

**SURFACE MODIFICATION AND
CHROMOPHORE ATTACHMENT VIA
IONIC ASSEMBLY AND COVALENT FIXATION**

A Dissertation
Presented to
The Academic Faculty

by

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In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy in the
School of Polymer, Textile and Fiber Engineering

Georgia Institute of Technology
May 2009

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IONIC ASSEMBLY AND COVALENT FIXATION**

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To my son, Carter, for giving me a new focus on life.

ACKNOWLEDGEMENTS

I would like to express my gratitude to my advisors, Dr. Haskell Beckham and Dr. Fred Cook, for the opportunity to be a member of such a great research effort. I am tremendously grateful for their guidance and encouragement throughout my graduate studies. Thanks for never giving up on me!

I would like to thank my committee members, Dr. Anselm Griffin, Dr. Uwe Bunz and Dr. David Collard for their valuable time, constructive criticisms and suggestions. I would also like to extend thanks to my research group members, both past and present, for all of their help and discussions: Dr. Swati Singla, Dr. Kimberlee Thompson, Dr. Deepali Palta, Dr. Sunghyun Nam, Dr. Philip Watson, Craig Simile, Ryan Kincer and Bo Xu. Special thanks go out to former group member, Dr. Marcus Foston, for trudging through this experience with me and showing me that it can be done.

I am also grateful to Dr. Yasuyuki Tezuka of the Tokyo Institute of Technology for pioneering the electrostatic self-assembly and covalent fixation process on which this work is focused.

I would like to thank my parents for always believing in me and pushing me to make the most out of life. Thank you for your love and support. But, most of all, I would like to thank my loving wife, Anna. She is my rock and without her none of this would have been possible.

TABLE OF CONTENTS

DEDICATION.....	iii
ACKNOWLEDGEMENTS.....	iv
LIST OF TABLES.....	ix
LIST OF FIGURES.....	x
LIST OF ABBREVIATIONS	xvi
SUMMARY.....	xviii
CHAPTER 1 INTRODUCTION.....	1
1.1 Motivations and Objectives.....	1
1.2 Current Finishing and Dyeing Technologies.....	4
1.2.1 Traditional Fiber Finishes.....	4
1.2.2 Traditional Dyes and Coloration Methods.....	6
1.2.3 Reducing the Salt Demand in Reactive Dyeing.....	16
1.3 Materials and Methods.....	25
1.3.1 Background on Ionic Self-Assembly and Covalent Fixation.....	25
1.3.2 Cyclic Ammonium Reactions.....	26
1.3.3 Cyclic Tertiary Amine Candidates for Formation of the Cyclic Ammonium Salt.....	33
1.3.4 Suitable Substrates.....	34
1.3.5 Formation of the Quaternary Ammonium Group.....	37
1.4 Scope of the Dissertation.....	38
1.5 References.....	39
CHAPTER 2 SYNTHESIS, CHARACTERIZATION AND APPLICATION OF A REACTIVE-IONIC ALKYL (WAX) FINISH.....	43
2.1 Introduction.....	43
2.1.1 Material Selection.....	44
2.1.2 Synthetic Methods.....	46

2.2	Experimental Section.....	48
2.2.1	Materials.....	48
2.2.2	Instrumentation.....	49
2.2.3	Synthesis of Octadecyl Triflate (reactive-ionic precursor).....	49
2.2.4	Synthesis and Purification of Reactive-Ionic Alkyl Finish.....	50
2.2.5	Application of Reactive-Ionic Alkyl Finish to a Glass Slide.....	51
2.2.6	Evaluation of Surface-Modified Glass Slide.....	52
2.3	Results and Discussion.....	52
2.3.1	Synthesis and Characterization of Octadecyl Triflate (reactive-ionic precursor).....	52
2.3.2	Synthesis and Characterization of Reactive-Ionic Alkyl (Wax) Finish.....	54
2.3.3	Application of Reactive-Ionic Alkyl (Wax) Finish to a Glass Slide.....	57
2.3.4	Evaluation of the Surface-Modified Glass Slide.....	59
2.4	Conclusions.....	62
2.5	References.....	62
CHAPTER 3	SYNTHESIS, CHARACTERIZATION AND APPLICATION OF A REACTIVE-IONIC FLUORINATED FINISH.....	64
3.1	Introduction.....	64
3.1.1	Material Selection.....	66
3.1.2	Synthetic Methods.....	68
3.2	Experimental Section.....	70
3.2.1	Materials.....	70
3.2.2	Instrumentation.....	71
3.2.3	Synthesis of 1H,1H,2H,2H-Perfluoro-1-Octyl Triflate (Precursor).....	71
3.2.4	Synthesis and Purification of Reactive-Ionic Fluorinated Finish.....	72
3.2.5	Application of Reactive-Ionic Fluorinated Finish to Cationic-Dyeable Nylon Carpet.....	73
3.2.6	Evaluation of Surface-Modified Carpet Sample.....	73

3.3	Results and Discussion.....	74
3.3.1	Synthesis and Characterization of 1H,1H,2H,2H-Perfluoro-1-Octyl Triflate (Precursor).....	74
3.3.2	Synthesis and Characterization of Reactive-Ionic Fluorinated Finish.....	76
3.3.3	Application of Reactive-Ionic Fluorinated Finish to Cationic-Dyeable Nylon Carpet.....	79
3.3.4	Evaluation of the RI-F Surface-Modified Carpet.....	81
3.4	Conclusions.....	85
3.5	References.....	86
CHAPTER 4	SYNTHESIS, CHARACTERIZATION AND APPLICATION OF A REACTIVE-IONIC ALKYL (WAX) FINISH.....	88
4.1	Introduction.....	88
4.1.1	Material Selection.....	89
4.1.2	Synthetic Methods.....	92
4.2	Experimental Section.....	93
4.2.1	Materials.....	93
4.2.2	Instrumentation.....	94
4.2.3	Purification of Disperse Red.....	94
4.2.4	Synthesis of Disperse Red 1 tosylate.....	95
4.2.5	Synthesis of Reactive-Ionic Chromophore (RI-Dye).....	95
4.2.6	Application of RI-Dye to Cellophane Film.....	96
4.2.7	Application of RI-Dye to Nylon 6,6 Film.....	97
4.2.8	Application of RI-Dye to Cationic- and Regular-Dyeable Nylon Carpet Yarns.....	97
4.2.9	Application of RI-Dye to Multi-Fiber Test Fabric.....	98
4.2.10	Application of RI-Dye to Nylon Fabric.....	98
4.2.11	Application of RI-Dye to Bleached Cotton Fabric.....	99
4.2.12	Application of RI-Dye to Silk Fabric.....	99
4.3	Results and Discussion.....	100
4.3.1	Purification of C.I. Disperse Red 1.....	100
4.3.2	Synthesis and Characterization of Disperse Red 1 tosylate (precursor).....	101

