 3.17. Found: C, 60.09; H, 4.56; N, 3.23.
7,8-N-4-(11-(2-bromo-2-methyl-propionic acid)-undecyl ester-1-oxy)phenylsuccinimide \textit{endo}-Tricyclo[4.2.2.0^{2.5}]deca-3,9-diene (M-22). To 7,8-N-4-(11-hydroxy-undecyl-1-oxy)phenylsuccinimide \textit{endo}-Tricyclo[4.2.2.0^{2.5}]deca-3,9-diene (0.43 mmol, 200 mg), 2 bromo-2 methyl propionic acid (0.45 mmol, 75 mg) and DPTS (0.09 mmol, 28 mg) dissolved in dry CH$_2$Cl$_2$ (4 mL) was added DCC (0.54 mmol, 114 mg) and the mixture was stirred at RT for 24 hours. The solution was then filtered and concentrated. The desired compound (200 mg, 46%) was recovered as a white crystalline solid after silica gel column chromatography (hexane / ethyl acetate, 1/1). $^1$H NMR (CDCl$_3$) $\delta$: 7.08 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 6.00 (m, 2H), 5.92 (s, 2H), 4.17 (t, J = 6.6 Hz, 2H), 3.95 (t, J = 6.6 Hz, 2H), 3.27 (bs, 2H), 2.94 (s, 2H), 2.87 (s, 2H), 1.94 (s, 6H), 1.77 (m, 2H), 1.69 (m, 2H), 1.5-1.3 (m, 14H); $^{13}$C $\{	ext{H}\}$ NMR $\delta$: 178.33, 171.28, 159.21, 128.14, 128.56, 127.82, 124.42, 115.07, 68.32, 66.31, 56.19, 44.25, 43.44, 37.13, 30.93, 29.64, 29.59, 29.47, 29.29, 29.27, 28.47, 26.12, 25.91. IR 3041, 2921, 2851, 1733, 1713, 1698, 1607, 1514, 1467, 1388, 1253, 1182, 1165, 1108, 838, 821, 791, 716, 682. Anal. Calcd for C$_{33}$H$_{42}$O$_5$NBr: C, 64.70; H, 6.91; N, 2.29. Found: C, 64.47; H, 7.01; N, 2.33.

Preparation of a 20-mer polymer from M-21 with Ru-III. To M-21 (0.067 mmol, 29.8 mg) in CH$_2$Cl$_2$ (0.3 mL) was added a CH$_2$Cl$_2$ solution (0.140 mL) of Ru-III (3.4 µmol, 2.8 mg) and the mixture was stirred at room temperature for 16 h. After quenching with a few drops of ethyl vinyl ether and stirring for 1 h, the solution was added dropwise to 75 mL methanol. After centrifugation and several washing with methanol, the polymer was recovered as a white powder (quantitative yield). $^1$H NMR
(CDCl₃) δ: 7.15 (m, 4H), 6.50, 6.39 (m, 2H), 5.29, 5.20 (m, 2H), 3.39, 3.29, 3.06, 2.80 (m, 6H), 2.07 (s, 6H). GPC Mₙ = 6943, PDI = 1.12. DSC T_g = 37.1°C.

**Preparation of a 20-mer polymer from M-22 with Ru-III.** To M-22 (0.052 mmol, 31.7 mg) in CH₂Cl₂ (0.25 mL) was added a CH₂Cl₂ solution (0.10 mL) of Ru-III (2.45 µmol, 2.0 mg) and the mixture was stirred at RT for 16 h. After quenching with a few drops of ethyl vinyl ether and stirring for 1 h, the solution was added dropwise to 75 mL methanol. After centrifugation and several washing with methanol, the polymer was recovered as a white powder (quantitative yield). ¹H NMR (CDCl₃) δ: 6.98, 6.83 (m, 4H), 6.50, 6.37 (m, 2H), 5.25, 5.17 (m, 2H), 4.17 (t, J = 6.6 Hz, 2H), 3.92 (m, 2H), 3.31, 3.25, 3.03 (m, 6H), 1.93 (s, 6H), 1.77 (m, 2H), 1.68 (m, 2H), 1.43, 1.31 (m, 14H). GPC Mₙ = 11770, PDI = 1.14.

