ABSTRACT

WANG, GUAN. Synthesis of Bleach Activators with Varying Cationic Groups. (Under the direction of David Hinks.)

Bleaching is a key method for preparing natural textile fibers for dyeing and finishing. The process removes colored and non-colored impurities in the fiber. It whitens the fiber and provides a more uniform base to enable high quality dyeing.

Hydrogen peroxide is an abundant, low-cost and commonly used oxidizing agent that oxidizes a range of organic compounds by dissociation into perhydroxyl anion under alkaline conditions. Relatively high temperature and alkali conditions are necessary for rapid hydrogen peroxide bleaching. These conditions produce a loss of fabric strength, result in relatively high energy consumption, and generate large amounts of electrolyte upon neutralization of the bleach solution.

Bleach activators have been employed for several decades in laundry detergent and dishwashing formulations, and their investigation as commercially viable bleaching systems for textile wet processing has been on-going for approximately 15 years. The most commonly used peroxide bleach activators are tetraacetyl ethylene diamine (TAED) and sodium nonanoyloxybenzenesulfonate (NOBS). While these bleach activators enable hydrogen peroxide bleaching at relative low temperature (approximately 60-80 °C) these activators still require alkali conditions for good bleaching performance and TAED has low solubility, which limits its use.
Cationic bleach activators have been investigated as next generation bleach activators that exhibit inherent substantivity towards cellulosic fibers. N-[4-(triethylammoniomethy)benzoyl]caprolactam chloride) (TBCC) is a cationic bleach activator that has been shown to exhibit improved hydrogen peroxide bleaching in relative low temperature and under neutral conditions. For enhance the water stability, another cationic bleach activator was used, N-[4-(triethylammoniomethy)benzoyl]butyrolactam chloride (TBBC) which exhibits equivalent bleaching performance to TBCC. However, the use of cationically charged compounds often leads to aquatic toxicity and other negative environmental concerns. Triethylamine (TEA) is the amine used to confer cationic charge to TBCC and TBBC, and this amine is toxic.

However, some tertiary amines are far less toxic than TEA. The purpose of this thesis research was to investigate the effect of varying the type of cationic group used for synthesis of a butyrolactam- and caprolactam-based bleach activators. The following cationic groups were used, each of which are known to have substantially less toxicity than TEA: Pyridine, 1,4-Diazabicyclo(2.2.2)octane, nicotinamide, and 3-methylpyridine.

The new cationic bleach activators were synthesized and characterized by $^1$H NMR, melting point, and via mass spectrometry. The new activators were then used in comparative bleaching experiments and their performance was compared to TBCC and TBBC.

The bleaching experiment results showed that all of the new cationic bleach activators exhibited bleaching at relatively low temperature and neutral conditions. When 3-
methylpyridine was employed as the cationizing amine the bleach performance was comparable to that of the current best bleach activator, TBBC. Importantly, the toxicity of 3-methyl pyridine is substantially lower than the triethylamine used for the synthesis of TBBC.
© Copyright 2012 by Guan Wang

All Rights Reserved
Synthesis of Bleach Activators with Varying Cationic Groups

by

Guan Wang

A thesis submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the degree of Master of Science

Textile Chemistry

Raleigh, North Carolina

2012

APPROVED BY:

_________________________  _______________________
Peter Bloomfield           Peter Hauser

_________________________
David Hinks
Chair of Advisory Committee
BIOGRAPHY

Guan Wang, the only son of Sifeng Wang and Ying Wang, was born on January 4th, 1989 in Zhejiang, China. He graduated from Huzhou High school in June, 2007, and received a Bachelor of Engineering degree in Textile Engineering from Donghua University, Shanghai, China in June 2011. In undergraduate study, he conducted research on 3D-weaving ramie polypropylene enforced composite under the guidance of Dr. Yiping Qiu. He was one of the Donghua “3+X” program students who took three years to complete the B.S. degree and then entered the Master of Science in Textile Chemistry in the College of Textiles at North Carolina State University in August, 2010.
ACKNOWLEDGMENTS

Firstly, I want to thank sincerely my advisor, Dr. David Hinks, who gave me a lot of help throughout my educational experience and research work as a student in the Textile Chemistry Master’s degree program. I appreciate his advice and encouragement when I met problems. I am also very thankful to other members of my advisory committee, Dr. Peter Hauser and Dr. Peter Bloomfield, whose knowledge and expertise greatly contributed to my graduate education.

I would like to acknowledge other professors and friends in our college: Dr. Harold S. Freeman and Dr. Renzo Shamey, who taught me textile dyeing and color theory, where I learned the basic theory needed for my thesis research; Dr. Keith R. Beck and Ms. Samantha Blake who helped me perform the LC/MS analysis for my products; Dr. Changhai Xu, who taught me how to use the lab equipment and gave me a great deal of help and advice for my thesis; Ms. Sasha Ormond, who helped me to conduct NMR analysis; and Ms. Birgit Andersen, who helped me to test the melting point of my products.

Special thanks go to my whole family, especially my parents, who gave me enormous support both in spirit and finance. I hope I can repay their kindness and care for them in the future.

Finally, I will give my most sincerely thanks to my girlfriend, Tong Yao. Thanks for your encouragement during the difficult times while in America. Thanks for the help both in my life and study. Thank you for accepting me even when I was in a bad mood.
# TABLE OF CONTENTS

LIST OF TABLES ........................................................................................................... xi

LIST OF FIGURES ......................................................................................................... xii

Chapter 1 INTRODUCTION ............................................................................................... 1

1.1 Thesis Outline ........................................................................................................... 1

1.2 Research Objectives ................................................................................................. 1

Chapter 2 LITERATURE REVIEW .................................................................................. 3

2.1 Impurities in Cotton ................................................................................................. 3

2.2 Conventional Bleaching .......................................................................................... 4

2.2.1 Chlorine-Based Bleaching .................................................................................... 5

2.2.2 Peroxide-Based Bleaching ................................................................................... 6

2.3 Bleach Activators .................................................................................................... 8

2.3.1 Bleach Activator Mechanism .............................................................................. 12

2.3.1.1 Tetra Acetyl Ethylene Diamine, TAED .......................................................... 13

The effect of H₂O₂ dosage ............................................................................................ 14

TAED dosage ................................................................................................................ 14

The effect of pH ............................................................................................................ 15

2.3.1.2 Nonanoylbenzenesulfonate, NOBS ............................................................... 15

2.3.1.3 Cationic Bleach Activators .......................................................................... 17
The effect of Temperature, NaOH concentration and activator concentration...... 22

2.3.2 Synthesis of Cationic Bleach Activators Process .................................... 25

2.3.2.1 Process for Making lactam–based cationic Bleach Activators ........ 25

2.3.3 Toxicity of Cationic Compounds.......................................................... 26

2.4 Chemical Analysis ..................................................................................... 29

2.4.1 Time-of-Flight Mass Spectrometry ....................................................... 29

2.4.2 High-Performance Liquid Chromatography .......................................... 29

2.4.3 Nuclear Magnetic Resonance ................................................................. 30

2.5 Whiteness Measurement .......................................................................... 31

2.5.1 Whiteness .............................................................................................. 31

2.5.2 Whiteness Index .................................................................................... 32

Chapter 3 EXPERIMENTAL ............................................................................. 33

3.1 Materials ................................................................................................... 33

3.2 Instrumentation .......................................................................................... 33

3.3 Synthesis .................................................................................................... 33

3.3.1 TBCC Synthesis ................................................................................... 34

3.3.1.1 Synthesis of the Intermediate, 4-Chloromethyl benzoyl caprolactam . 34

3.3.1.2 Synthesis of TBCC ........................................................................... 35
3.3.2 Pyridine-based Bleach Activator with Caprolactam as the Leaving Group

3.3.2.1 Synthesis of the Intermediate, 4-Chloromethyl benzoyl caprolactam

3.3.2.2 Synthesis of N-[4-(pyridiniummethyl)benzoyl] caprolactam chloride, PBCC

3.3.3 1,4-diazabicyclo[2.2.2] octane-based Bleach Activator with Caprolactam as the Leaving Group

3.3.3.1 Synthesis of the Intermediate, 4-chloromethyl benzoyl caprolactam

3.3.3.2 Synthesis of N-[4-(1,4-diazabicyclo[2.2.2] octane-methyl)benzoyl] caprolactam chloride, DOBCC

3.3.4 Nicotinamide-based Bleach Activator with Caprolactam as the Leaving Group

3.3.4.1 Synthesis of the Intermediate, 4-Chloromethyl benzoyl caprolactam

3.3.4.2 Synthesis of N-[4-(nicotinamide-methyl) benzoyl] caprolactam chloride, NABCC

3.3.5 3-Picoline-based Bleach Activator with Caprolactam as the Leaving Group

3.3.5.1 Synthesis of the Intermediate, 4-Chloromethyl benzoyl caprolactam
3.3.5.2 Synthesis of N-[4-(3-picoline-methyl)benzoyl] caprolactamchloride, PBCC

3.3.6 Pyridine-based Bleach Activator with Butyrolactams the Leaving Group

3.3.6.1 Synthesis of the Intermediate, 4-Chloromethyl benzoyl butyrolactam

3.3.6.2 Synthesis of N-[4-(pyridinmethyl)benzoyl] butyrolactamchloride, PBBC

3.3.7 1,4-Diazabicyclo[2.2.2] Octane-based Bleach Activator with Butyrolactams the Leaving Group

3.3.7.1 Synthesis of the Intermediate, 4-Chloromethyl benzoyl butyrolactam

3.3.7.2 Synthesis of N-[4-(1,4-diazabicyclo[2.2.2] octane-methyl)benzoyl] butyrolactamchloride, DOBBC

3.3.8 Nicotinamide-based Bleach Activator with Butyrolactams the Leaving Group

3.3.8.1 Synthesis of the Intermediate, 4-Chloromethyl benzoyl butyrolactam

3.3.8.2 Synthesis of N-[4-(nicotinamide-methyl)benzoyl] butyrolactamchloride, NABBC
3.3.9 3-Picoline-based Bleach Activator with Butyrolactamas the Leaving Group

3.3.9.1 Synthesis of the Intermediate, 4-Chloromethyl benzoyl butyrolactam

3.3.9.2 Synthesis of N-[4-(3-picoline-methyl) benzoyl] butyrolactamchloride, 3-PBBC

3.4 Bleaching Performance

3.4.1 Materials

3.4.2 Bleaching Method

3.4.4 Whiteness Measurement

3.4.5 Water Absorbency Measurement

3.4.6 Mote Counting Test

Chapter 4 RESULTS AND DISCUSSION

4.1 Synthesis and Characterization

4.1.1 Synthesis of 4-Chloromethyl benzoyl Caprolactam Intermediate

4.1.2 Synthesis of N-[4-(triethylammoniomethyl)benzoyl] CaprolactamChloride, TBCC

4.1.3 Synthesis of N-[4-(pyridiniummethyl)benzoyl] CaprolactamChloride, PBCC
4.1.4 Synthesis of N-[4-(1,4-diazabicyclo[2.2.2]octane-methyl)benzoyl] CaprolactamChloride, DOBCC .......................................................... 55

4.1.5 Synthesis of N-[4-(nicotinamide-methyl)benzoyl] CaprolactamChloride, NABCC .......................................................... 58

4.1.6 Synthesis of N-[4-(3-picoline-methyl)benzoyl] CaprolactamChloride, 3-PBCC .......................................................... 60

4.1.7 Synthesis of N-[4-(pyridiniummethyl)benzoyl] ButyrolactamChloride, PBBC .......................................................... 63

4.1.8 Synthesis of N-[4-(1,4-diazabicyclo[2.2.2]octane-methyl)benzoyl] ButyrolactamChloride, DOBCC .......................................................... 65

4.1.9 Synthesis of N-[4-(nicotinamide-methyl)benzoyl] ButyrolactamChloride, NABCC .......................................................... 68

4.1.10 Synthesis of N-[4-(3-picoline-methyl)benzoyl] ButyrolactamChloride, 3-PBCC .......................................................... 70

4.2 Scouring and Bleaching Performance .......................................................... 73

4.3 Water Absorbency .................................................................................. 77

4.4 Mote Counting .................................................................................... 78

Chapter 5 CONCLUSIONS ........................................................................ 79

Chapter 6 FUTURE WORK ......................................................................... 81
LIST OF TABLES