4.3.3	Synthesis and Characterization of Reactive-Ionic Chromophore (RI-Dye).....	104
4.3.4	Application of RI-Dye to Cellophane Film.....	110
4.3.5	Application of RI-Dye to Nylon 6,6 Film.....	111
4.3.6	Application of RI-Dye to Cationic- and Regular-Dyeable Nylon Carpet Yarns.....	114
4.3.7	Application of RI-Dye to Multi-Fiber Test Fabric.....	115
4.3.8	Application of RI-Dye to Nylon Fabric.....	117
4.3.9	Application of RI-Dye to Bleached Cotton Fabric.....	121
4.3.10	Application of RI-Dye to Silk Fabric.....	124
4.4	Conclusions.....	126
4.5	References.....	127
CHAPTER 5	CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK.....	128
5.1	Conclusions.....	128
5.2	Recommendations for Future Work.....	132
5.3	References.....	135
APPENDIX.....		136
VITA.....		139

LIST OF TABLES

Table 1.1 –	Summary of physical characteristics of fiber reactive vinylsulfone dyes developed by Hinks and coworkers. (py+ = pyridinium chloride).....	21
Table 1.2 –	Possible nucleophiles for incorporation into a reactive-ionic molecule and the temperatures at which the ring- opening reaction takes place after formation of the corresponding quaternary ammonium group.....	33
Table 2.1 –	Measured contact angles of 1 μ L drops of deionized water on glass slides which had been (A) precleaned with no treatment, (B) treated with reactive-ionic wax finish then covalently fixed at 80 $^{\circ}$ C and (C) treated with reactive-ionic wax with no covalent fixation.	59
Table 4.1 –	Chemical composition of dyebaths used to dye bleached cotton print cloth using reactive-ionic dye.....	99
Table 4.2 –	Reflectance measurement data (<i>L</i> , <i>a</i> , <i>b</i> , <i>dE</i> values) of nylon fabrics dyed with RI-dye.	120
Table 4.3 –	Reflectance measurement data (<i>L</i> , <i>a</i> , <i>b</i> , <i>dE</i> values) of bleached cotton fabrics dyed with 1% owf RI-dye both with and without salt added during the dyeing processes.	123
Table 4.4 –	K/S values of RI-dyed samples along with chemical composition of dyebaths used to dye bleached cotton print cloth.	123

LIST OF FIGURES

Figure 1.1 –	Diagram showing the principles of ionic assembly followed by covalent fixation at elevated temperatures.	3
Figure 1.2 –	General structure of the perfluoroethylmethacrylate copolymers used by Goetz et al. as a repellent finish for cotton where R_f is a perfluorinated chain of length 4-20 carbon atoms.	6
Figure 1.3 –	The chemical structure of C.I. Acid Yellow 69—an azo-type acid dye with two sodium sulfonate groups.	8
Figure 1.4 –	The chemical structure of C.I. Basic Blue 22—an anthraquinone-type basic dye with one quaternary ammonium group.	9
Figure 1.5 –	(TOP) A monochlorotriazinyl-type reactive dye reacting with a cellulosate ion to form a covalent bond between the dye and the substrate. (BOTTOM) The same dye molecule undergoing dye hydrolysis due to reaction with hydroxide.	11
Figure 1.6 –	(TOP) A VS-type reactive dye reacting with a cellulosate ion to form a covalent bond between the dye and the substrate. (BOTTOM) The same dye molecule undergoing dye hydrolysis due to reaction with hydroxide.	12
Figure 1.7 –	General scheme used to synthesize triazinyl halide type reactive dyes. Diazotization of an aromatic amine is followed by diazonium coupling to form the water soluble chromophore. Cyanuric chloride is then reacted across the bridge to form the reactive dye.	13
Figure 1.8 –	Representation of a diffuse electrical double layer consisting of a negatively charged substrate in water. Counterions reside at the interface and decrease in concentration as distance from surface, r , increases. Whereas, co-ion concentration increases with r	14
Figure 1.9 –	An example of a heterobifunctional reactive dye containing a permanent quaternary ammonium group where $z = \text{halogen}$	19
Figure 1.10 –	General vinylsulfone dye structure developed by Hinks and coworkers where R_1 and R_2 are $\text{SO}_3(-)$, H or pyridinium(+) groups.....	20

Figure 1.11 – Chemical structure of GTMAC—the cationic reactant used for fiber modification.	22
Figure 1.12 – Chemical structure of NMA-HTCC—the water-soluble chitosan derivative used to surface modify cotton.	23
Figure 1.13 – Synthetic scheme used by Tezuka and coworkers for electrostatic self-assembly followed by covalent fixation of poly(THF) with an <i>N</i> -methylpyrrolidinium salt end group and sodium benzoate.	26
Figure 1.14 – A typical Hofmann elimination reaction involving the decomposition of a cyclic ammonium salt in the presence of base at elevated temperatures.	27
Figure 1.15 – A ring-opening nucleophilic substitution reaction between a cyclic ammonium ion and a nucleophile.	28
Figure 1.16 – An exocyclic nucleophilic substitution reaction involving the demethylation of an <i>N,N</i> -dimethyl-substituted cyclic ammonium salt.	29
Figure 1.17 – Possible reactions of cyclic quaternary ammonium species in the presence of methoxide ion include demethylation, ring-opening and Hofmann elimination.	29
Figure 1.18 – Distribution of products from reactions of <i>N</i> -methyl- <i>N</i> -phenylpiperidinium (left) and <i>N</i> -methyl- <i>N</i> -phenylpyrrolidinium (right) with methoxide ion at temperatures of 90 °C and 130 °C.....	32
Figure 1.19 – Potential substrates for reactive-ionic surface modification including the chain structure and a surface schematic of each detailing the necessary functional groups.	36
Figure 2.1 – The chemical structure of 1-octadecanol (stearyl alcohol)—the starting material for the reactive-ionic wax finish.	44
Figure 2.2 – The target chemical structure of the reactive-ionic wax finish— <i>N</i> -octadecyl- <i>N</i> -phenyl pyrrolidinium triflate salt.	45
Figure 2.3 – General reaction scheme for the triflation of stearyl alcohol using triflic anhydride.	53
Figure 2.4 – ¹ H NMR spectrum of the reactive-ionic alkyl finish precursor, stearyl triflate, with proton labels to identify location in the structure. (CDCl ₃ solvent peak @ 7.24 ppm not shown)	54

