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- [54] **OLEFIN METATHESIS REACTIONS IN CARBON DIOXIDE MEDIUM**
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**Related U.S. Application Data**

- [63] Continuation-in-part of Ser. No. 423,501, Apr. 13, 1995, abandoned.
- [51] **Int. Cl.**<sup>6</sup> ..... **C07C 6/04**; C07C 6/00
- [52] **U.S. Cl.** ..... **526/169**; 526/89; 526/93; 526/115; 526/281; 526/250; 526/283; 526/941; 585/643; 585/646
- [58] **Field of Search** ..... 526/89, 281, 941, 526/93, 169, 250, 283; 585/643, 646

[56] **References Cited**

## U.S. PATENT DOCUMENTS

- |           |         |                      |           |
|-----------|---------|----------------------|-----------|
| 2,963,447 | 12/1960 | Peters et al. .      |           |
| 3,074,918 | 1/1963  | Sousa et al. .       |           |
| 3,471,463 | 10/1969 | Kagiya et al. .      |           |
| 3,880,945 | 4/1975  | Kramer .             |           |
| 4,250,063 | 2/1981  | Kotani et al. .      |           |
| 4,496,668 | 1/1985  | Newburg .....        | 521/91    |
| 4,496,669 | 1/1985  | Leach .....          | 521/93    |
| 4,568,660 | 2/1986  | Klosiewicz .....     | 502/169   |
| 4,568,788 | 2/1986  | Kukes .....          | 585/646   |
| 4,592,933 | 6/1986  | Meyerson et al. .... | 427/255.1 |
| 4,891,387 | 1/1990  | Janda .....          | 521/54    |
| 4,959,395 | 9/1990  | Janda .....          | 521/54    |
| 4,977,226 | 12/1990 | Sagawara et al. .... | 526/122   |
| 5,210,336 | 5/1993  | Gaffney .....        | 568/860   |
| 5,312,882 | 5/1994  | DeSimone et al. .... | 526/201   |
| 5,312,940 | 5/1994  | Grubbs et al. ....   | 556/136   |
| 5,328,972 | 7/1994  | Dada et al. ....     | 526/227   |
| 5,342,909 | 8/1994  | Grubbs et al. ....   | 526/171   |
| 5,376,744 | 12/1994 | Kennedy .....        | 526/89    |
| 5,382,623 | 1/1995  | DeSimone et al. .... | 524/557   |
| 5,406,018 | 4/1995  | Sherman .....        | 585/729   |

## FOREIGN PATENT DOCUMENTS

- |            |         |        |
|------------|---------|--------|
| WO93/20116 | 10/1993 | WIPO . |
| WO95/03346 | 2/1995  | WIPO . |
| WO96/01850 | 1/1996  | WIPO . |
| WO96/10851 | 1/1996  | WIPO . |

## OTHER PUBLICATIONS

- G. Odian, "Principles of Polymerization", (1991), 577, Wiley New York.
- C.J. Hardiman of Monsanto (U.S. Pat. No. 5,266,665)(Abstract).
- W. L. Truett et al.; *Polynorbornene by Coordination Polymerization*, 82:2337-2340 (May 5, 1960).
- F. W. Michelotti et al.; Coordinated Polymerization of the Bicyclo[2.2.1]-heptene-2 Ring System (Norbornene) in Polar Media, *J. of Polymer Science: Part A*, 3:895-905 (1965).

K. J. Ivin; Olefin Metathesis, *Dept. of Chemistry, The Queen's University of Belfast, Belfast, Northern Ireland* (1983).

B. M. Novak et al.; Catalytic Organometallic Chemistry in Water: The Aqueous Ring-Opening Metathesis Polymerization of 7-Oxanorbornene Derivatives, *J. Am. Chem. Soc.*, 110:7543-7544 (1988).

R. Streck; Olefin Metathesis in Industry—A Status Report, *J. of Molecular Catalysis*, 46:305-316 (1988).

B. M. Novak et al.; The Ring Opening Metathesis Polymerization of 7-Oxabicyclo[2.2.1]-hept-5-ene Derivatives: A New Acyclic Polymeric Ionophore, *J. Am. Chem. Soc.*, 110:960-961 (1988).

R. H. Grubbs et al.; Polymer Synthesis and Organotransition Metal Chemistry, *Science*, 243:907-915 (1989).

W. J. Feast et al.; Aqueous ring-opening metathesis polymerizations of heteropolycyclic carboxylic acids with transition-metal chlorides, *Polymer*, 32:558-563 (1991).

Shui-Yu Lu et al.; Aqueous Ring-Opening Metathesis Polymerization of *exo,exo*-2,3-Bis(methoxymethyl)-7-oxanorbornene Catalyzed by Ruthenium Trichloride, *Macromolecules*, 25:2692-2697 (1992).

E. Zenkl et al.; The aqueous ring-opening metathesis polymerization of 7-oxa-norbornene-2,3-dicarboxylic acid dimethyl ester and norbornene with Ru catalysts, *J. of Molecular Catalysis*, 76:1-14 (1992).

M. B. France et al.; Initiation of Ring-Opening Metathesis Polymerization in Protic Media. Extension of  $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$  Catalyzed Polymerizations to Less-Strained Cyclic Monomers, *Macromolecules*, 26:4739-4741 (1993).

M. B. France et al.; Chain Transfer during the Aqueous Ring-Opening Metathesis Polymerization of 7-Oxanorbornene Derivatives, *Macromolecules*, 26:4742-4747 (1993).

V. C. Gibson; Metathesis Polymerization: ROMPing Towards New Materials, *Advanced Materials*, 6:37-42 (1994).

R. H. Grubbs; The Development of Functional Group Tolerant ROMP Catalysts, *J.M.S.—Pure Appl. Chem.*, A31(11):1829-1833 (1994).

C. D. Mistele et al.; The Ring-Opening Metathesis Polymerization of Norbornene in Supercritical Carbon Dioxide, *Dept. of Chemistry, Univ. of North Carolina at Chapel Hill*, 507-508.

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[57] **ABSTRACT**

The present invention provides a process for olefin metathesis. The process comprises (a) providing a reaction mixture comprising an olefin, a metathesis initiator, and a reaction medium comprising carbon dioxide, and (b) reacting the reaction mixture to provide a metathesis modified olefin. The olefin metathesis reaction may be an olefin metathesis exchange reaction, an olefin metathesis degradation reaction, or a metathesis polymerization reaction. The carbon dioxide medium may be liquid, supercritical, and gaseous carbon dioxide.

**20 Claims, No Drawings**