Table 1. Summary of Main Components Present in Raw Cotton Fibers ........................................ 3
Table 2. Summary of Steps in the Preparation of Cotton ................................................................. 4
Table 3. Toxicity Classes: Hodge and Sterner Scale ......................................................................... 28
Table 4. Toxicity of the Amine Groups ............................................................................................. 28
Table 5. Chromaticity Coordinates for the CIE Standard Illuminant and Source Used ............. 32
Table 6. Tertiary Amino Compounds Used ......................................................................................... 34
Table 7. Bleach Performance of Each Activator ............................................................................... 75
Table 8. Water Absorbency ................................................................................................................ 77
Table 9. Mote Number of Each Fabric ............................................................................................... 78
LIST OF FIGURES

Figure 1. Extracted Ion Chromatogram of 4-Chloromethyl benzoyl caprolactam .......... 47
Figure 2. Positive-ion ESI MS spectrum of 4-Chloromethyl benzoyl caprolactam .......... 48
Figure 3. $^1$H NMR spectrum of N-[4-(triethylammoniomethyl)benzoyl] caprolactam chloride, TBCC .................................................................................................................................... 50
Figure 4. Extracted Ion Chromatogram of N-[4-(triethylammoniomethyl)benzoyl]
caprolactam chloride, TBCC ............................................................................................... 51
Figure 5. Positive-ion ESI MS spectrum of N-[4-(triethylammoniomethyl)benzoyl]
caprolactam chloride, TBCC ............................................................................................... 51
Figure 6. $^1$H NMR spectrum of N-[4-(pyridiniummethyl)benzoyl] caprolactam
caprolactam chloride, PBCC ............................................................................................... 53
Figure 7. Extracted Ion Chromatogram of N-[4-(pyridiniummethyl)benzoyl] caprolactam
caprolactam chloride, PBCC ............................................................................................... 54
Figure 8. Positive-ion ESI MS spectrum of N-[4-(pyridiniummethyl)benzoyl] caprolactam
caprolactam chloride, PBCC ............................................................................................... 54
Figure 10. Extracted Ion Chromatogram of N-[4-(1,4-diazabicyclo[2.2.2] octane-
 methyl)benzoyl] caprolactam chloride, DOBCC ............................................................... 57
Figure 11. Positive-ion ESI LC-MS spectrum of N-[4-(1,4-diazabicyclo[2.2.2] octane-
methyl)benzoyl] caprolactam chloride, DOBCC ............................................................... 57
Figure 13. Extracted Ion Chromatogram of N-[4-(nicotinamide-methyl)benzoyl] caprolactam chloride, NABCC ................................................................. 60

Figure 14. Positive-ion ESI MS spectrum of N-[4-(nicotinamide-methyl)benzoyl] caprolactam chloride, NABCC ................................................................. 60

Figure 15. $^1$H NMR spectrum of N-[4-(3-picoline-methyl)benzoyl] caprolactam chloride, 3-PBCC ................................................................................................................................. 61

Figure 16. Extracted Ion Chromatogram of N-[4-(3-picoline-methyl)benzoyl] caprolactam chloride, 3-PBCC ................................................................................................................................. 62

Figure 17. Positive-ion ESI LC-MS spectrum of N-[4-(3-picoline-methyl)benzoyl] caprolactam chloride, 3-PBCC ................................................................................................................................. 62

Figure 18. $^1$H NMR spectrum of N-[4-(pyridiniummethyl) benzoyl] butyrolactam chloride, PBBC ................................................................................................................................. 64

Figure 19. Extracted Ion Chromatogram of N-[4-(pyridiniummethyl) benzoyl] butyrolactam chloride, PBBC ................................................................................................................................. 65

Figure 20. Positive-ion ESI LC-MS spectrum of N-[4-(pyridiniummethyl) benzoyl] butyrolactam chloride, PBBC ................................................................................................................................. 65

Figure 21. $^1$H NMR spectrum of N-[4-(1,4-diazabicyclo[2.2.2] octane-methyl)benzoyl] butyrolactam chloride, DOBCC ................................................................................................................................. 66

Figure 22. Extracted Ion Chromatogram of N-[4-(1,4-diazabicyclo[2.2.2] octane-methyl)benzoyl] butyrolactam chloride, DOBCC ................................................................................................................................. 67
Figure 23. Positive-ion ESI LC-MS spectrum of N-[4-(1,4-diazabicyclo[2.2.2] octane-methyl)benzoyl] butyrolactam chloride, DOBBC ................................................................. 67

Figure 24. $^1$H NMR spectrum of N-[4-(nicotinamide-methyl)benzoyl] butyrolactam chloride, NABBC .................................................................................................................. 69

Figure 25. Extracted Ion Chromatogram of N-[4-(nicotinamide-methyl)benzoyl] butyrolactam chloride, NABBC .................................................................................................................. 70

Figure 26. Positive-ion ESI LC-MS spectrum of N-[4-(nicotinamide-methyl)benzoyl] butyrolactam chloride, NABBC .................................................................................................................. 70

Figure 27. $^1$H NMR spectrum of N-[4-(3-picoline-methyl)benzoyl] butyrolactam chloride, 3-PBBC .................................................................................................................. 71

Figure 28. Extracted Ion Chromatogram of N-[4-(3-picoline-methyl)benzoyl] butyrolactam chloride, 3-PBBC .................................................................................................................. 72

Figure 29. Positive-ion ESI LC-MS spectrum of N-[4-(3-picoline-methyl)benzoyl] butyrolactam chloride, 3-PBBC .................................................................................................................. 72

Figure 30. CIE Whiteness Index values for control sample and fabric treated with current and new cationic bleach activators .................................................................................. 76
Chapter 1  INTRODUCTION

1.1 Thesis Outline

This thesis consists of six chapters. In Chapter 1, the general format of the thesis is discussed and the main research objectives are described. Chapter 2 provides a literature review of conventional bleaching, research on the bleaching with so-called bleach activators by reaction with hydrogen peroxide, and basic chemical analysis undertaken in this work. Chapter 3 is the experimental section, describing the design, synthesis of a series of novel cationic bleach activators, and equipment and methods used to analyze the performance of the new activators. Chapter 4 presents the results and discussion of the synthesis and application of the new bleach activators. Chapter 5 provides the conclusions and Chapter 6 provides a short discussion on recommended future work. Chapter 7 is a list of references cited throughout the thesis.

1.2 Research Objectives

The main objectives of this research are:

1) Design and synthesize novel cationic bleach activators containing varying cationic groups
2) Investigate the performance of the novel bleach activators in terms of whiteness measurement by comparison to cationic bleach activators already in the prior art.
Chapter 2

LITERATURE REVIEW

2.1 Impurities in Cotton

Cotton is grown and processed into commercial products in various locations throughout the world. Approximately 123.6 million of 480 lb. bales of cotton were processed in 2011 [1]. It is the most important natural fiber by far, owing to its perceived comfort, relatively low cost, bright hues and good fastness properties when dyed.

All natural fibers contain significant levels of impurities that may interfere with the dyeing and finishing process. Table 1 shows the main components present in cotton [2].

<table>
<thead>
<tr>
<th>COMPONENTS</th>
<th>PERCENTAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>91.00%</td>
</tr>
<tr>
<td>water</td>
<td>7.85%</td>
</tr>
<tr>
<td>Protoplasm, pectins</td>
<td>0.55%</td>
</tr>
<tr>
<td>Waxes, fatty substances</td>
<td>0.40%</td>
</tr>
<tr>
<td>Mineral salts</td>
<td>0.20%</td>
</tr>
</tbody>
</table>

Wet processing of textiles is commonly performed in three stages: Preparation, Dyeing and Finishing. Preparation is a critical phase in the wet processing of fibers, yarns, fabrics or garments that aims to remove some or all of the impurities in the fiber, thereby enabling effective dyeing and finishing in the subsequent stages. In some cases, fibers are not dyed,
but are left in a whitened state. Table 2. shows the primary stages of preparation for cotton [3].

<table>
<thead>
<tr>
<th>PROCESS</th>
<th>DESCRIPTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Size application</td>
<td>Warp yarns are treated with size agents to protect them during weaving</td>
</tr>
<tr>
<td>Desizing</td>
<td>For woven fabrics only, size is removed most commonly via amylase</td>
</tr>
<tr>
<td>Singeing</td>
<td>Surface fibers are burned off fabric to improve appearance</td>
</tr>
<tr>
<td>Scouring</td>
<td>Oils and waxes are saponified and emulsified to improve absorbency</td>
</tr>
<tr>
<td>Bleaching</td>
<td>Fibers are oxidized to improve whiteness uniformity of appearance</td>
</tr>
</tbody>
</table>

### 2.2 Conventional Bleaching

In textile industry, whiteness of the fabric is very important not only for daily application but also for post processing of textile such as dyeing and finishing. However most of the textile materials contain impurities which will detract from their white appearance [4-7]. Bleaching is a key process used to remove colored and non-colored impurities present in natural fibers such as cotton, ramie, and wool. In addition to whitening fibers, bleaching improves water absorbency (wetting) and uniformity of appearance, which assist in the generation of high quality, level dyeings.

Bleaching may be performed using a variety of continuous or batch applications [8]. It is most commonly performed rapidly (at elevated temperatures), but it may also be undertaken
commercially by a relatively slow process (at room temperature). Two main bleaching mechanisms are possible: oxidation or reduction. The most common types of oxidative bleaching are based on hydrogen peroxide (H₂O₂) and sodium hypochlorite (NaOCl). Reductive bleaching may be performed using reducing agents such as sodium dithionite (also known as sodium hydrosulfite, or “hydro”, and sodium sulfoxylate) [9]. The two main types of oxidative bleaching are reviewed below.

2.2.1 Chlorine-Based Bleaching

Historically, chlorine bleaching agents have been widely used and they are still used for low cost bleaching such as whitening of socks and other inexpensive textile products. However, the use of chlorine has been reduced owing to the environmental impact from the release of organohalogens (AOX) during chlorine bleaching.

The most common form of chlorine bleach uses sodium hypochlorite (NaOCl). The mechanism of chlorine bleaching is shown in Equation 1[10].

\[
\begin{align*}
\text{NaOCl} + \text{H}_2\text{O} & \rightleftharpoons \text{NaOH} + \text{HOCl} \\
4\text{NaOCl} + 2\text{H}_2\text{O} & \rightleftharpoons 4\text{NaOH} + 2\text{Cl}_2 + \text{O}_2
\end{align*}
\]
The main bleaching species is hypochlorous acid (HOCl), which is a powerful oxidizing agent that lends hypochlorite excellent bleaching and disinfecting abilities. Excess chlorine at the end of the bleaching must be removed prior to dyeing as chlorine can oxidize certain dyes during dyeing. An “antichlor” treatment is commonly used, which typically involves addition of sodium thiosulfate, as shown in Equation 2 [48].

\[
\text{Na}_2\text{S}_2\text{O}_3 + 4\text{Cl}_2 + 5\text{H}_2\text{O} \rightarrow 8\text{HCl} + 2\text{NaHSO}_4 \quad (2)
\]

### 2.2.2 Peroxide-Based Bleaching

The most common conventional bleaching process employs a perhydroxyl anion as the primary oxidation species. The generation of the perhydroxyl group may be obtained in a number of ways, using \(\text{H}_2\text{O}_2\) and sodium perborate (\(\text{NaBO}_3 \cdot n\text{H}_2\text{O}\)) [16]. Of these, \(\text{H}_2\text{O}_2\) is the most commonly used in diluted form (e.g. 35% w/w), owing to its very low cost, abundance, and ease of application from a solution.

\(\text{H}_2\text{O}_2\) is a weak acid that exists in equilibrium with its conjugate base, as shown in Equation 3.

\[
\text{H}_2\text{O}_2 \rightleftharpoons \text{H}^+ + \text{HO}^- \quad (3)
\]
In order to shift the equation to the right so that the perhydroxyl anion is established in high concentration, alkaline conditions are required, typically in the range pH 11-12. The perhydroxyl anion destroys many impurities via oxidation in substrates, although the exact mechanism is unclear [12-15].