Figure 2.5 –	General reaction scheme for the formation of the cyclic ammonium group by reaction of stearyl triflate with N-phenyl pyrrolidine.	55
Figure 2.6 –	¹ H NMR spectrum of the reactive-ionic alkyl finish with proton labels to identify corresponding location in the structure.	56
Figure 2.7 –	Diagram depicting the ionic assembly of the reactive-ionic alkyl (wax) finish on a surface containing deprotonated hydroxyl groups and subsequent covalent fixation at 80 °C.	58
Figure 2.8 –	Video capture of a 1 μL drop of deionized water sitting on the surface of an untreated, clean glass slide.	60
Figure 2.9 –	Video capture of a 1 μL drop of deionized water sitting on the surface of a glass slide which had been treated with the reactive-ionic wax finish and covalently fixed at 80 °C.	61
Figure 2.10 –	Video capture of a 1 μL drop of deionized water sitting on the surface of a glass slide which had been treated with the reactive-ionic wax finish but rinsed with THF before the covalent fixation step.....	61
Figure 3.1 –	The chemical structure of 1H,1H,2H,2H-perfluoro-1-octanol—the starting material for the reactive-ionic fluorinated finish.	67
Figure 3.2 –	The target chemical structure of the reactive-ionic fluoro-finish—N-phenyl-N-(1H,1H,2H,2H-perfluoro-1-octyl)-pyrrolidinium triflate salt.....	68
Figure 3.3 –	General reaction scheme for the triflation of 1H,1H,2H,2H-perfluoro-1-octanol using triflic anhydride.	74
Figure 3.4 –	¹ H NMR spectrum of the reactive-ionic fluorinated finish precursor, 1H,1H,2H,2H-perfluoro-1-octyl triflate, with proton labels to identify location in the structure.	76
Figure 3.5 –	General reaction scheme for the formation of the cyclic ammonium group by reaction of 1H,1H,2H,2H-perfluoro-1-octyl triflate with N-phenyl pyrrolidine.	77
Figure 3.6 –	¹ H NMR spectrum of the reactive-ionic fluorinated finish with proton labels to identify corresponding location in the structure.....	78

Figure 3.7 –	Diagram depicting the ionic assembly of the reactive-ionic fluorinated finish on a nylon surface containing carboxylate groups and subsequent covalent fixation at 80 °C.	80
Figure 3.8 –	Photo of a drop of DI water containing Direct Red 80 dye sitting atop a cationic-dyeable nylon carpet sample which had been surface-modified with the reactive-ionic fluorinated finish. (Elapsed time = 1 minute)	82
Figure 3.9 –	Close-up of the same drop sitting on the RI-F surface-modified carpet sample. (Elapsed time = 60 minutes)	82
Figure 3.10 –	Photo of a drop of DI water containing Direct Red 80 dye which has penetrated the tufts of an untreated cationic-dyeable carpet sample. (Elapsed time = < 1 minute)	83
Figure 3.11 –	Cationic-dyeable carpet samples subjected to stain-resistance test. Immersed 1 cm from bottom of sample which relates is about 2 rows of tufts. (LEFT): Unmodified sample (RIGHT): RI-F-modified sample.	84
Figure 4.1 –	The chemical structure of C.I. Disperse Red 1 dye—the starting material for the reactive-ionic chromophore.	90
Figure 4.2 –	The target chemical structure of the reactive ionic dye—a quinuclidinium tosylate salt of C.I. Disperse Red 1.	91
Figure 4.3 –	¹ H NMR spectrum of purified C.I. Disperse Red 1 dye with peaks labeled to corresponding protons in chemical structure.	101
Figure 4.4 –	General reaction scheme for the tosylation of Disperse Red 1 using tosyl chloride.	102
Figure 4.5 –	¹ H NMR spectrum of the reactive-ionic dye precursor, DR1-tosylate, with peak labels to identify proton location within chemical structure.....	104
Figure 4.6 –	General reaction scheme for the preparation of the reactive-ionic dye by reaction of DR1-tosylate with quinuclidine.....	105
Figure 4.7 –	¹ H NMR spectrum of the reactive-ionic dye with peak labels to identify proton location within the chemical structure.....	106
Figure 4.8 –	Photos of purified DR1 solids (LEFT), RI-dye solids (CENTER) and RI-dye crystals (RIGHT)	107

Figure 4.9 – Visible light absorbance measurements as a function of wavelength for 50 ppm solutions of Disperse Red 1 and RI-dye in DMSO. The points were measured and the lines were added to aid the eye.	108
Figure 4.10 – (a) Cellophane film dyed by reactive-ionic dye. (b) Cellophane film dyed by reactive-ionic dye after boiling in water and then THF. (c) Cellophane film dyed by DR1. (d) Cellophane film dyed by DR1-OTs.....	111
Figure 4.11 – (LEFT) Nylon 6,6 film dyed by reactive-ionic dye at room temperature. (RIGHT) Nylon 6,6 film dyed by reactive-ionic dye at 60 °C. After dyeing, the samples were extracted for 15 minutes in THF at the boil.	112
Figure 4.12 – Diagram depicting the ionic assembly of the reactive-ionic dye on nylon containing carboxylate groups and subsequent fixation at 120 °C.	113
Figure 4.13 – (TOP) Regular-dyeable nylon carpet yarn dyed with RI-dye at 25 °C. (BOTTOM) Cationic-dyeable nylon carpet yarn dyed with RI-dye at 25 °C.	115
Figure 4.14 – A multi-fiber fabric test strip dyed with 1% owf RI-Dye at 80 °C for 30 minutes.	116
Figure 4.15 – Schematic of the dyeing method developed for application of RI-dye to nylon fabric.	118
Figure 4.16 – Nylon fabrics dyed with 1% owf RI-Dye at 80 °C for 45 minutes followed by covalent fixation at 120 °C. (LEFT): No post-dye extraction (RIGHT): 15 minutes extraction in THF.	119
Figure 4.17 – Schematic of the dyeing method developed for application of RI-dye to cotton fabric.	121
Figure 4.18 – Bleached cotton fabrics dyed with 1% owf RI-Dye at 80 °C for 45 minutes. (LEFT): No NaCl added to dyebath. (RIGHT): 40 g/L NaCl added to dyebath.	122
Figure 4.19 – Silk fabrics dyed with RI-Dye at 80 °C for 30 minutes. (LEFT): 1% owf (RIGHT): 2% owf	125
Figure 5.1 – The chemical structure of polyamideamine-epichlorohydrin (PAE) resin.	133

Figure 5.2 – A schematic of the proposed use of reactive-ionic technology in LBL assembly of cationic PAE and anionic PAA polymers followed by covalent crosslinking at elevated temperatures. 134

LIST OF ABBREVIATIONS

AATCC	American Association of Textile Chemists and Colorists
AM-PS	Aminomethylated-polystyrene
BP	Boiling point
CCl ₄	Carbon tetrachloride
CDCl ₃	Deuterated chloroform
CH ₂ Cl ₂	Dichloromethane or methylene chloride
CH ₃ Cl	Chloroform
CH ₃ CN	Acetonitrile
CI	Colour Index
CIE	International Commission on Illumination
(CF ₃ SO ₂) ₂ O	Triflic anhydride
DI	Deionized
DMSO	Dimethyl sulfoxide
DMSO- <i>d</i> ₆	Deuterated DMSO
DR1	Disperse Red 1
DR1-OTs	Disperse Red 1 tosylate
DSC	Differential scanning calorimetry
EPA	Environmental Protection Agency
Et ₃ N	Triethylamine
GTMAC	Glycidyltrimethylammonium chloride
HCl	Hydrochloric acid
HTCC	<i>N</i> -[(2-hydroxy-3-trimethylammonium)-propyl]-chitosan chloride
K/S	Color strength value (unitless)
λ_{\max}	Wavelength of maximum absorbance
LBL	Layer-by-layer
LS	Low salt
MCT	Monochlorotriazinyl
MFT	Monofluorotriazinyl