**General procedure for the copolymerization of M-21 (or M-22) with MMA using Ru-III.** To the desired ATRP initiator dissolved in toluene in a Screw-cap vial equipped with a stirring-bar was added the desired amount of freshly distilled MMA with a syringe. To the stirred mixture a monomers was then added an aliquot of a freshly prepared toluene solution of Ru-III at room temperature. The vial was taken out of the dry box, sealed with Parafilm and place in a pre-heatediggler with a temperature set at 65°C. After 24 h, the vial was cooled down to room temperature. The visquous solution was diluted with a few drops of CH₂Cl₂ and added dropwise to a methanol solution under vigorous stirring. After centrifugation and several washing with methanol, the polymer was dried under high vacuum at 40°C for 12 h and recovered as a white filament-like solid.
Preparation of Poly(M-22-co-M-3)-graft-PMMA polymers. The desired amounts of M-22 and M-3 were dissolved with toluene in a Screw-cap vial. To this solution was added an aliquot of a freshly prepared toluene solution of Ru-III. The conditions were adjusted so that \([\text{M-22}] = 0.1\ \text{M}\) and \([\text{M-22}] / [\text{Ru-III}] = 20\). After a complete copolymerization as indicated by the \(^1\text{H}\) NMR analysis of a quenched aliquot (13 h, overnight), freshly distilled MMA was added via a syringe to the yellow slightly viscous copolymer solution ([MMA] / [M-22] = 40). The vial was taken out of the dry box, sealed with Parafilm and place in a pre-heatediggler with a temperature set at 65°C. After 30 h, the vial was cooled down to room temperature. The orange viscous solution was diluted with a few drops of CH\(_2\)Cl\(_2\) and added dropwise to a methanol solution under vigorous stirring. After centrifugation and several washing with methanol, the polymer was dried under high vacuum at 40°C for 12 h and recovered as a white fibrous solid.

Determination of the kinetics of the copolymerization by \(^1\text{H}\) NMR. In a vial were mixed M-22 (15.4 mg, 25.1 \(\mu\text{mol}\)), MMA (105 \(\mu\text{L}, 0.98\ \text{mmol}\)) and naphthalene (4.7 mg). The mixture was diluted with 420 \(\mu\text{L}\) of toluene-d\(_8\) and transferred with a pipette in a NMR tube equipped with a Teflon valve. To this mixture was then added 80 \(\mu\text{L}\) of a freshly prepared Ru-III stock solution (2.5 mg, 100 \(\mu\text{L}\) of toluene-d\(_8\)) and a timer was started. The NMR tube was rapidly taken out of the dry box and immersed in oil bath thermostated at 65°C. At repeated intervals, the NMR tube was removed from the oil bath for \(^1\text{H}\) NMR analysis. The conversion of MMA was measured by following the
disappearance of the olefinic proton signal at 5.98 ppm versus the naphthalene reference signal at 7.6 ppm.

4.4. References

(1) Controlled Radical Polymerization; Matyjaszewski, K., Ed.; ACS Symposium Series 685; American Chemical Society: Washington, DC, 1998


(6) Grimaud, T.; Matyjaszewski, K Macromolecules 1997, 30, 2216


(8) Ando, T.; Kamigaito, M.; Sawamoto, M. Macromolecules 2000, 33, 2819


APPENDICES
Figure A1.1. $^1$H NMR (in CDCl$_3$) and $^{13}$C NMR (in DMSO-$d_6$) spectra of M-1.
Figure A1.2. $^1$H NMR and $^{13}$C NMR spectra of M-2 in CDCl$_3$. 
Figure A1.3. $^1$H NMR and $^{13}$C NMR spectra of M-3 in CDCl$_3$. 
Figure A1.4. $^1$H NMR and $^{13}$C NMR spectra of M-4 in CDCl$_3$. 
Figure A1.5. $^1$H NMR and $^{13}$C NMR spectra of M-5 in CDCl$_3$. 
Figure A1.6. $^1$H NMR and $^{13}$C NMR spectra of M-6 in CDCl$_3$. 
**Figure A1.7.** $^1$H NMR and $^{13}$C NMR spectra of M-7 in CDCl$_3$. 
Figure A1.8. $^1$H NMR and $^{13}$C NMR spectra of M-8 in CDCl$_3$. 
Figure A1.9. $^1$H NMR and $^{13}$C NMR spectra of M-9 in CDCl$_3$. 