Rapid bleaching is undertaken at relatively high pH and at elevated temperatures, typically 95°C. These conditions consume significant amounts of energy and lead to reduction of fiber strength up to approximately 10% [11], via reduction in degree of polymerization. Furthermore, neutralization of the alkaline bleach bath is required at the end of the process, which generates electrolytes that have a negative environmental impact. In large dyeing and finishing mills, the effluent must be treated in lagoons prior to discharge to receiving waters. Hence, conventional bleaching is significantly costly.

Over the last 40 years, attempts have been made to increase bleaching efficiency of textile materials and reduce the environmental impact of bleaching processes. One approach that has been made commercial in laundry detergent formulations and is showing promise as a new method of bleaching textiles during the manufacturing process is the use of so-called bleach activators.
2.3 Bleach Activators

Bleach activators are compounds with O- or N-bounded acetyl groups which are able to react with the strongly nucleophilic perhydroxyl anion to yield a peroxycetic acid functional group. Since 1970 sodium perborate has been used as a bleaching compound in European laundry detergents. Sodium perborate decomposes rapidly in aqueous solution to yield H₂O₂, as shown in Equation 4.

\[
\text{Na}_2\text{(H}_4\text{B}_2\text{O}_8) + 4\text{H}_2\text{O} \rightarrow 2\text{Na[B(OH)_4]} + 2\text{H}_2\text{O}_2
\]

(4)

Sodium perborate by itself is active at temperatures above 80°C, but less so at 40-60°C. Hence, the bleach activators in the presence of which sodium perborate acts as a bleaching agent already at temperatures below 80°C were developed [21]. The peroxycetic acid is decomposed in weakly basic media in a bimolecular reaction forming singlet oxygen [21], as shown in Equation 5.

\[
2\text{AcOOH} \xrightarrow{\text{OH}} 2\text{AcOH} + \text{O}_2
\]

(5)

Many organic bleach activator candidates have been considered for use with laundry powders. In Europe, for example, compounds such as tetraacetylglycoluril (TAGU, 1), diacetyldioxohexahydrotriazine (DADHT, 2), and glucose pentaacetate (PAG, 3) were all
commercially produced, but because of environmental impact, manufacturing or processing cost, they eventually became obsolete [21].

Other potential activators were also considered in the United States. Today, two peroxyl activators are in widespread commercial use: tetraacetylenediamine (TAED, 4), mostly
used in Europe, Asia and South America, and the sodium salt of nonanoylbenzenesulphonic acid (NOBS, 5), used mainly by The Procter & Gamble Company (P&G) in the US, Japan and certain other countries.

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{O} \\
\text{O} & \quad \text{N} \quad \text{N} \quad \text{C} \quad \text{H}_3 \\
\text{CH}_3 & \quad \text{O} \\
\text{O} & \quad \text{N} \quad \text{N} \quad \text{C} \quad \text{H}_3 \\
\text{CH}_3 & \quad \text{O} \\
\text{O} & \quad \text{N} \quad \text{N} \\
\text{C} & \quad \text{H}_3 \\
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{N} \quad \text{N} \\
\text{C} & \quad \text{H}_3
\end{align*}
\]

\[\text{4}\]

\[
\text{H}_3\text{C} - \text{O} - \text{C} - \text{H}_3 \quad \text{O} - \text{SO}_3\text{Na}
\]

\[\text{5}\]

Cai et al. [30] reported a new class of peroxide activator and its application in the textile bleaching process. The new activators are guanidine derivatives, in which at least one amine hydrogen atom is substituted with an alkyl or acyl group. Suitable acyl groups include the benzoyl, formyl and acetyl groups.

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{N} \quad \text{H}_2\text{N} \\
\text{HO} & \quad \text{SO}_3\text{H}
\end{align*}
\]

\[\text{6}\]

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{N} \quad \text{H}_2\text{N} \\
\text{H}_2\text{N} & \quad \text{N} \quad \text{H}_2\text{N}
\end{align*}
\]

\[\text{7}\]

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{N} \quad \text{H}_2\text{N} \\
\text{HN} & \quad \text{C} \quad \text{H}_2
\end{align*}
\]

\[\text{8}\]

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{N} \quad \text{H}_2\text{N} \\
& \quad \text{O} \quad \text{CH}_3
\end{align*}
\]

\[\text{9}\]
Examples of the activators described in this paper include 1,1-dimethylguanidine sulphate (1,1-DMG, 6), 1,1-dimethylbiguanide hydrochloride (1,1-DMBG, 7), 1-benzoylguanidine hydrochloride (1-BOG, 8) and 1-acetylguanidine (1-ACG, 9). The performance of each new activator was evaluated on various cellulosic textiles and compared with the performance of TAED. The results demonstrated that the whiteness of the substrate bleached using any of the alkyl-substituted guanidine additives is higher than that obtained without an activator. Among the alkyl guanidines and biguanides evaluated, 1,1-DMG and 1,1-DMBG were found to be the most effective activators and performed better than TAED.

The whiteness of cotton was found to increase with increasing bleach temperature. The improvement in whiteness became smaller as the temperature increased beyond 70 °C. The whiteness of cotton increased with increasing alkali concentration. However, the addition of TAED caused a higher pH drop compared with the same concentration of 1,1-DMG. 1,1-DMG was superior to TAED in cotton bleaching, but this superiority was less evident at higher alkali concentrations in the bleaching bath. Although it seems like the guanidine compounds exhibited better performance than TAED, it still required relatively high pH when bleaching the cotton.
2.3.1 Bleach Activator Mechanism

The general reaction mechanism for the generation of the bleaching species is shown in Scheme 1.

![Scheme 1. Mechanism of bleach activator reaction](image)

In an alkaline aqueous solution, H$_2$O$_2$ first dissociates to yield perhydroxyl anion; the bleach activator reacts with the formed perhydroxyl anion to generate peracid, which is a more kinetically potent bleaching specie than H$_2$O$_2$ and thus can be used for bleaching under mild conditions such as low temperature and reduced the time [16-18].
2.3.1.1 Tetra Acetyl Ethylene Diamine, TAED

In the first stage of the bleach reaction for TAED, the two compounds are rapidly dissolved in the detergent wash water at a solution pH \( \approx 10 \), and a temperature in excess of 40 \(^\circ\)C. The liberated \( \text{H}_2\text{O}_2 \) reacts with TAED to form peracetic acid (Scheme 2) and diacetylethlenediamine (DAED) in a rapid reaction, which is almost independent of temperature [31].

In the second stage of the bleaching reaction, which is temperature-dependent, peracetic acid is generated as the oxidative bleaching agent. This reaction ideally occurs at a slightly lower solution pH of 8.5-9.5. The reduced pH of the wash water at this stage is achieved by careful powder formulation and the contributing acidity of the soiled fabrics.

![Scheme 2. Reaction of TAED with H\textsubscript{2}O\textsubscript{2} to produce a peracid.](image)

Shao et al. [33] reported the bleaching performance of cotton fabric bleached with a TAED/H\textsubscript{2}O\textsubscript{2} activated system. The whiteness was calculated using the blue reflectance whiteness formula [34].
The effect of $H_2O_2$ dosage

Shao et al. showed that whiteness increased sharply with increasing $H_2O_2$ concentration until above a $H_2O_2$ dosage of 30g/L, a maximum whiteness level of 86% was reached. As the $H_2O_2$ dosage increased, the amount of peracid increased, thereby increasing whiteness. When the $H_2O_2$ dosage exceeded 30g/L, the whiteness did not increase further because, presumably, the rate of peracetic acid formation exceeded the rate of the oxidative bleaching reaction.

TAED dosage

Shao et al. showed that whiteness was improved as a function of increasing mol ratio of TAED to peroxide until the fabric whiteness reached 87.7%, when the mol ratio was 1:2 at which point no further change was observed. The increase in TAED dosage was accompanied by an increase in peracetic acid concentration, resulting in the increase in fabric whiteness. However, because of poor water solubility, the amount of peracetic acid appeared to reach a maximum level and the resultant fabric whiteness could not be improved further. Furthermore, excess TAED may have reacted with the peracetic acid, it might consume both active peracetic acid and perhydroxy anion, resulting in reduced bleaching efficiency.
The effect of pH

Shao et al. also showed that the fabric whiteness increased initially while NaOH dosage was increased between 0 and 3 g/L. At this point, a maximum level of whiteness 86.1% was reached, after which further increase in NaOH led to a decrease in whiteness. The presence of NaOH was beneficial to disassociation of $\text{H}_2\text{O}_2$ and the creation of peraectic acid, leading to improved fabric whiteness. However, if the NaOH dosage was beyond a reasonable amount, it might cause hydrolysis of TAED (Scheme 3), resulting in an ineffective bleaching process.

\[
\begin{align*}
\text{N} & \text{N} \text{CH}_3 \text{CH}_3 \\
& \text{CH}_3 \\
& \text{O} \\
& \text{O} + 2\text{H}_2\text{O} \\
\text{NaOH} & \text{H} \\
& \text{N} \text{N} \text{H} \text{C} \text{H}_3 \text{CH}_3 \\
& \text{O} \\
& \text{O} + 2\text{H}_2\text{O} \\
\text{NaOH} & \text{H}_2\text{N} \text{NH}_2 + 2\text{CH}_3\text{COONa}
\end{align*}
\]

Scheme 3. TAED partial hydrolysis and side reactions

2.3.1.2 Nonanoylbenzenesulfonate, NOBS

In the case of the NOBS-perborate system, in a similar manner to the percarboxylic acid generation for TAED, pernonanoic acid is produced by reaction of $\text{NaBO}_3$·$\text{aB}_2\text{O}$ with NOBS, also forming the soluble sodium phenolsulphonate as the leaving group, as shown in Scheme
A secondary characteristic of the NOBS perhydrolysis reaction (Scheme 5) is the possible formation of small amounts of a secondary bleach compound, a diacyl peroxide (DAP), produced in a competing reaction of the already formed peracid anion with an excess of the nonanoyloxybenzenesulphonate. Regulation of these reactions can be achieved by control of the perborate/NOBS ratio and the pH of the wash solution. Peracid formation is favored by high perborate ratios and high solution pH values.

\[
\begin{align*}
\text{C}_8\text{H}_{17} \text{C} \text{O} \text{S} \text{O}_3\text{Na} + \text{HOO}^- & \rightarrow \text{C}_8\text{H}_{17} \text{C} \text{O} \text{OH} + \text{O} \text{S} \text{O}_3\text{Na} \\
\text{Pernonanoic acid}
\end{align*}
\]

Scheme 4. Reaction of NOBS with H\textsubscript{2}O\textsubscript{2} to produce pernonanoic acid

\[
\begin{align*}
\text{C}_8\text{H}_{17} \text{C} \text{O} \text{S} \text{O}_3\text{Na} + \text{C}_8\text{H}_{17} \text{C} \text{O} \text{N} \text{O} \text{B} & \rightarrow \text{C}_8\text{H}_{17} \text{C} \text{O} \text{OO} \text{C} \text{O} \text{C}_8\text{H}_{17} \\
\text{DAP}
\end{align*}
\]

Scheme 5. NOBS side reaction to produce DAP

NOBS is claimed to give a superior bleach performance over TAED at low temperatures, possibly owing to its higher solubility than TAED, which is only sparingly soluble in water. However, equivalence in bleach performance is reached at temperatures above 40°C [24]. Bleach activators are usually added to laundry powders at levels of 2-5% (w/w) [24].
In the late 1990s, Miracle and co-workers at P&G patented a series of new activators with cationic groups [37].