MgSO ₄	Magnesium sulfate
NaCl	Sodium chloride
NaHCO ₃	Sodium bicarbonate
NaOH	Sodium hydroxide
NMA	<i>N</i> -methylolacrylamide
NMA-HTTC	<i>O</i> -acrylamidomethyl-HTCC
NMR	Nuclear magnetic resonance
NPP	<i>N</i> -phenyl pyrrolidine
PAA	Polyacrylic acid
PAE	Polyamideamine-epichlorohydrin
PFBS	Perfluorobutane sulfonate
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonate
ppm	Parts per million
PVP	Poly(4-vinyl pyridine)
R _f	Perfluorinated alkyl
RI	Reactive-ionic
RI-F	RI-fluorinated
SES	Sulfatoethylsulfone
S _N 2	Bimolecular nucleophilic substitution
THF	Tetrahydrofuran
TsCl	Tosyl chloride
VCA	Video contact angle
VS	Vinyl sulfone
XPS	X-ray photoelectron spectroscopy

SUMMARY

Ionic assembly followed by covalent fixation offers a novel method for the application of finishes and colorants to fibrous substrates. This reactive-ionic chemistry utilizes electrostatic interactions to assemble species with complementary charges and offers a subsequent permanent link between them by conversion of the ionic bond to a covalent bond via a ring-opening reaction at elevated temperatures. This dissertation focuses on the high-yield, permanent application of reactive-ionic processing chemicals to negatively charged substrates. A reactive-ionic alkyl (wax) finish, a reactive-ionic fluorinated finish and a reactive-ionic chromophore were prepared and applied to suitable substrates.

The first part of the dissertation focuses on the synthesis and characterization of a reactive-ionic wax finish. A moderately strained, cyclic ammonium group was incorporated into the structure of stearyl alcohol via triflation of the alcohol and subsequent reaction with *N*-phenyl pyrrolidine. The RI wax was successfully applied to a glass slide to increase the hydrophobic nature of the surface. Contact angle measurements indicated an increase in average contact angle of approximately 45°, from 18.7° for an untreated slide to 63.0° after application of the permanent RI finish.

The second part of the dissertation focuses on the synthesis and characterization of a reactive-ionic fluorinated finish to be used as an anti-wetting and anti-stain agent. The reactive-ionic group was incorporated into the structure of 1H,1H,2H,2H-perfluoro-1-octanol via triflation of the fluorous alcohol and subsequent reaction with *N*-phenyl pyrrolidine. The RI-F finish was successfully applied to a cationic-dyeable nylon carpet

sample. The permanent treatment rendered the modified sample completely non-wetting and stain resistant.

The third part of the dissertation focuses on the synthesis and characterization of a reactive-ionic chromophore to be used as a colorant for polyamide and cellulosic fibers. The reactive-ionic group was incorporated into the structure of C.I. Disperse Red 1 via tosylation of the alcohol group and subsequent reaction with quinuclidine. The wavelength of maximum absorbance for the RI dye shifted 40 nm towards the blue region compared to the starting material, thus the dye is more of an orange color. The RI chromophore was used to dye nylon, bleached cotton and silk fabrics. Studies of the dyeing behavior indicated that fixation of the dye to fiber was indeed permanent as little dye was lost during multiple post-fixation, solvent extractions. The addition of electrolyte to aid the exhaustion of RI dye onto cotton was not necessary, unlike the case with traditional reactive dyes on cotton.

CHAPTER 1

INTRODUCTION

1.1 MOTIVATIONS AND OBJECTIVES

Since its inception, the textile industry has relied on the use of chemicals and colorants to alter the appearance and functionality of products. In particular, dyes and finishes have been used to give textiles specific visual, mechanical and functional properties. Chemical finishes impart to a wide variety of fibers anti-static, hydrophilic/hydrophobic, soil-repellent, etc., properties. However, modern concerns involving the environment have placed increasing pressure on the industry to respond with more eco-friendly practices. The wet processing of textiles inevitably creates a large volume of plant effluent in the form of wastewater (and the chemicals contained therein) due to high liquor ratios and the dramatic excess of chemicals required during application. A straightforward approach to help reduce the amount of chemicals in the plant effluent is to simply use smaller amounts of chemicals in the application step. This requires a high level of exhaustion from the bath to the substrate thus reducing the amount of chemicals in the effluent.

Traditionally, textile finishes are non-ionic molecules which rely on concentration gradients and secondary forces to promote exhaustion, adsorption, binding and fastness. This binding is fairly weak due to lack of a covalent bond between chemical and substrate, resulting in most finishes being non-permanent in nature. In addition, there are

weak thermodynamic driving forces for exhaustion; therefore, adequate adsorption requires large excesses of finish during application, increasing the cost and waste associated with these types of processes. Incorporating a reactive-ionic entity into the structure of a traditional finish should help to solve these problems by utilizing ionic interactions to assemble the finish on the substrate in high yield. The ionic bond is then converted to a permanent covalent bond at elevated temperatures.

Current reactive dyes utilize a chromophore which is attached to a reactive group that will covalently bond to an appropriate chemical moiety on the polymer backbone of the substrate. Although this does provide for a covalent bond between dye molecule and substrate, the main disadvantage of the dyes is that a high percentage (15 – 40%) is destroyed under the basic fixation conditions. To increase the exhaustion of reactive dyes to substrates, large amounts of salt (usually NaCl) are added. The salt helps mask the inherent negative charge on the substrate and aid in adsorption of dye to substrate. Traditional dyeing recipes require 50-80 g/L of salt, and unless considerable amounts of time, energy and money are spent to remove the salt through water treatment, the salt will be released in the plant effluent. Globally, 2.7 billion pounds of salt are discharged from reactive dyebaths annually,¹ all of which is detrimental to plant and animal life.

Various efforts have been employed in an attempt to reduce the salt demand in reactive dyeing. Low-salt reactive dyes have been produced which incorporate multiple reactive groups onto the dye structure. Often these molecules are large and flat with multiple hydrogen bonding sites which helps to increase affinity for cotton, thereby lowering the liquor ratio (mass based ratio of water to goods) and as a result reducing the salt requirement. Other methods which aim to reduce the overall salt requirement for

reactive dyes include cellulose surface modification and the use of chemical auxiliaries. However, these approaches have not been commercialized due to the high added cost associated with each.

Ionic self-assembly followed by covalent fixation utilizes electrostatic interactions to assemble species with complementary charges. This creates a driving force for chemicals to leave the processing bath and adsorb on the substrate surface. Once assembled, the ionic bond is then converted to a covalent bond at elevated temperatures. A general diagram describing the process is shown in Figure 1.1. The pathway affords a process with high-yield adsorption of the chemical entity onto the substrate surface and a subsequent permanent link between the two.