202
Figure A1.10. $^1$H NMR and $^{13}$C NMR spectra of M-10 in CDCl$_3$. 
Figure A1.11. $^1$H NMR and $^{13}$C NMR spectra of M-11 in CDCl$_3$. 
Figure A1.12. $^1$H NMR and $^{13}$C NMR spectra of M-12 in CDCl₃.
Figure A1.13. $^1$H NMR and $^{13}$C NMR spectra of M-13 (major isomer) in CDCl$_3$. 
Figure A1.14. $^1$H NMR spectrum of M-13 (minor isomer) in CDCl$_3$. 

207
Figure A1.15. $^1$H NMR and $^{13}$C NMR spectra of M-14 in CDCl$_3$. 
Figure A1.16. $^1$H NMR and $^{13}$C NMR spectra of M-15 in CDCl$_3$. 
Figure A1.17. $^1$H NMR and $^{13}$C NMR spectra of M-16 in CDCl$_3$. 
Figure A1.18. $^1$H NMR (in CD$_3$OD) and $^{13}$C NMR (in DMSO-d$_6$) spectra of M-17.
Figure A1.19. $^1$H NMR and $^{13}$C NMR spectra of M-18 in CDCl$_3$. 
Figure A1.20. $^1$H NMR and $^{13}$C NMR spectra of M-19 in CDCl$_3$. 
Figure A1.21. $^1$H NMR and $^{13}$C NMR spectra of M-20 in CDCl$_3$. 
Figure A1.22. $^1$H NMR and $^{13}$C NMR spectra of M-21 in CDCl$_3$. 
Figure A1.23. $^1$H NMR and $^{13}$C NMR spectra of M-22 in CDCl$_3$. 
Figure A2.1. $^1$H NMR and $^{13}$C NMR spectra of DM-1 in CDCl$_3$. 
Figure A2.2. $^1$H NMR and $^{13}$C NMR spectra of DM-1B in CDCl$_3$. 
Figure A2.3. $^1$H NMR and $^{13}$C NMR spectra of DM-2 in CDCl$_3$. 
Figure A2.4. $^1$H NMR and $^{13}$C NMR spectra of **DM-3** in CDCl$_3$. 
Figure A2.5. $^1$H NMR and $^{13}$C NMR spectra of DM-4 in CDCl$_3$. 
Figure A2.6. $^1$H NMR and $^{13}$C NMR spectra of DM-5 in CDCl$_3$. 
Figure A2.7. $^1$H NMR and $^{13}$C NMR spectra of DM-6 in CDCl$_3$. 
Figure A2.8. $^1$H NMR and $^{13}$C NMR spectra of DM-7 in CDCl$_3$. 

224
Figure A2.9. $^1$H NMR and $^{13}$C NMR spectra of DM-8 in CDCl$_3$. 
Figure A3.1. DSC thermogram of DM-1.
Figure A3.2. DSC thermogram of DM-1B.
Figure A3.3. DSC thermogram of DM-2.
Figure A3.4. DSC thermogram of DM-3.
Figure A3.5. DSC thermogram of DM-4.
Figure A3.6. DSC thermogram of DM-5.
**Figure A3.7.** DSC thermogram of DM-6.
Figure A3.8. DSC thermogram of DM-7.
Figure A3.9. DSC thermogram of DM-8.
Figure A4.1. $^1$H NMR spectra of poly-2 (top) and hydrogenated poly-2 (bottom) in CDCl$_3$. 
Figure A4.2. $^{13}$C NMR spectra of poly-2 (top) and hydrogenated poly-2 (bottom) in CDCl$_3$. 
Figure A5.1. TGA thermogram of poly-2.
Figure A5.2. TGA thermogram of hydrogenated poly-2.
Figure A6. DSC thermogram of hydrogenated poly-2.