2.3.1.3 Cationic Bleach Activators

TAED and NOBS are anionic bleach activators, and have certain limitations considering the negative charge on cellulosic fibers. Hence, cationic bleach activators have potential to exhibit inherent substantivity for the fiber which at the same time exhibiting the same mechanism of activating peroxide. All of them react with peroxide to produce peracid which has higher efficiency in bleaching compared to the perhydroxyl anion obtained from the dissociation of H₂O₂ under alkaline conditions. The mechanism of each bleach activator has been studied in previous research. Hofmann reported the mechanism of the TAED and NOBS [24]. Lee et al. and later Xu et al. studied the mechanism of cationic bleach activators. Cationic bleach activators contain at least one cationic group, which can provide high water solubility. Compared to anionic bleach activators, cationic bleach activators have potential to exhibit better performance because they exhibit inherent substantivity to the negatively charged surface of cellulosic fibers in neutral to alkaline conditions to provide enhanced bleaching efficiency, especially in low temperature [27]. Cationic bleach activators can be applied in cold pad-batch or rapid hot peroxide bleaching for cotton [27,28]. N-[4-(triethylammoniomethyl)benzoyl]caprolactam chloride (TBCC, 10) is one kind of cationic
bleach activator that exhibited satisfactory bleaching performance in a shorter time and at lower temperatures than conventional peroxide bleaching. This kind of bleach activator may improve the performance of rapid \( \text{H}_2\text{O}_2 \) hot bleaching [27]. The performance of TBCC was superior to that of NOBS, possibly due to its higher substantivity toward negatively charged cotton in the bleach solution. Also the bleach activator system produced substantially less chemical damage than conventional bleaching [27]. However, TBCC was found to be unstable in aqueous solution.

\[
\text{Cl}^\ominus \quad \text{O} \quad \text{O} \\
\text{N} \quad \text{N} \quad \text{C} \quad \text{l}
\]

10

The oxidizing power of \( \text{H}_2\text{O}_2 \) or peracids can be assessed by measurement of available oxygen. The AvO of \( \text{H}_2\text{O}_2 \) is determined by titration of an acidified aqueous solution against a standard potassium permanganate solution. Lim et al. set up three storage solutions at varying pH and measured available oxygen (AvO) of each solution every five days [27].

The sample solution was titrated with 0.025 N sodium thiosulphate solution until it turned colorless. The AvO of the sample (ppm) was determined from the volume of sodium thiosulphate solution consumed, using Equation 6.
AvO[total](ppm) = \frac{\text{ml Na}_2\text{S}_2\text{O}_3 \times \text{normality of Na}_2\text{S}_2\text{O}_3 \times 8}{\text{sample volume in litres}}

= \frac{\text{ml Na}_2\text{S}_2\text{O}_3 \times 0.025 \times 8}{200/1000} = \text{ml Na}_2\text{S}_2\text{O}_3

(6)

After bleaching the fabric, the whiteness of each group was tested and the correlation between AvO of TBCC solution and CIE WI was determined. AvO correlated to storage time and pH. The AvO decreased with the increase in storage time of the TBCC solution, as a result of hydrolysis. The initial rate of decrease in AvO and CIE WI was more rapid at high pH. While the solid form of TBCC is stable, aqueous solutions are not. Since the rate of hydrolysis was found to be related to the leaving group of a bleach activator, similar derivatives containing different leaving groups produced varying hydrolytic stability. TBBC is an alternative activator that was found to exhibit high hydrolytic stability and good bleaching performance [25]. Lee et al. synthesized, characterized and tested five cationic bleach activators containing lactam-based leaving groups of varying ring size. The hydrolytic stability of each activator was determined via HPLC-based analysis of hydrolysis products, titration of AvO and whiteness assessment of cellulosic fibers using a peroxide-activator bleaching system following solution storage for various times under controlled conditions. All the cationic bleach activators exhibited good oxidative power before aqueous storage, as exhibited by CIE Whiteness Index measurement of cellulosic fibers bleached with each activator and alkaline H_2O_2. After comparing the effect, stability and cost of each lactam, the
N-[4-(triethylammoniomethyl)benzoyl] butyrolactam chloride (TBBC) was determined to be the most promising practical substitute to the more hydrolytically unstable TBCC.

The prior art shows that TAED and NOBS both need alkaline condition for effective fabric bleaching, which requires neutralization, and reduces fabric strength. TBCC, on the other hand, has been shown to be effective when applied under neutral conditions. Also, as cationic compound, TBCC has a better absorption on the cellulose than TAED and NOBS, which likely contributes to enhanced bleach performance. However, the instability makes it hard to store for industry use. TBBC has a similar structure to TBCC, except for the leaving group.

The bleach mechanism for these cationic activators is the same, whiles the stability and, to a certain extent bleach performance of TBBC is better than TBCC.

TBCC (10) and TBBC(11) increase the reactivity of a H₂O₂ bleach bath by reacting with perhydroxyl anions (OOH⁻) to form a reactive peracid oxidant. It has potential to be a more effective bleaching system than H₂O₂ alone. A leaving group is expelled in the process. In TBCC, caprolactam is the leaving group while in TBBC, the butyrolactam is the leaving group. Incorporating a cationic group facilitates the potential inherent affinity for negatively charged substitutes in addition to water solubility. The scheme 6 shows the reaction of TBBC with H₂O₂ to produce a cationic peracid.
Scheme 6. Reaction of TBBC with H$_2$O$_2$ to produce a cationic peracid

Scheme 7. A proposed sorption-activation peroxide bleaching model for TBBC [20]
Xu et al.[20] reported the sorption of a novel cationic bleach activator TBBC on regenerated bamboo fiber (Scheme 7). At the sorption equilibrium, bleaching was initiated by addition of sodium perborate to liberate $\text{H}_2\text{O}_2$, which reacted with TBBC to generate a peracid that is a more kinetically active oxidant than peroxide. The result supports their hypothesis that the cationic group brings the activator in close proximity of cellulosic fibers and associated colored impurities and that this proximity is important for efficient oxidation to take place.

Sang-Hoon Lim et al. [28] reported and compared the bleaching performances of NOBS activated and TBCC activated peroxide system.

*The effect of Temperature, NaOH concentration and activator concentration*

In the NOBS system, Lim et al. found that whiteness increases with temperature and NaOH concentration, similar to the TBCC system. The performance does not increase as a function of NOBS concentration. This indicates that the increase in NOBS concentration does not increase perhydrolysis under the conditions used. Hence, the NOBS system appears more complex than the TBCC system and there is an optimal NOBS concentration that will vary as a function of the other major factors.
The whiteness increases as temperature, NaOH concentration and TBCC concentration increase. The effect of TBCC concentration decreases as the temperature increases. This is possibly because the hydrolysis of bleach activators and diacylperoxide (DAP) formation produce inactive and less active species that are more dominant as the temperature is increased.

At a lower concentration of activator, the performance of TBCC and NOBS activators were close to each other. However, as the activator concentration was increased, the whiteness obtained using TBCC increased while the whiteness using NOBS actually decreased. At a temperature of 100 °C and at a high concentration of NOBS, the whiteness was actually inferior to that without activators. Although higher concentrations of TBCC resulted in higher whiteness values, the concentration effect decreased as the temperature increased.

Whiteness increased as the concentration of NaOH was increased for both activator systems. The whiteness increase was slightly decreased as the concentration of NaOH increased. This trend was very close to that of a conventional bleaching system and was not affected by the activators.

Presumably, NOBS has a negative charge on its leaving group, which leads to low substantivity for cotton. Therefore, perhydrolysis occurs in the bleach bath rather than on the surface of cotton. However, TBCC has a positive charge and will likely exhibit higher
substantivity for cotton than NOBS. The perhydrolysis of TBCC may thus occur at both the fiber surface and in bleach bath, thereby increasing the efficiency of oxidation of impurities on cotton compared to NOBS.

Xu et al. [20], reported that regenerated bamboo fibers were bleached with TBBC as the bleach activator. When TBBC was added in the H₂O₂ bleach system, the whiteness values increased substantially at pH 7.0. However, the whiteness values dropped as pH value increased from 7.0 to 11.0, indicating that hydrolysis of TBCC or decomposition of TBCC peracid occurs at a high pH value.

The ratio of TBCC to H₂O₂ and pH were found to be critical to achieving effective bleaching at low temperature. Using equimolar amounts of TBCC and H₂O₂ at pH 7 and 50 °C, comparable whiteness and less fiber damage compared with conventional peroxide bleaching was obtained.

Lavrič et al. [36] assessed the performance of TBBC by following the consumption of PAA and H₂O₂ and the formation of peracids during cotton bleaching was studied. To assess the influence of TBBC on bleaching performance with PAA, the concentrations of both oxidants during the bleaching process were measured as a function of time, and the kinetics compared with a blank bath in which no cotton sample was present. The result showed that the additional TBBC had a slight increase in peracid formation in both the PAA and
H$_2$O$_2$ system. The reaction rate for PAA consumption decreased with increasing TBBC concentration in bleaching and blank baths due to the formation of probably more reactive peracid. However, the consumption of PAA increased with temperature and was more rapid in the blank bath than in the bleaching bath. The rate constant for H$_2$O$_2$ consumption increased with higher TBBC concentrations and temperatures.

2.3.2 Synthesis of Cationic Bleach Activators Process

2.3.2.1 Process for Making lactam–based cationic Bleach Activators

Lee et al. reported the synthesis method for making lactam-based cationic bleach activators [21]. The first step is to make the intermediate: 4-chloromethyl benzoyl lactam. Scheme 8 summarizes the process.

![Scheme 8. Process for making 4-chloromethyl benzoyl lactam](image)

The second step is the intermediate reacted with triethylamine to get the final bleach activators: the 4-chloromethyl benzoyl lactam was dissolved in acetonitrile under argon and reacted with triethylamine. The solution was stirred under reflux for 4 hours then cooled to
room temperature. The solvent was evaporated and the mixture was washed using acetone.

Scheme 9 summarizes the process.

![Scheme 9. Process for making the lactam based bleach activator.](image)

### 2.3.3 Toxicity of Cationic Compounds

Cationically charged compounds are often flagged by the US Environmental Protection Agency as being potentially toxic. Toxicity is a key characteristic of all new compounds developed for commercial application. The cationic group in TBCC and TBBC is triethylamine, which is a toxic chemical. Additional research to discover reduced toxicity bleach activators may be necessary. LC$_{50}$ and LD$_{50}$ are the two key indexes of toxicity. LC stands for “lethal concentration”, LC$_{50}$ values refer to the concentration of a chemical that kills 50% of the test animals in a given time. LD stands for “Lethal Dose”. LD$_{50}$ is the amount of a material, given all at once, which causes the death of 50% of a group of test animals. LD$_{50}$ is one way to measure the short-term poisoning potential of a material.

Bleach activators are consumed during bleaching and therefore cannot be recycled after use. The cationic chemical will therefore release to the environment and it is important to
decrease the impact of the chemical on the environment for industry use. The cationic groups in both TBCC and TBBC are triethylamine. The toxicity of triethylamine is LC$_{50}$ 60mg/L and LD$_{50}$ 460mg/kg. Table 3. summarizes toxicity classifications of molecules. The toxicity rating of triethylamine is a rating of two, or highly toxic. Therefore, it is desirable to replace triethylamine with a low toxicity cationic group to help make the bleach activator more environmentally responsible. Table 4. shows several amine groups with relatively low toxicity. It is feasible that the toxicity of bleach activators may be decreased by replacing triethylamine with a low toxicity tertiaryamino group.