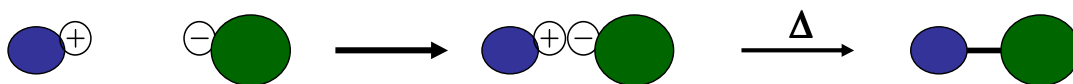


Figure 1.1 – Diagram showing the principles of ionic assembly followed by covalent fixation at elevated temperatures.

The reactive-ionic method described in this dissertation should allow a drastic reduction in the amount of salt needed for dye exhaustion due to complementary electrostatic interactions between dye and substrate. Reactive-ionic dye fastness on fibers should be similar to that of traditional reactive dyes, as both attach to the substrate via covalent bonds.

The aim of the present work is the application of novel functional groups to commercially useful chemicals for enhanced surface modification and material properties, and also to gain insight into how reactive-ionic chemistry can be used to

benefit the field of material science. Reactive-ionic molecules, when properly applied to a substrate, can exhibit functionalizing properties to the bulk material with satisfactory loadings, coverage and permanency. The main objectives of this research are fourfold:

- i. Synthesis of a reactive-ionic alkyl (wax) finish to serve as a proof of concept/model compound for further reactions and subsequent application of the finish to a suitable substrate.
- ii. Synthesis of a reactive-ionic fluoro-finish and subsequent application to nylon polyamide to serve as a non-wetting, anti-stain finish.
- iii. Synthesis of a reactive-ionic dye and subsequent application to various substrates like nylon, cotton and silk in several physical forms including films, fibers, woven fabrics and tufted carpet samples.
- iv. Physical testing of the substrates which have been surface-modified or dyed by the various reactive-ionic molecules.

1.2 CURRENT FINISHING AND DYEING TECHNOLOGIES

1.2.1 Traditional Fiber Finishes

Chemical finishes are used to modify the surface of a substrate thus giving surface properties different from that of the bulk material. Traditional fiber finishes are usually applied in an exhaustive or pad method in which there is little or no driving force for adsorption of the finish on the fiber surface. As a result large excesses of materials are required. Furthermore, most textile finishes are temporary because there is not a covalent bond between fiber and the target chemical. In the case of ionic finishes, the finish is usually applied in an exhaustive method and the finish is fixed to the fiber via an ionic bond. When the finish is non-ionic, secondary forces are used to attach the finish to the

fiber. These forces are generally weak and the finish can be removed without much effort. Recently, reactive finishes have been developed which, upon application, form a covalent bond between finish and substrate, thereby making them permanent.

Reactive Finishes

One requirement for the use of reactive finishes on fibers is that the substrate surface must contain appropriate reactive groups. Cotton, for instance, has a multitude of hydroxyl and carboxylic acid groups along the cellulose chain which can serve as reactive sites for the finish. Nylon polyamide contains both carboxylic acid as well as amine groups located at polymer chain ends which can react with appropriate moieties of a finish molecule. Polypropylene is an example of a fiber which bears no potentially reactive sites because it is composed completely of hydrocarbon groups.

Goetz and coworkers from the Clariant Corporation have developed a series of perfluoroalkylethylmethacrylate copolymers to be used as oil-, water-, and soil-repellent finishes on cotton.² The general structure of the components used in the reactive finish is shown in Figure 1.2. The double bonds of the finish molecules are reactive towards the deprotonated hydroxyl groups of cotton in an alkaline environment at elevated temperatures. The reaction indeed yields a permanent finish as a covalent bond is formed between the perfluorinated molecules and the cotton surface. R_f chain lengths of 4-20 perfluorinated carbon atoms are used in the study. While the application of finish is permanent, levelness and surface coverage remain issues of concern because the loading of the surface is purely statistical and no reshuffling or migration of active species is allowed prior to fixation.

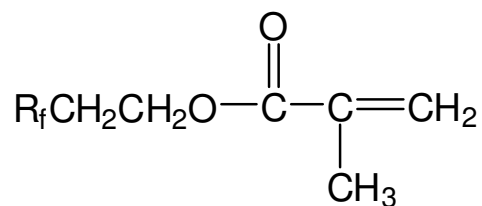


Figure 1.2 – General structure of the perfluoroethylmethacrylate copolymers used by Goetz et al. as a repellent finish for cotton where R_f is a perfluorinated chain of length 4-20 carbon atoms.

Michielsen and coworkers have developed a novel method for the finishing of nylon films and fibers via a reactive process.³⁻⁵ First, polyacrylic acid (PAA) was adsorbed on the surface of the nylon fiber to serve as a scaffold for subsequent reactions. An amide-forming, condensation catalyst was then used to graft the adsorbed PAA chains to nylon by reaction of the amine groups of nylon with the carboxylic acid groups of PAA. A perfluorinated amine was then adsorbed onto the grafted PAA chains followed by covalent fixation with the aforementioned catalyst. By using a PAA chain, the number of active binding sites (carboxylic acid groups) for reactions with the perfluorinated amine was amplified thus enhancing the overall surface coverage of the fluororous material on nylon. The method has been shown to be effective on nylon films, carpet and woven structures.

1.2.2 Traditional Dyes and Coloration Methods

The majority of dyes used for the coloration of textiles share similarities in both chemical structure and physical characteristics. All textile dyes contain a chromophore which consists of a conjugated aromatic pi system. The two most prevalent types of

chromophores used in textile dyes include anthraquinone-based structures and azo compounds. Most anthraquinone-based dyes are blue while azo-type dyes are generally a red hue. By varying the chemical constituents attached to the aromatic structure the light absorbing characteristics of the molecule are changed, thus providing the ability to tune the visible color. Another similarity among most textile dyes is the incorporation of solubilizing groups to impart water solubility since most dyeings take place in an aqueous medium. The most common anionic water solubilizing group used in textile dye synthesis is the sulfonic acid group or more specifically the conjugate base of this acid—sodium sulfonate. The group has excellent water solubilizing properties and has little effect on the color of a dye.⁶ Cationic groups also impart water solubility to chromophores and generally consist of a cationized nitrogenous salt.

Textile dyes are typically grouped into classes by application method. For instance, acid dyes are generally applied to substrates which have ionizable groups which can be protonated with acid. The negatively charged dye molecule then forms an ionic bond with the positively charged substrate and becomes “fixed”. Other textile dye classes include cationic (basic) dyes, direct dyes and reactive dyes to name a few. The dyeing of generic nylon polyamide is usually performed with acid dyes, while the fiber variant cationic-dyeable nylon is colored with basic dyes. The dyeing of cotton and other cellulose is dominated by the use of vat, direct and reactive dyes.

The following discussion will focus on three distinct dye application classes—acid, basic and reactive. Acid and basic dyes both utilize ionic interactions for adsorption of dye on the substrate. These dyes are fixed to the fiber by the formation of ionic bonds.

Reactive dyes form a covalent bond between the dye and substrate; however, there is little inherent driving force for surface adsorption.

Acid Dyes

Acid dyes are generally used for the dyeing of polyamide fibers like nylon, wool and silk. Numerous sodium sulfonate groups incorporated into the structure of acid dyes work both to impart water solubility to the molecule as well as to serve as binding sites for the ionic dyeing process. In the case of nylon, the end groups are composed of either carboxylic acid or primary amine groups. In an acidic medium the primary amines are protonated to form cationic centers. Acid dye molecules bond to the protonated chain ends through ionic interactions. Figure 1.3 shows the structure of C.I. Acid Yellow 69.

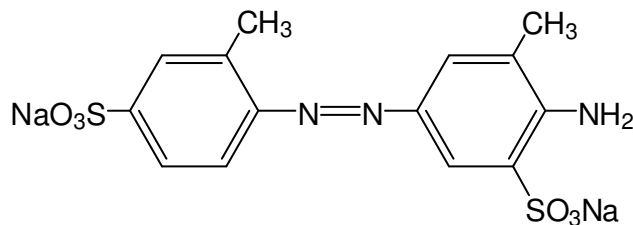


Figure 1.3 – The chemical structure of C.I. Acid Yellow 69— an azo-type acid dye with two sodium sulfonate groups.

Generally, acid dyes exhibit high levels of affinity for polyamides and as a result have excellent dyebath exhaustion properties. Good dyebath exhaustion reduces waste in the form of unused dye. This is a benefit not only for limiting material cost but also for wastewater and effluent cleanup and control. One drawback to acid dyeing is limited

wash fastness. Since the bond holding the dye to the substrate is an ionic bond, an ion-exchange reaction can readily take place in the presence of water or steam, effectively removing the dye from the substrate. Dye removal can occur with every washing or steaming, causing the overall color of the material to gradually fade. This problem can be remedied with the use of fixing agents or metal complexes.

Basic Dyes

Basic dyes are cationic, water-soluble dyes containing one or more positively charged groups which will interact with negatively-charged species on the substrate. Basic dyes are most commonly used on acrylics but find some use on wool and silk. Basic dyes are also effective on cationic-dyeable derivatives of nylon and polyester. As a class, basic dyes are prone to poor light fastness thought to be a result of the net positive charge on the molecule. Basic dyes are also susceptible to poor wash fastness for the same reasons described for the acid dye class and as a result fixing agents are often required after dyeing. An example of a basic dye is shown in Figure 1.4.

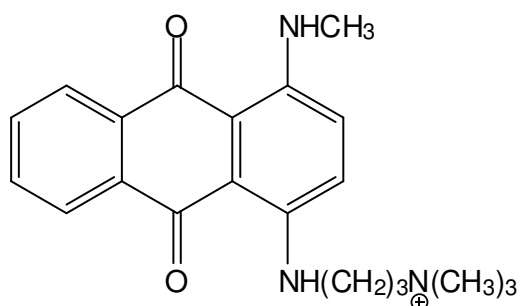


Figure 1.4 – The chemical structure of C.I. Basic Blue 22—an anthraquinone-type basic dye with one quaternary ammonium group.

Reactive Dyes

Reactive dyes are generally used to dye cotton and other cellulose fibers. Reactive dyes contain a fiber reactive group attached to a water-soluble chromophore. Two major types of reactive dyes exist with the difference being the type of reactive group employed—triazinyl halide or vinyl sulfone. Triazinyl halide reactive dyes contain a triazinyl ring with halide substituents which are easily attacked in an S_N2 nucleophilic displacement reaction by a cellulose anion, forming a permanent ether linkage between the substrate and the triazinyl ring. Another possible reaction between a triazinyl halide type reactive dye in a basic medium involves displacement of the halide by a hydroxide ion which renders the dye unreactive. This is referred to as reactive dye hydrolysis or “kill off” and can be responsible for up to a 50% loss in dye which can be covalently fixed to the substrate. Reactions involving a triazinyl halide type reactive dye are shown in Figure 1.5.

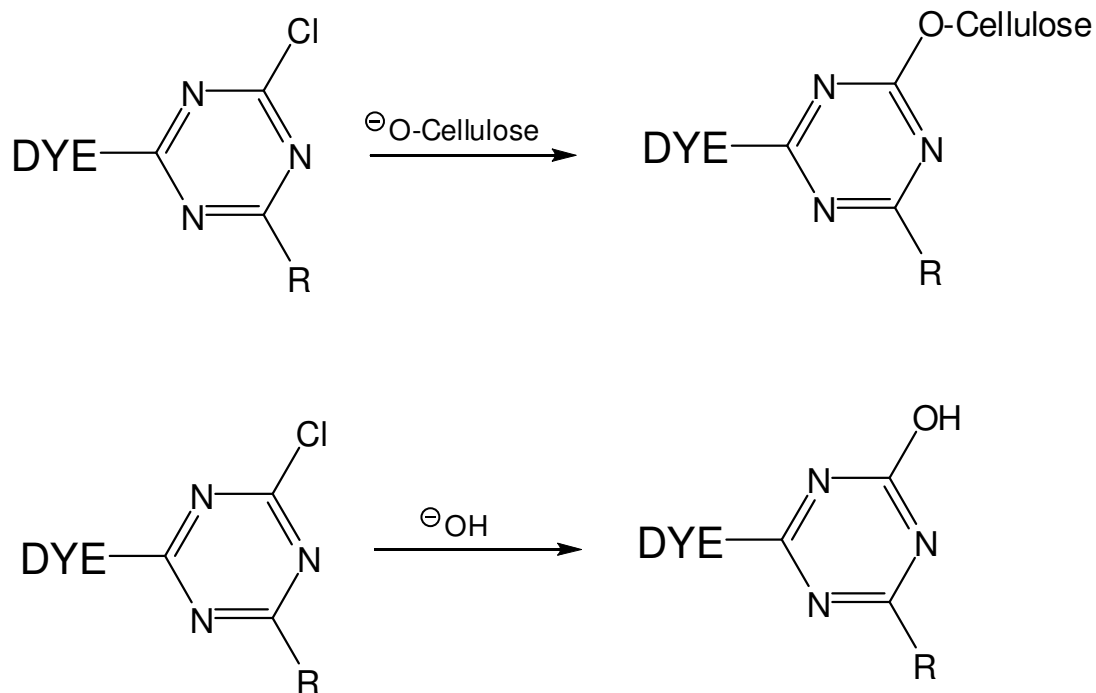


Figure 1.5 – (TOP) A monochlorotriazinyl-type reactive dye reacting with a cellulose ion to form a covalent bond between the dye and the substrate. (BOTTOM) The same dye molecule undergoing dye hydrolysis due to reaction with hydroxide.

Vinyl sulfone (VS) reactive dyes contain a VS group attached to the water-soluble chromophore. The VS group is reactive towards strong nucleophiles at elevated temperatures. VS reactive dyes form a covalent bond between the dye molecule and the fiber via a Michael addition process. As is the case with triazinyl halide type reactive dyes, VS reactive dyes are also susceptible to dye hydrolysis in the presence of strong base. Reactions involving a VS reactive dye are shown in Figure 1.6.