The nicotinoyl series of tertiary amines could be employed as the substituent that confers cationic character to a molecule with relatively low toxicity. The toxicity of 1,4-Diazabicyclo(2.2.2)octane is also relatively low. 3-Picoline is the main precursor of niacin, one of the B vitamins. Nicotinamide is also one of the B vitamins. Although pyridine is a highly toxic chemical, it is still less toxic than triethylamine. These chemicals can be incorporated into bleach activators as the cationic group during synthesis. The reaction sequence for the synthesis of new cationic bleach activators is similar to the synthetic method for the preparation of to TBBC. The chlorine substituent in the benzoyl chloride moiety will react with the nitrogen in the amine group to produce cationic chemicals. After synthesis of the new cationic bleach activators, optimizing the bleach recipe, comparing the toxicity and bleach performance with current bleach activators are necessary.
### Table 3. Toxicity Classes: Hodge and Sterner Scale

<table>
<thead>
<tr>
<th>TOXICITY RATING</th>
<th>DESCRIPTION</th>
<th>ROUTES OF ADMINISTRATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Extremely Toxic</td>
<td>LC50(ppm)</td>
</tr>
<tr>
<td>2</td>
<td>Highly Toxic</td>
<td>1-50</td>
</tr>
<tr>
<td>3</td>
<td>Moderately Toxic</td>
<td>50-500</td>
</tr>
<tr>
<td>4</td>
<td>Slightly Toxic</td>
<td>500-5000</td>
</tr>
<tr>
<td>5</td>
<td>Practically Non-toxic</td>
<td>5000-15,000</td>
</tr>
<tr>
<td>6</td>
<td>Relatively Harness</td>
<td>15,000 or more</td>
</tr>
</tbody>
</table>

### Table 4. Toxicity of the Amine Groups

<table>
<thead>
<tr>
<th>NAME</th>
<th>STRUCTURE</th>
<th>LC50(ppm)</th>
<th>LD50(ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triethylamine</td>
<td>[Structure Image]</td>
<td>600</td>
<td>460</td>
</tr>
<tr>
<td>Pyridine</td>
<td>[Structure Image]</td>
<td>4000</td>
<td>866</td>
</tr>
<tr>
<td>Nicotinamide</td>
<td>[Structure Image]</td>
<td>NA</td>
<td>3500</td>
</tr>
<tr>
<td>1,4-Diazabicyclo(2.2.2)octane</td>
<td>[Structure Image]</td>
<td>1510-1980</td>
<td>1700</td>
</tr>
<tr>
<td>3-Picoline</td>
<td>[Structure Image]</td>
<td>3300</td>
<td>400</td>
</tr>
</tbody>
</table>

Note: mg/kg = 0.001/1000 = 0.000001 = 1/1000000 = ppm
2.4 Chemical Analysis

2.4.1 Time-of-Flight Mass Spectrometry

Time-of-flight Mass Spectrometry (TOFMS) was first introduced by Wiley et al. in 1955 [38]. TOFMS can determine the mass-to-charge ratio (m/Q) of an ion via a highly accurately measured time measurement. In TOFMS, ions are accelerated by an electric field. The ions that have the same charge will have the same kinetic energy and the velocity of ion depends on the mass-to-charge ratio. The time that the ion subsequently takes to reach a detector at a known distance is measured. From this time and the known experimental parameters one can find the mass-to-charge ratio of the ion. Based on this technique, some other methods such as matrix-assisted laser desorption/ionization (MALDI), californiumplasma desorption, static secondary ion mass spectrometry (SIMS) [39-42] were invented and are now quite widely used. An important enhancement to mass spectrometry is combining it with chromatographic separation techniques. The chromatographic separation system will separate the compounds first followed by ionization, which pass into the mass spectrometer's analyzer and eventually detected.

2.4.2 High-Performance Liquid Chromatography

In 1966, Horvath developed reverse-phase separations to high-performance liquid chromatography (HPLC) [43]. Reverse-phase HPLC is one chromatographic technique that
can be used for identifying, quantifying and purifying the individual components in a mixture.

2.4.3 Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) is a physical phenomenon. It was first described and measured in molecular beams by Rabi et al. in 1938 [44]. For all nucleons, that is neutrons and protons, composing any atomic nucleus, have the intrinsic quantum property of spin. The overall spin of the nucleus is determined by the spin quantum number $S$. If the number of both the protons and neutrons in a given nuclide $S = 0$, a non-zero spin is associated with a non-zero magnetic moment ($\mu$) via the relation shown in Equation $7$ [45]. The symbol, $\gamma$, is the gyromagnetic ratio, which is this magnetic moment that allows the observation of NMR absorption spectra caused by transitions between nuclear spin levels.

$$\mu = \gamma S$$ (7)

For instance, $^{18}O$ has both an even number of protons and an even number of neutrons with zero nuclear magnetic moments. Hence, such nuclides do not exhibit any NMR absorption spectra.

Nuclear “shielding” effect [46] is because of the surrounding shells of electrons. Electrons will also charge and rotate with a spin to produce a magnetic field opposite to the magnetic
field produced by the nucleus. This kind of shield will reduce the magnetic field at the nucleus which is what determines the NMR frequency. As a result, the frequency to achieve resonance is also reduced.

The magnetic nuclei absorb and re-emit the electromagnetic radiation in a magnetic field. The resonance frequency depends on the strength of the magnetic field and the magnetic properties of the atoms. Different atomic nuclei within a molecule resonate at different (radio) frequencies for the same magnetic field strength. NMR spectroscopy is one technique to obtain the structural information of molecules. $^1$H is the most common chemical element used for NMR analysis, because hydrogen is highly abundant and it is the nucleus most sensitive to a NMR signal. By studying the peaks of nuclear magnetic resonance spectra, the structure of many compounds can be inferred.

2.5 Whiteness Measurement

2.5.1 Whiteness

In colorimetry, whiteness is the degree of which a surface is determined to be perceived as white [47]. Whiteness is fundamentally an attribute of the human visual system of whose “color” is devoid of hues and grayness [11].
2.5.2 Whiteness Index

In 1931, the CIE (the International Commission on Illumination) introduced the instrumental color measurement for specifying color numerically. All colors, including white, can be defined by tristimulus values. Whiteness index is a single scale of whiteness and allows users to identify and compare the level of whiteness of two or more objects, shown as Equation 8 [49].

\[
\text{WI CIE} = Y + 800 \left( x_n - x \right) + 1700 \left( y_n - y \right) \tag{8}
\]

Where \(Y, x, y\) are the luminance factor and chromaticity coordinates of the specimen, and \(x_n\) and \(y_n\) are the chromaticity coordinates for the CIE standard illuminant and source used. These values are provided in the Table 5 below based on the illuminant and observer used. Whiteness Index can only be calculated for illuminants C, D50, and D65. Currently, no additional illuminants are incorporated into the standard.

<table>
<thead>
<tr>
<th>VALUE</th>
<th>C/2°</th>
<th>D50/2°</th>
<th>D65/2°</th>
<th>C/10°</th>
<th>D50/10°</th>
<th>D65/10°</th>
</tr>
</thead>
<tbody>
<tr>
<td>(x_n)</td>
<td>0.3101</td>
<td>0.3457</td>
<td>0.3127</td>
<td>0.3104</td>
<td>0.3477</td>
<td>0.3138</td>
</tr>
<tr>
<td>(y_n)</td>
<td>0.3161</td>
<td>0.3585</td>
<td>0.3290</td>
<td>0.3191</td>
<td>0.3595</td>
<td>0.3310</td>
</tr>
</tbody>
</table>
Chapter 3  EXPERIMENTAL

3.1 Materials

ε-Caprolactam (99%), γ-Butyrolactam (98%) and 4-chloromethylbenzoyl chloride(98%) were purchased from TCI America. Triethylamine(99.5%) was purchased from Sigma-Aldrich Co. Nicotine amide (98%), 3-picoline (98%), 1,4-Diazabicyclo(2.2.2)octane (99%) and Pyridine (97%) was purchased from Acros Organics Co.

3.2 Instrumentation

Melting points were recorded using a Perkin Elmer Diamond DSC with Intercooler. Proton nuclear magnetic resonance (1H NMR) spectra were recorded in DMSO using a 500MHz BrukerAvance Spectrometer. Mass spectra were recorded on Agilent Technologies 1200 SL Liquid Chromatograph with Evaporative Light Scattering (ELS) detector and 6520 QTOF mass spectrometer. The following reverse phase C18 column was employed: Agilent ZorbaxEclipse plus (2.1 mmx 100 mm, 3.5 µm particle size).

3.3 Synthesis

Table 6. summarizes the tertiary amino compounds used in the synthesis of novel cationic bleach activators.
Table 6. Tertiary Amino Compounds Used

<table>
<thead>
<tr>
<th>NAME</th>
<th>STRUCTURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triethylamine</td>
<td><img src="image1" alt="Structure" /></td>
</tr>
<tr>
<td>Pyridine</td>
<td><img src="image2" alt="Structure" /></td>
</tr>
<tr>
<td>DABCO</td>
<td><img src="image3" alt="Structure" /></td>
</tr>
<tr>
<td>Nicotinamide</td>
<td><img src="image4" alt="Structure" /></td>
</tr>
<tr>
<td>3-picoline</td>
<td><img src="image5" alt="Structure" /></td>
</tr>
</tbody>
</table>

3.3.1 TBCC Synthesis

3.3.1.1 Synthesis of the Intermediate, 4-Chloromethyl benzoyl caprolactam

Caprolactam (22.6 g, 0.2 mol) was mixed with triethylamine (30.5 g, 0.3 mol) and toluene (225 mL) under argon, and heated to reflux. 4-Chloromethyl benzoyl chloride (38.6 g, 0.2 mol) was dissolved in toluene (75 mL) and added slowly to the solution. The solution was stirred under reflux for 6 h, cooled to room temperature and filtered. The filtrate was cooled
and stored overnight in a refrigerator. The white precipitated product was filtered, washed with 5 % NaHCO₃ solution 300 mL and dried in an oven at 40 °C for 12 h.

3.3.1.2 Synthesis of TBCC

4-Chloromethyl benzoyl caprolactam(26.95 g, 0.1 mol) were dissolved in 150 mL of acetonitrile under argon. Triethylamine (0.2 mol) was added dropwise to the solution and the solution was stirred under reflux for 4 h. The solution was cooled to room temperature and the solvent evaporated using a rotary evaporator. Acetone (100 mL) was added and the mixture was heated briefly and cooled to room temperature. The white product was filtered, washed with acetone and dried to give 29.2 g of product, a theoretical yield of 79.6 %.

3.3.2 Pyridine-based Bleach Activator with Caprolactam as the Leaving Group

3.3.2.1 Synthesis of the Intermediate, 4-Chloromethyl benzoyl caprolactam

Caprolactam (22.6 g, 0.2 mol) was mixed with triethylamine (30.5 g, 0.3 mol) and toluene (225 mL) under argon, and heated to reflux. 4-Chloromethyl benzoyl chloride (38.6 g, 0.2 mol) was dissolved in toluene (75 mL) and added slowly to the solution. The solution was stirred under reflux for 6 h, cooled to room temperature and filtered. The filtrate was cooled and stored overnight in a refrigerator. The white precipitated product was filtered, washed with 5 % NaHCO₃ solution (300 mL) and dried in an oven at 40 °C for 12 h.
3.3.2.2 Synthesis of N-[4-(pyridiniummethyl)benzoyl] caprolactam chloride, PBCC

The intermediate described in 3.3.2.1, 4-chloromethyl benzoyl caprolactam (26.95 g, 0.1 mol) was dissolved in 150 mL acetonitrile under argon. Pyridine (16.3 mL, 0.2 mol) was added dropwise to the solution and the solution was stirred under reflux for 4 h. The solution was cooled to room temperature and the solvent evaporated using a rotary evaporator. Acetone (100 mL) was added and the mixture was heated briefly and cooled to room temperature. The white product was filtered, washed with acetone and dried to give 30.3 g of product, a theoretical yield of 88.1%.

3.3.3 1,4-diazabicyclo[2.2.2] octane-based Bleach Activator with Caprolactam as the Leaving Group

3.3.3.1 Synthesis of the Intermediate, 4-chloromethyl benzoyl caprolactam

Caprolactam (22.6 g, 0.2 mol) was mixed with triethylamine (30.5 g, 0.3 mol) and toluene (225 mL) under argon, and heated to reflux. 4-Chloromethyl benzoyl chloride (38.6 g, 0.2 mol) was dissolved in toluene (75 mL) and added slowly to the solution. The solution was stirred under reflux for 6 h, cooled to room temperature and filtered. The filtrate was cooled and stored overnight in a refrigerator. The white precipitated product was filtered, washed with 5% NaHCO₃ solution 300 mL and dried in an oven at 40 °C for 12 h.
3.3.3.2 Synthesis of N-[4-(1,4-diazabicyclo[2.2.2] octane-methyl)benzoyl] caprolactam chloride, DOBCC

*Intermediate and 1, 4-diazabicyclo[2.2.2] octane mol ratio 1:1*

The intermediate described in 3.3.3.1, 4-chloromethyl benzoyl caprolactam (13.5 g, 0.05 mol) was dissolved in 75 mL acetonitrile under argon. 1, 4-diazabicyclo[2.2.2] octane(0.05 mol) was added dropwise to the solution and the solution was stirred under reflux for 4h. The solution was cool the room temperature and the solution evaporated using a rotary evaporator. Acetone (80 mL) was added and stirred. The solution was filtered and the filtrate was mixed with acetone (80 mL) and the mixture was heated briefly then cooled to room temperature. The white produce was filtered, washed with acetone and dried to give 18.55 g of product, a theoretical yield of 98.91 %.