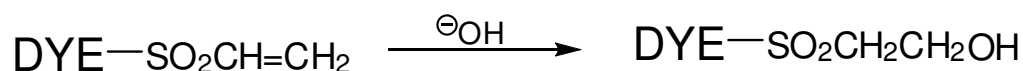
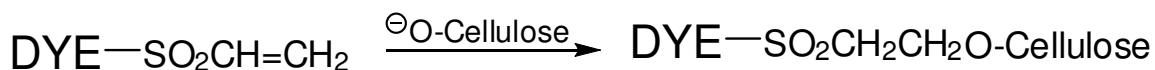


Figure 1.6 – (TOP) A VS-type reactive dye reacting with a cellulosate ion to form a covalent bond between the dye and the substrate. (BOTTOM) The same dye molecule undergoing dye hydrolysis due to reaction with hydroxide.

Traditional reactive dye syntheses involve diazonium coupling of two water-soluble precursors thus forming a water-soluble chromophore. Depending on the desired type of reactive functionality—triazinyl halide⁷ or vinyl sulfone⁸—the appropriate reactive group is added via the aromatic amine of the water-soluble chromophore. The resulting secondary amine is termed the “bridge” between the reactive group and the “dye base” or soluble chromophore. In the case of triazinyl chloride reactive dyes, cyanuric chloride is reacted across the bridge as seen in Figure 1.7.

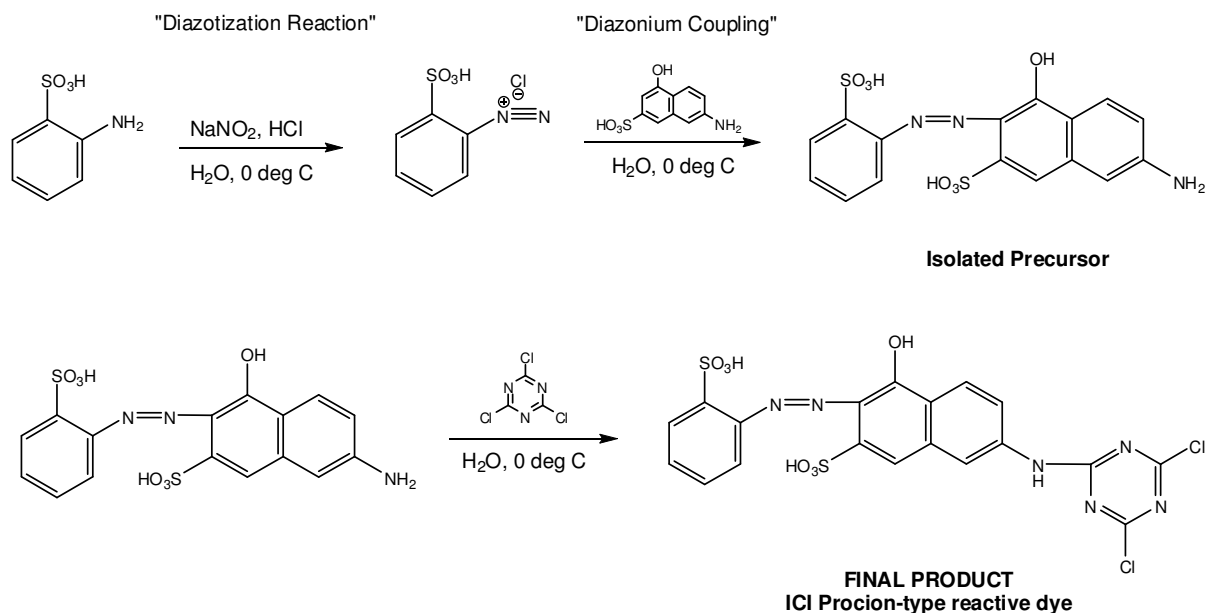


Figure 1.7 – General scheme used to synthesize triazinyl halide type reactive dyes. Diazotization of an aromatic amine is followed by diazonium coupling to form the water soluble chromophore. Cyanuric chloride is then reacted across the bridge to form the reactive dye.

The major advantage of using reactive dyes to dye cotton and other cellulose is excellent fastness properties. The dye molecule is permanently attached to the fiber because a covalent bond is formed between two. Thus, little to no dye is removed during subsequent washings and the color does fade. However, there are several drawbacks to using reactive dyes on cotton. The first is active dye loss in the bath through hydrolysis as previously discussed. The other disadvantage of reactive dyes is the high level of salt (usually NaCl) necessary for proper adsorption of reactive dyes on negatively charged substrates. This problem arises due to the formation of an electrical double layer.

When a substrate containing charged groups is immersed in water the surface acquires an electrical potential. Even if the solid possesses no intrinsic charge, the

adsorption of ions from the water will result in generation of an electrical potential. The presence of such a potential will result in oppositely charged ions (counterions) being attracted to the surface while similarly charged ions (co-ions) will be repelled.⁹ As a result, there will be an imbalance of ions near the charged surface with counterions dominating the space. The effect of the electrical potential falls as distance from the surface increases, causing the concentration of counterions to decrease and the number of co-ions to increase. This led to development of the diffuse electrical double layer model in which the layer of adsorbed ions and the diffuse volume are together known as the diffuse double layer. A diagram depicting the diffuse double layer is shown in Figure 1.8.

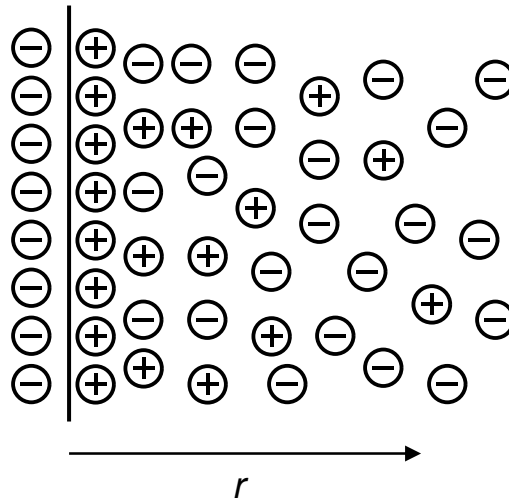


Figure 1.8 – Representation of a diffuse electrical double layer consisting of a negatively charged substrate in water. Counterions reside at the interface and decrease in concentration as distance from surface, r , increases. Whereas, co-ion concentration increases with r .

The region near the surface can be divided into two parts. The first being a compact, immobile, surface layer containing a limited number of counterions per unit area known as the Stern layer. Adjacent to the Stern layer is the diffuse layer where ions are mobile within the medium. The thickness of the double layer is proportional to the electrical potential. Reducing the thickness of the double layer will serve to reduce the repulsive influence that the negatively charged surface has on the negatively charged dye molecule. Increasing the ionic strength of the solution acts to compress the double layer, and thus large amounts of electrolyte are added to reactive dyebaths to increase adsorption of dye on fiber.¹⁰

If there is relative motion between a charged surface and bulk solution a plane of slip will exist in the diffuse layer, so that there is a separation of ions, and thus of charge, which in turn gives rise to a potential difference. The plane of slip is usually known as the shear plane and the potential at that plane as the electrokinetic or zeta potential.⁹ This zeta potential must be overcome in order to adsorb negatively-charged dyes on to the surface and this can be achieved by increasing the ionic strength of the solution. Thus an increase in ionic strength of the dyebath has two related benefits for dye adsorption: a narrow diffuse layer and a lower zeta potential. Both of these offer a greatly reduced electrical resistance to dye adsorption.