*Intermediate and 1, 4-diazabicyclo[2.2.2] octane mol ratio 2:1*

The intermediate described in 3.3.3.1, 4-chloromethyl benzoyl caprolactam (13.5 g, 0.05 mol) was dissolved in 75 mL of acetonitrile under argon. 1,4-diazabicyclo[2.2.2] octane (0.025 mol) was added dropwise to the solution and the solution was stirred under reflux for 4 h. The solution was cool the room temperature and the solution evaporated using a rotary evaporator. Acetone (80 mL) was added and stirred. The solution was filtered and the filtrate was mixed with acetone (80 mL) and the mixture was heated briefly then cooled to room
temperature. The white produce was filtered, washed with acetone and dried to give 15.40 g of product, a theoretical yield of 48.3 %.

3.3.4 Nicotinamide-based Bleach Activator with Caprolactam as the Leaving Group

3.3.4.1 Synthesis of the Intermediate, 4-Chloromethyl benzoyl caprolactam

Caprolactam (22.6 g, 0.2 mol) was mixed with triethylamine (30.5 g, 0.3 mol) and toluene (225 mL) under argon, and heated to reflux. 4-Chloromethyl benzoyl chloride (38.6 g, 0.2 mol) was dissolved in toluene (75 mL) and added slowly to the solution. The solution was stirred under reflux for 6 h, cooled to room temperature and filtered. The filtrate was cooled and stored overnight in a refrigerator. The white precipitated product was filtered, washed with 5 % NaHCO$_3$ solution 300 ml and dried in an oven at 40 °C for 12 h.

3.3.4.2 Synthesis of N-[4-(nicotinamide-methyl) benzoyl] caprolactam chloride, NABCC

The intermediate described in 3.3.4.1, 4-chloromethyl benzoyl caprolactam (26.95 g, 0.1 mol) were dissolved in 150 mL of THF under argon. Nicotinamide (0.2 mol) was dissolved in THF 50 mL and added dropwise to the solution and the solution was stirred under reflux for 4 h. The solution was cooled to room temperature and the solvent evaporated using a rotary evaporator. Acetone (100 mL) was added and the mixture was heated briefly and
cooled to room temperature. The white product was filtered, washed with acetone and dried to give 17.65 g of product, a theoretical yield of 45.62%.

### 3.3.5 3-Picoline-based Bleach Activator with Caprolactam as the Leaving Group

#### 3.3.5.1 Synthesis of the Intermediate, 4-Chloromethyl benzoyl caprolactam

Caprolactam (22.6 g, 0.2 mol) was mixed with triethylamine (30.5 g, 0.3 mol) and toluene (225 mL) under argon, and heated to reflux. 4-Chloromethyl benzoyl chloride (38.6 g, 0.2 mol) was dissolved in toluene (75 mL) and added slowly to the solution. The solution was stirred under reflux for 6 h, cooled to room temperature and filtered. The filtrate was cooled and stored overnight in a refrigerator. The white precipitated product was filtered, washed with 5% NaHCO₃ solution 300 mL and dried in an oven at 40 °C for 12 h.

#### 3.3.5.2 Synthesis of N-[4-(3-picoline-methyl)benzoyl] caprolactamchloride, 3-PBCC

The intermediate described in 3.3.5.1, 4-chloromethyl benzoyl caprolactam (26.95 g, 0.1 mol) were dissolved in 150 mL of acetonitrile under argon. 3-Picoline (10 mL, 0.1 mol) was dissolved in solution and added dropwise to the solution and the solution was stirred under reflux for 4 h. The solution was cooled to room temperature and then the solvent evaporated using a rotary evaporator. Acetone (100 mL) was added and the mixture was heated briefly.
and cooled to room temperature. The white product was filtered, washed with acetonitrile and dried to give 14.32 g of product, a theoretical yield of 40.2 %

3.3.6 Pyridine-based Bleach Activator with Butyrolactams the Leaving Group

3.3.6.1 Synthesis of the Intermediate, 4-Chloromethyl benzoyl butyrolactam

Butyrolactam (17.2 g, 0.2 mol) was mixed with triethylamine (30.5 g, 0.3 mol) and toluene (225 mL) under argon, and heated to reflux. 4-Chloromethyl benzoyl chloride (38.6 g, 0.2 mol) was dissolved in toluene (75 mL) and added slowly to the solution. The solution was stirred at reflux for 6 h, cooled to room temperature and filtered. The filtrate was cooled and stored overnight in a refrigerator. The white precipitated product was filtered, washed with 5 % NaHCO₃ solution 300 mL and dried in an oven at 40 °C for 12 h.

3.3.6.2 Synthesis of N-[4-(pyridinmethyl)benzoyl] butyrolactam chloride, PBBC

The intermediate described in 3.3.6.1, 4-Chloromethyl benzoyl butyrolactam (24.15 g, 0.1 mol) were dissolved in 150 mL of acetonitrile under argon. Pyridine (16.3 mL, 0.2 mol) was added dropwise to the solution and the solution was stirred under reflux for 4 h. The solution was cooled to room temperature and the solvent evaporated using a rotary evaporator. Acetone (100 mL) was added and the mixture was heated briefly and cooled to room
temperature. The white product was filtered, washed with acetone and dried to give 23.62 g of product, a theoretical yield of 74.52 %.

3.3.7 1,4-Diazabicyclo[2.2.2] Octane-based Bleach Activator with Butyrolactamas the Leaving Group

3.3.7.1 Synthesis of the Intermediate, 4-Chloromethyl benzoyl butyrolactam

Butyrolactam (17.2 g, 0.2 mol) was mixed with triethylamine (30.5 g, 0.3 mol) and toluene (225 mL) under argon, and heated to reflux. 4-Chloromethyl benzoyl chloride (38.6 g, 0.2 mol) was dissolved in toluene (75 mL) and added slowly to the solution. The solution was stirred under reflux for 6 h, cooled to room temperature and filtered. The filtrat overnighted and stored overnight in a refrigerator. The white precipitated product was filtered, washed with 5 % NaHCO₃ solution 300 mL and dried in an oven at 40 °C for 12 h.

3.3.7.2 Synthesis of N-[4-(1,4-diazabicyclo[2.2.2] octane-methyl)benzoyl] butyrolactam chloride, DOBBC

The intermediate described in 3.3.7.1, 4-chloromethyl benzoyl butyrolactam (16.8 g, 0.05 mol) were dissolved in 75 mL of acetonitrile under argon. 1, 4-diazabicyclo[2.2.2] octane (5.6 g, 0.05 mol) was added dropwise to the solution and the solution was stirred under reflux for 4 h. The solution was cool the room temperature and the solution evaporated using a
rotary evaporator. Acetone 80 mL was added and stirred. Remove the acetone from the beaker and add another 80 mL acetone and the solution was heated briefly then cooled to room temperature. The white produce was filtered, washed with acetone and dried to give 13.38 g of product, a theoretical yield of 76.23 %.

### 3.3.8 Nicotinamide-based Bleach Activator with Butyrolactam as the Leaving Group

#### 3.3.8.1 Synthesis of the Intermediate, 4-Chloromethyl benzoyl butyrolactam

Butyrolactam (17.2 g, 0.2 mol) was mixed with triethylamine (30.5 g, 0.3 mol) and toluene (225 mL) under argon, and heated to reflux. 4-Chloromethyl benzoyl chloride (38.6 g, 0.2 mol) was dissolved in toluene (75 mL) and added slowly to the solution. The solution was stirred under reflux for 6 h, cooled to room temperature and filtered. The filtrate was cooled and stored overnight in a refrigerator. The white precipitated product was filtered, washed with 5 % NaHCO$_3$ solution 300 mL and dried in an oven at 40 °C for 12 h.

#### 3.3.8.2 Synthesis of N-[4-(nicotinamide-methyl)benzoyl] butyrolactam chloride, NABBC

The intermediate described in 3.3.8.1, 4-Chloromethyl benzoyl butyrolactam (23.7 g, 0.1 mol) were dissolved in 150 mL of THF under argon. Nicotinamide (5.6 g, 0.05 mol) was dissolved in THF 50 mL and added dropwise to the solution and the solution was stirred
under reflux for 24 h. The solution was cooled to room temperature and the solvent evaporated using a rotary evaporator. Acetone (100 mL) was added and the mixture was heated briefly and cooled to room temperature. The white product was filtered, washed with acetone and dried to give 13.44 g of product, a theoretical yield of 37.45 %.

3.3.9 3-Picoline-based Bleach Activator with Butyrolactamas the Leaving Group

3.3.9.1 Synthesis of the Intermediate, 4-Chloromethyl benzoyl butyrolactam

Butyrolactam (17.2 g, 0.2 mol) was mixed with triethylamine (30.5 g, 0.3 mol) and toluene (225 mL) under argon, and heated to reflux. 4-Chloromethyl benzoyl chloride (38.6 g, 0.2 mol) was dissolved in toluene (75 mL) and added slowly to the solution. The solution was stirred under reflux for 6 h, cooled to room temperature and filtered. The filtrate was cooled and stored overnight in a refrigerator. The white precipitated product was filtered, washed with 5 % NaHCO₃ solution 300 mL and dried in an oven at 40 °C for 12 h.

3.3.9.2 Synthesis of N-[4-(3-picoline-methyl) benzoyl] butyrolactam chloride, 3-PBBC

The intermediate described in 3.3.9.1, 4-Chloromethyl benzoyl caprolactam (24.15 g, 0.1 mol) were dissolved in 150 mL of acetonitrile under argon. 3-Picoline (30 mL, 0.3 mol) was dissolved in solution and added dropwise to the solution and the solution was stirred under
reflux for 4 h. The solution was cooled to room temperature and then the solvent evaporated using a rotary evaporator. Acetone (100 mL) was added and the mixture was heated briefly and cooled to room temperature. The white product was filtered, washed with acetonitrile and dried to give 13.30 g of product, a theoretical yield of 40.2%.

### 3.4 Bleaching Performance

#### 3.4.1 Materials

Cationic bleach activators were synthesized and purified by recrystallized in acetonitrile and washed with acetone, then dried in the oven at 40 °C for 12 h. 100% Desized unscoured cotton knit fabric was purchased from Testfabrics (West Pittston, PA, USA). H₂O₂, 35% w/w and sodium bicarbonate (NaHCO₃, 99.5%) were purchased from Sigma-Aldrich Co. (St.Louis, MO, USA). The wetting agent (Kieralon MFB) and stabilizer (Prestogen N-D) were purchased from BASF (Charlotte, NC, USA).

#### 3.4.2 Bleaching Method

The following bleaching method was used: Bleach activator: 5 g/L; stabilizer: 1 g/L; wetting agent: 1 g/L; H₂O₂: 6 g/L; sodium bicarbonate: 6.25 g/L; Liquor-to-goods ratio: 20:1. All bleaching experiments were performed using an Ahiba Nuance Infrared Laboratory Dyeing Machine (Datacolor international, USA). The desired amount of the bleach activators and
chemicals were dissolved in a 200 mL bleach bath, 10 g knit fabric was added. The bath was heated to 50 °C at the rate of 4 °C/min. After 30 min, the fabric was removed from the bleach bath and rinsed with copious amounts of cold water, then dried under ambient conditions.

### 3.4.4 Whiteness Measurement

CIE Whiteness Index (CIE WI) values were calculated from the reflectance data of each sample using AATCC Test Method 110 [49]. For each sample, four layers of fabric were measured and each sample was measured four times by rotating the sample at 90 degrees between each measurement. The average value was recorded.

### 3.4.5 Water Absorbency Measurement

AATCC Test Method 79 was used to determine water absorbency. In this standard measurement, the fabric sample is placed over the top of a beaker so that the center is unsupported. A measured drop of water is placed on the fabric 1 cm from the surface. Time is recorded until the water drop absorbs completely. Each sample fabric is tested five times and the average time is calculated [50].
3.4.6 Mote Counting Test

Mote counting was not performed according to a standard method. A 25 cm² fabric sample was placed in the viewing booth at 45° to the plane of the light source. The sample was then viewed perpendicular to the plane of the sample using a calibrated daylight simulator, according to AATCC Evaluation Procedure 9 [51]. The motes on the fabric were counted. The visual assessment was performed three times and the average mote count was calculated.
Chapter 4  RESULTS AND DISCUSSION

A series of new cationic bleach activators were synthesized and their bleaching properties investigated by comparing to activators reported in the prior art. Eight new compounds were synthesized as described in the next section.

4.1 Synthesis and Characterization

4.1.1 Synthesis of 4-Chloromethyl benzoyl Caprolactam Intermediate

4-Chloromethylbenzoyl caprolactam was synthesized as a primary intermediate for the subsequent synthesis of the series of cationic bleach activators. The method reported previously was used [25], and produced the target compound in 84.58 % yield, with m.p. 212.4 °C. Extracted Ion Chromatogram (EIC) analysis showed the presence of two peaks at mass = 266.094, which corresponds to the intermediate, with a retention time of 6.337 min, as shown in Figure 1. The mass spectrum is shown in Figure 2 and the m/z value 266.094 was assigned to the product [M+H]^+.

![Figure 1. Extracted Ion Chromatogram of 4-Chloromethyl benzoyl caprolactam](image-url)
4.1.2 Synthesis of N-[4-(triethylammoniomethyl)benzoyl] Caprolactam Chloride, TBCC

TBCC (10) was previously synthesized by Miracle et al. [37] and later Lee et al. [25]. Scheme 9 shows the reaction sequence. The product was synthesized successfully using the Lee method to give 79.6% theoretical yield and m.p. 218.81 °C.
Scheme 9. Reaction scheme for the synthesis of amino group based cationic bleach activators

\[(\text{ClO}_2\text{C})_3\text{N} + \text{N}((\text{C}_2\text{H}_5)_3)\rightarrow \text{ClO}_2\text{C}N((\text{C}_2\text{H}_5)_3)\]

\[\text{R} + \text{Cl}((\text{C}_6\text{H}_4)\text{N}((\text{CH}_2)_n)\rightarrow \text{R}((\text{C}_6\text{H}_4)\text{N}((\text{CH}_2)_n)\]

\(^1\text{H NMR} \) analysis was consistent with the structure of the target compound: \(\delta_\text{H}(\text{DMSO})/\text{ppm}\)

1.30-1.32 (9H, t, N(CH\_2\_CH\_3)_\_3), 1.74-1.76 (6H, m, COCH\_2(CH\_2)_\_3), 2.68-2.70 (2H, t, COCH\_2),

3.15-3.31 (6H, q, N(CH\_2\_CH\_3)_\_3), 3.93-3.95 (2H, t, NCH\_2CH\_2), 4.53 (1H, s, ArCH\_2), 7.58-

7.59 (2H, d, ArH), 7.60 (2H, d, ArH), the signal at 3.3 is water, signal at 2.1 is acetone;

\(m/\text{z}(\text{FAB-MS})331.2[(\text{M-Cl})^+]\) Calc. for C\_20H\_31ClN\_2O\_2: 331.2]. Figure 3 shows the \(^1\text{H NMR}\) spectrum of TBCC.
Extracted Ion Chromatogram (EIC) analysis showed the presence of one peak at mass = 331.24, which corresponds to TBCC, with a retention time of 4.014 min, as shown in Figure 4. The mass spectrum is shown in Figure 5 and the m/z value 331.23 was assigned to TBCC [M-Cl]^+ and the product is pure enough so there is no any other noise signal in the mass spectrum.
Figure 4. Extracted Ion Chromatogram of N-[4-(triethylammoniomethyl)benzoyl] caprolactam chloride, TBCC

Figure 5. Positive-ion ESI MS spectrum of N-[4-(triethylammoniomethyl)benzoyl] caprolactam chloride, TBCC
4.1.3 Synthesis of N-[4-(pyridiniummethyl)benzoyl] Caprolactam Chloride, PBCC

PBCC (12) was synthesized with the same method as TBCC synthesis. The product was synthesized successfully using the Lee method to give yield: 88.11%; mp 226.90 °C; $^1$H NMR analysis was consistent with the structure of the target compound: $\delta_H$(DMSO)/ppm 1.72-1.74(6H, m, COCH$_2$(CH$_2$)$_3$), 2.65-2.67(2H, t, COCH$_2$), 3.90-3.92(2H, t, NCH$_2$CH$_2$), 5.94(1H, s, ArCH$_2$), 7.52-7.53(4H, d, ArH), 8.20-8.22(2H, d, NCHCH), 8.65 (1H, d, NCHCHCH), 9.27-9.28(2H, d, NCH), the signal at 3.3 is water; signal at 2.1 is acetone; m/z(FAB-MS)309.16[(M-Cl)$^+$]. Calc. for C$_{19}$H$_{21}$ClN$_2$O$_2$: 309.16]; Figure 6 shows the $^1$H NMR spectrum of PBCC.
EIC analysis showed the presence of one peak at mass = 309.16, which corresponds to PBCC, with a retention time of 3.695 min, as shown in Figure 7. The mass spectrum is shown in Figure 8 and the m/z value 309.16 was assigned to PBCC [M-Cl]^+ and the product is pure enough so there is no any other noise signal in the mass spectrum.
Figure 7. Extracted Ion Chromatogram of N-[4-(pyridiniummethyl)benzoyl] caprolactam chloride, PBCC

Figure 8. Positive-ion ESI MS spectrum of N-[4-(pyridiniummethyl)benzoyl] caprolactam chloride, PBCC
4.1.4 Synthesis of N-[4-(1,4-diazabicyclo[2.2.2] octane-methyl)benzoyl] Caprolactam Chloride, DOBCC

DOBCC (13) was synthesized with the same method as TBCC synthesis. The product was synthesized successfully using the Lee method to give yield: 98.91%; mp 213.98°C; $^1$H NMR analysis was consistent with the structure of the target compound: $\delta_H$(DMSO)/ppm 1.72-1.74(6H, m, COCH$_3$(CH$_2$)$_3$), 2.63-2.64(2H, t, COCH$_2$), 3.28-3.31(12H, t, NCH$_2$) 3.88-3.93(2H, t, NCH$_2$CH$_2$), 4.55(1H, s, ArCH$_2$), 7.51-7.55(4H, d, ArH), the signal at 3.3 is water, signal at 2.1 is acetone; m/z(FAB-MS)342.22[(M-Cl)$^+$. Calc. for C$_{20}$H$_{28}$ClN$_3$O$_2$: 342.22]; Figure 9 shows the $^1$H NMR spectrum of DOBCC.
EIC analysis showed the presence of one peak at mass =342.21, which corresponds to DOBCC, with a retention time of 3.190 min, as shown in Figure 10. The mass spectrum is shown in Figure 11 and the m/z value 342.21 was calculated and assigned to DOBCC [M-Cl]^+. The product appears relatively pure.
Figure 10. Extracted Ion Chromatogram of N-[4-(1,4-diazabicyclo[2.2.2]octane-methyl)benzoyl] caprolactam chloride, DOBCC

Figure 11. Positive-ion ESI LC-MS spectrum of N-[4-(1,4-diazabicyclo[2.2.2]octane-methyl)benzoyl] caprolactam chloride, DOBCC

The EIC/MS and NMR results of the different mol ratio experiments produced the same results. Only one nitrogen in the DABCO was shown to react with the intermediate.
4.1.5 Synthesis of N-[4-(nicotinamide-methyl)benzoyl]Caprolactam Chloride, NABCC

NABCC (14) was synthesized with the same method as TBCC synthesis. The product was synthesized successfully using the Lee method to give yield: 45.62%; mp 218.90°C; $^1$H NMR analysis was consistent with the structure of the target compound: $\delta_{\text{H}}$(DMSO)/ppm 1.72-1.74(6H, m, COCH$_2$(CH$_2$)$_3$), 2.66-2.68(2H, t, COCH$_2$), 3.90-3.92(2H, t, NCH$_2$CH$_2$), 4.82(1H, s, ArCH$_2$), 7.50-7.51(4H, m, ArH), 8.19-8.22(1H, m, NCHCH), 8.67-8.70(H, d, NCHCHCH), 9.03-9.06(H, d, NCHCH), 9.31-9.33(H, d, NCH), the signal at 3.3 is water, the signal at 2.1 is acetone; [(M-Cl)$^+$, Calc. for C$_{20}$H$_{22}$ClN$_3$O$_3$: 352.17]; Figure 12 shows the $^1$H NMR spectrum of NABCC.
Figure 12. $^1$H NMR spectrum of N-[4-(nicotinamide-methyl)benzoyl] caprolactam chloride, NABCC

EIC analysis showed the presence of one peak at mass = 352.16, which corresponds to NABCC, with a retention time of 2.153 min, as shown in Figure 13. The mass spectrum is shown in Figure 14 and the m/z value 352.16 was calculated and assigned to NABCC [M-Cl]$^+$. The product appears relatively pure.
Figure 13. Extracted Ion Chromatogram of N-[4-(nicotinamide-methyl)benzoyl] caprolactam chloride, NABCC

Figure 14. Positive-ion ESI MS spectrum of N-[4-(nicotinamide-methyl)benzoyl] caprolactam chloride, NABCC

4.1.6 Synthesis of N-[4-(3-picoline-methyl)benzoyl] Caprolactam Chloride, 3-PBCC
3-PBCC (15) was synthesized with the same method as TBCC synthesis. The product was synthesized successfully using the Lee method to give yield: 40.2%; mp191.31 °C; $^1$H NMR analysis was consistent with the structure of the target compound: $\delta_H$(DMSO)/ppm 1.77-1.82(6H, m, COCH$_2$(CH$_2$)$_3$), 2.71-2.74(3H,d, CH$_3$), 3.96-3.99(2H, t, NCH$_2$CH$_2$), 4.13(2H, s, COCH$_2$), 5.93-5.94(2H, d, ArCH$_2$), 7.62(4H, s, ArH), 8.16-8.19(1H, t, NCHCHCH), 8.55-8.57(1H, d, NCHCH), 9.16-9.19(1H, t, NCHCH), 9.27-9.30(H, t, NCHC), the signal at 3.3 is water, the signal at 2.1 is acetone; [(M-Cl)$^+$]. Calc. for C$_{20}$H$_{23}$ClN$_2$O$_2$: 323.18]; Figure 15 shows the $^1$H NMR spectrum of 3-PBCC.
EIC analysis showed the presence of one peak at mass $=323.18$, which corresponds to 3-PBCC, with a retention time of 2.637 min, as shown in Figure 16. The mass spectrum is shown in Figure 17 and the m/z value 323.17 was calculated and assigned to 3-PBCC [M-Cl]$^+$. The product appears relatively pure.

Figure 16. Extracted Ion Chromatogram of N-[4-(3-picoline-methyl)benzoyl] caprolactam chloride, 3-PBCC

Figure 17. Positive-ion ESI LC-MS spectrum of N-[4-(3-picoline-methyl)benzoyl] caprolactam chloride, 3-PBCC
4.1.7 Synthesis of N-[4-(pyridiniummethyl)benzoyl] Butyrolactam Chloride, PBBC

PBBC (16) was synthesized with the same method as TBCC synthesis. The product was synthesized successfully using the Lee method to give yield: 74.52%; mp106.67°C; $^1$H NMR analysis was consistent with the structure of the target compound: δ$_H$(DMSO)/ppm 1.25-1.27(2H, m, CH$_2$CH$_2$CH$_2$), 3.85-3.87(2H, d, NCH$_2$CH$_2$), 4.82-4.83(2H, d, COCH$_2$), 5.89-5.93(1H, m, ArCH$_2$), 7.60-7.67(4H, m, ArH), 8.28-8.30(2H, m, NCHCH), 8.72-8.73(1H, m, NCHCHCH), 9.32-9.37(2H, m, NCH), the signal at 3.3 is water, the signal at 2.1 is acetone;[(M-Cl)$^+$]. Calc. for C$_{17}$H$_{17}$ClN$_2$O$_2$: 281.13. Figure 18 shows the NMR spectrum of PBBC.
HPLC analysis showed the presence of one peak at mass =281.13, which corresponds to PBBC, with a retention time of 0.803 min, as shown in Figure 19. The mass spectrum is shown in Figure 20 and the m/z value 281.13 was calculated and assigned to PBBC [M-Cl]^+. The product appears relatively pure.
Figure 19. Extracted Ion Chromatogram of N-[4-(pyridiniummethyl) benzoyl] butyrolactam chloride, PBBC

Figure 20. Positive-ion ESI LC-MS spectrum of N-[4-(pyridiniummethyl) benzoyl] butyrolactam chloride, PBBC

4.1.8 Synthesis of N-[4-(1,4-diazabicyclo[2.2.2] octane-methyl)benzoyl] Butyrolactam Chloride, DOBBC

\[
\begin{align*}
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N}
\end{align*}
\]
DOBBC (17) was synthesized with the same method as TBCC synthesis. The product was synthesized successfully using the Lee method to give yield: 76.23%; mp 218.26°C; $^1$H NMR analysis was consistent with the structure of the target compound: $\delta_H$(DMSO)/ppm 1.25-1.27(2H, m, CH$_2$CH$_2$CH$_2$), 4.88-4.92(2H, m, COCH$_3$), 3.10-3.12(12H, t, NCH$_2$) 3.88-3.96(2H, t, NCH$_2$CH$_2$), 4.64-4.66(1H, s, ArCH$_3$), 7.62-7.75(4H, m, ArH), the peak at 2.1 is acetone; [(M-Cl)$^+$, Calc. for C$_{18}$H$_{24}$ClN$_3$O$_2$: 314.19]. Figure 21 shows the $^1$H NMR spectrum of DOBBC.

![Figure 21. $^1$H NMR spectrum of N-[4-(1,4-diazabicyclo[2.2.2] octane-methyl)benzoyl] butyrolactam chloride, DOBBC](DOBBC.esp)
EIC analysis showed the presence of one peak at mass =314.19, which corresponds to DOBBC, with a retention time of 0.566 min, as shown in Figure 22. The mass spectrum is shown in Figure 23 and the m/z value 314.19 was calculated and assigned to DOBBC [M-Cl]^+. The product appears relatively pure.

Figure 22. Extracted Ion Chromatogram of N-[4-(1,4-diazabicyclo[2.2.2] octane-methyl)benzoyl] butyrolactam chloride, DOBBC

Figure 23. Positive-ion ESI LC-MS spectrum of N-[4-(1,4-diazabicyclo[2.2.2] octane-methyl)benzoyl] butyrolactam chloride, DOBBC
4.1.9 Synthesis of N-[4-(nicotinamide-methyl)benzoyl] Butyrolactam Chloride, NABBC

NABBC (18) was synthesized with the same method as TBCC synthesis. The product was synthesized successfully using the Lee method to give yield: 37.45%; mp203.30°C; 'H NMR analysis was consistent with the structure of the target compound: δH(DMSO)/ppm 1.25-1.26(2H, d, CH₂CH₂CH₂), 3.85-3.87(2H, t, NCH₃CH₂), 4.89(2H, s, COCH₂), 6.04(1H, s, ArCH₂), 7.55-7.66(4H, m, ArH), 8.28-8.36(1H, m, NCHCH), 8.77-8.80(H, d, NCHCHCH), 9.08-9.12(H, d, NCHCH), 9.31-9.33(H, d, NCH), the peak at 2.1 is acetone; [(M-Cl)⁺]. Calc. for C₁₈H₁₈ClN₃O₃: 324.13]. Figure 24 shows the 'H NMR spectrum of NABBC.
EIC analysis showed the presence of one peak at mass = 324.13, which corresponds to DOBBC, with a retention time of 0.688 min, as shown in Figure 25. The mass spectrum is shown in Figure 26 and the m/z value 324.13 was calculated and assigned to DOBBC [M-Cl]^+. The product appears relatively pure.
4.1.10 Synthesis of N-[4-(3-picoline-methyl)benzoyl] Butyrolactam Chloride, 3-PBBC
3-PBBC (19) was synthesized with the same method as TBCC synthesis. The product was synthesized successfully using the Lee method to give yield: 40.2%; This product is a gel-like compound under room temperature; $^1$H NMR analysis was consistent with the structure of the target compound: $\delta_H$(DMSO)/ppm 1.25-1.28(2H, m,CH$_2$CH$_2$CH$_2$), 3.85-3.87(2H, t, NCH$_2$CH$_2$), 4.82-4.83(2H, t, COCH$_2$), 6.08-6.11(2H, d, ArCH$_2$), 7.64-7.66(4H, m, ArH), 8.17-8.20(H, t, NCHCHCH), 8.55-8.57(1H, d, NCHCH), 9.40-9.43(1H, t, NCHCH), 9.56-9.57(H, t, NCHC);[(M-Cl)$^+$. Calculated for C$_{18}$H$_{24}$ClN$_3$O$_2$: 295.14]. Figure 27 shows the $^1$H NMR spectrum of 3-PBBC.

![Figure 27. $^1$H NMR spectrum of N-[4-(3-picoline-methyl)benzoyl] butyrolactam chloride, 3-PBBC](image-url)
EIC analysis showed the presence of one peak at mass = 295.14, which corresponds to 3-PBBC, with a retention time of 1.284 min, as shown in Figure 28. The mass spectrum is shown in Figure 29 and the m/z value 295.14 was calculated and assigned to 3-PBBC [M-Cl]^+. The product appears relatively pure.

Figure 28. Extracted Ion Chromatogram of N-[4-(3-picoline-methyl)benzoyl] butyrolactam chloride, 3-PBBC

Figure 29. Positive-ion ESI LC-MS spectrum of N-[4-(3-picoline-methyl)benzoyl] butyrolactam chloride, 3-PBBC
4.2 Scouring and Bleaching Performance

Desized, non-scoured woven cotton fabric was treated with the following combined scour/bleach process: Each bleach activator was applied separately to 10 g of desized fabric under the condition of 5 g/L bleach activator, 6 g/L 35% H₂O₂, 1 g/L H₂O₂ stabilizer, 1 g/L surfactant, 50 °C, pH 7.5 and bleaching time 30 minutes. The control sample was treated in a bath in the same way except no activator was added. All samples are repeated and the bleaching performance was evaluated using the CIE Whiteness Index formula, and data are summarized in Table 7 and Figure 30.
Table 7. Bleach Performance of Each Activator

<table>
<thead>
<tr>
<th>ACTIVATOR</th>
<th>GREIGE FABRIC</th>
<th>CONTROL</th>
<th>TBCC</th>
<th>PBCC</th>
<th>DOBCC</th>
<th>NABCC</th>
<th>3-PBCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAMPLE 1</td>
<td>10.58</td>
<td>39.23</td>
<td>71.2</td>
<td>66.3</td>
<td>55.3</td>
<td>63.12</td>
<td>70.56</td>
</tr>
<tr>
<td>SAMPLE 2</td>
<td>12.8</td>
<td>41.43</td>
<td>72.88</td>
<td>65.62</td>
<td>56.36</td>
<td>64.3</td>
<td>71.32</td>
</tr>
<tr>
<td>AVERAGE</td>
<td>11.69</td>
<td>40.33</td>
<td>72.04</td>
<td>65.96</td>
<td>55.83</td>
<td>63.71</td>
<td>70.94</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ACTIVATOR</th>
<th>TBBC</th>
<th>PBBC</th>
<th>DOBCC</th>
<th>NABBC</th>
<th>3-PBBC</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAMPLE 1</td>
<td>73.58</td>
<td>62.32</td>
<td>50.25</td>
<td>55.89</td>
<td>70.03</td>
</tr>
<tr>
<td>SAMPLE 2</td>
<td>73.32</td>
<td>65.32</td>
<td>54.43</td>
<td>60.07</td>
<td>72.47</td>
</tr>
<tr>
<td>AVERAGE</td>
<td>73.45</td>
<td>63.77</td>
<td>52.34</td>
<td>57.98</td>
<td>71.25</td>
</tr>
</tbody>
</table>
Figure 30. CIE Whiteness Index values for control sample and fabric treated with current and new cationic bleach activators

Compared with the control sample, all of the cotton samples treated with the bleach activator demonstrated an improvement in low temperature and neutral bleaching. While only the 3-picoline (PBCC and PBBC) activators exhibited similar bleaching performance to the current generation of bleach activator, TBBC, the differences are less than three WI units and are therefore likely imperceptible to most observers. Hence, the performance can be considered equivalent.

Importantly, a statistically designed experiment needs to be completed before conclusions on performance can be produced. Also, the low toxicity of the starting amine may lead to one of the new activators becoming the preferred next generation activators.
4.3 Water Absorbency

The water absorbency of raw fabric and the fabric bleached was shown in Table 8.

<table>
<thead>
<tr>
<th>ACTIVATOR</th>
<th>GREIGE FABRIC</th>
<th>CONTROL</th>
<th>TBCC</th>
<th>PBCC</th>
<th>DOBCC</th>
<th>NABCC</th>
<th>3-PBCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water Absorbency (second)</td>
<td>60+</td>
<td>60+</td>
<td>60+</td>
<td>60+</td>
<td>60+</td>
<td>60+</td>
<td>60+</td>
</tr>
</tbody>
</table>

One of the key factors in scouring and bleaching fabrics is to prepare the fabric for dyeing such that the material has high water absorbency. As Table 8 shows, under the conditions used to bleach the fabric, the absorbency of the samples did not improve compared to the control sample or the greige sample. This is surprising since it has been shown that the TBCC-based sample will establish acceptable water absorbency when applied with peroxide at neutral conditions and temperature of 50 °C. However, in order to achieve this, significant agitation of the fabric is needed during scouring/bleaching, which was not done for the experiments used in the present study. Hence, each of the bleach activators should be applied using agitation consistent with industrial processes. Of the fabrics, the raw and the bleached, have the poor water absorbability.
4.4 Mote Counting

The mote number of each 25 cm$^2$ fabric was counted three times and average mote number of each fabric is shown in Table 9.

<table>
<thead>
<tr>
<th>ACTIVATOR</th>
<th>GREIGE FABRIC</th>
<th>CONTROL</th>
<th>TBCC</th>
<th>PBCC</th>
<th>DOBCC</th>
<th>NABCC</th>
<th>3-PBCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mote number</td>
<td>4</td>
<td>4</td>
<td>1</td>
<td>1</td>
<td>5</td>
<td>4</td>
<td>1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ACTIVATOR</th>
<th>PBBC</th>
<th>DOBCC</th>
<th>NABCC</th>
<th>3-PBCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mote number</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>1</td>
</tr>
</tbody>
</table>

By chance, the greige fabric used for these experiments had relatively low mote count. Hence, while the bleach activators used for the experiments did reduce the number of motes in most cases, mote counting should be repeated using fabric with higher initial mote count. A larger fabric size (1 m$^2$) should also be treated in order to obtain a more accurate representation of the number of motes on a fabric per unit area.
Chapter 5 CONCLUSIONS

The synthesis of eight novel cationic bleach activators have been synthesized, four having a caprolactam leaving group and different cationic groups, and four having the same varying cationic groups but butyrolactam incorporated into the activator.

The cationic groups used were all reported to exhibit relatively less toxicity, according to the six toxicity scale, than the current cationic bleach activators, TBCC and TBBC. These new cationic bleach activators were characterized by NMR and mass spectrometry. While the structures were confirmed, some levels of impurities are possible. In the synthesis step, it was found that only one nitrogen of the 1, 4-diazabicyclo[2.2.2] octane will react with chlorine of the intermediate even though the intermediate was excess.

The bleaching performance of the prototype cationic bleach activators was measured. When 3-picoline was used as the cationic group similar bleaching performance was obtained compared to the current cationic bleach activator TBBC, while rest of new cationic bleach activators exhibited less improvement in low temperature neutral condition Hydrogen peroxide bleaching.

Absorbency of the treated fabric was not improved by the prototype cationic bleach activator, indicating that further research is needed to optimize the bleaching conditions. While
slightly fewer motes were found on the treated fabric compared to the greige fabric and control fabric, initial fabric with larger numbers of motes need to be tested before any conclusions can be drawn as to whether the new bleaching methods improve mote removal.
In this dissertation, a new series of cationic bleach activators was synthesized and characterized. For future work, more in-depth characterization will be needed, including elemental analysis. In addition, a statistically designed experiment to identify the key variables in bleaching performance and predict an optimum method for each new cationic bleach activator should be studied, even though the preliminary bleaching results show that some of the bleach activators do not have prominent improvement in low temperature and neutral condition H₂O₂ bleaching.

The toxicity of all the new bleach activators should be measured. The toxicities of all of the cationic starting compounds used in this dissertation are lower than triethylamine, which is the cationic group used in the current generation of cationic bleach activators, TBBC and TBCC. It is important to determine the toxicity of the final product and compare with the current cationic bleach activator.

In addition, the hydrolytic stability of the new cationic bleach activators should be studied. Although the leaving group in these new cationic bleach activators is not changed and there are some previous researches of the hydrolytic stability, the effect of the cationic group in regard to stability is unknown.
Chapter 7  REFERENCES


35. McDonald R. *Color research & application*, 1997, 22 (6), p. 418-419