Therefore in an effort to reduce the electrical effects of the negatively charged cotton surface in solution, copious amounts of electrolyte are added to aid adsorption of sulfonated reactive dyes. For darker shades, upwards of 100 g/L of NaCl are required with traditional reactive dyes in order to achieve satisfactory dyeings. Since the salt is discharged with the spent dyebath, it has become a concern from an economic viewpoint

as waste and also due to environmental concerns over increased salinity in our rivers and lakes.

1.2.3 Reducing the Salt Demand in Reactive Dyeing

The development of low-salt or no-salt dyeing processes for the reactive dyeing of cellulose has been approached by numerous research groups in an effort to reduce waste and minimize the environmental impact of these systems. Methods undertaken to tackle this problem include but are not limited to: development of new dyes, modification of cellulose fiber, use of dyeing auxiliaries and emerging dyeing technologies. However, the synthesis of new dyes and cellulose fiber surface modification represent the majority of work in this area.

Low-Salt Reactive Dyes

The Cibacron LS line of dyes and the Sumifix Supra dyes represent commercially-available lower salt alternatives to traditional reactive dyes. Both types are heterobifunctional meaning that each dye molecule contains two different types of reactive groups. In the case of the Sumifix Supra range, the reactive groups are monochlorotriazinyl (MCT) and sulfatoethylsulfone (SES), a vinyl sulfone precursor, moieties which bond to the fiber in alkaline medium by means of nucleophilic substitution and Michael addition, respectively. Cibacron LS dyes require only about 20 g/L of salt to achieve dyeing results comparable with traditional reactive dyes at 60-100 g/L. The main features of the Cibacron LS series include: high dye affinity and fixation, a stable fiber-dye bond, less dye to be removed from fabric after dyeing, a faster rinsing step with less water used and less dye effluent.¹¹ The higher cost of these dyes is said to

be offset by the cost savings from reduced salt in the system, less dye required for dyeing and a reduction in effluent clean up.

In an effort to decrease the salt requirements for reactive dyeing, Mokhtari et al. synthesized and evaluated a series of triazo, monochloro-*s*-triazinyl reactive dyes for cotton.¹² The group suggested that since tinctorial strength plays a role in overall color yield then increasing the tinctorial strength of a given dye should reduce the salt required to achieve a satisfactory color yield. Three new triazo, MCT dyes were synthesized with identical structures except for varying substituents attached to one of the phenyl rings. In addition to these moieties, each dye contained at least four sodium sulfonate groups to aid solubility. The color yield of cotton fabrics dyed with these dyes initially increased with salt concentration reaching a plateau between the concentrations of 15 g/L and 40 g/L of sodium chloride. Although this is a reduction in total salt when compared to traditional reactive dyeing processes in the 60-100 g/L concentration range, the work was not a total success. All three dyes gave a dull violet shade when applied to cotton. In addition, the dyes exhibited very poor build-up properties making it difficult to achieve a deep shade. This was attributed to their limited aqueous solubility and the presence of only one reactive group in each molecule.

Mousa and coworkers synthesized several polyfunctional bis(monochlorotriazine/sulphatoethylsulphone) reactive dyes in an attempt to reduce the salt required to achieve satisfactory dyeing of silk fiber.¹³ Dyes containing MCT and SES moieties give higher fixation efficiency than the corresponding dyes containing only one type of reactive group. As mentioned previously, the Sumifix Supra range of reactive dyes is an example of commercially-available, bi-functional, low-salt reactive

dyes containing one MCT group and one SES group. Mousa developed a dye which contained two SES groups and one MCT reactive group and applied it to silk fiber in an alkaline medium. The dye exhibited higher exhaustion and fixation when compared to a traditional bifunctional reactive dye, even at salt loadings as low as 20 g/L. Wash fastness tests showed that the twin SES/MCT polyfunctional dye exhibited similar wash fastness to that of the corresponding SES/MCT bifunctional dye.

Pedemonte et al. developed a series of three different dyes which when applied as a mixture showed good exhaustion on bleached cotton fabric with salt levels as low as 5 g/L for light to medium shades.¹⁴ This is a dramatic reduction in salt needed when compared to traditional reactive dyes. The three dye types that comprised the mixture in the study included a monochloro-difluoro-pyrimidine type reactive dye, a MCT reactive dye containing a quaternary ammonium group and a direct dye containing no reactive groups. Although, the mixture of dyes resulted in a dramatic drop in the amount of salt required it is quite difficult to prepare three different types of dyes with identical shades. Fastness was also a problem due to the use of a direct dye in the dye mixtures.

It is apparent that one could overcome the problem of low exhaustion of traditional reactive dyes in the absence of copious amounts of salt by changing the overall charge of the dye molecule from negative to positive. A positively charged molecule should have more affinity for a negatively charged surface than would a negatively charged molecule. Generally, sodium sulfonate groups are incorporated into the dye structure to impart water solubility to the highly hydrophobic chromophore. The addition of cationic groups, specifically quaternary ammoniums, to a dye molecule will help to give the dye more affinity for the negatively charged substrate. These cationic groups

could be added to a traditional reactive dye structure containing sulfonate groups, which might pose complexation issues, or they could replace the sulfonate groups and be present not only to increase dye affinity but also to serve as solubilizing groups.

Phillips et al. incorporated permanent quaternary ammonium groups into the structure of heterobifunctional reactive dyes which contained at least one monofluorotriazine (MFT) or MCT group and one SES reactive group.¹⁵ Phillips and coworkers synthesized numerous different dyes with quaternary ammonium cationic groups. A general structure of one of the dyes developed in this study is shown in Figure 1.9.

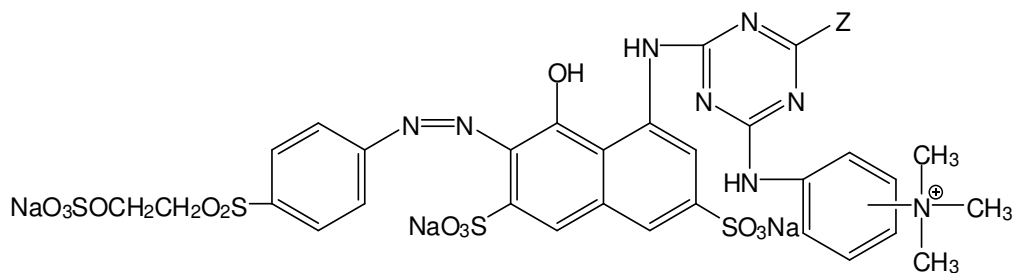


Figure 1.9 – An example of a heterobifunctional reactive dye containing a permanent quaternary ammonium group where z = halogen.

All dyes in the series possessed a single quaternary ammonium group in addition to several sulfonate groups. The overall charge of the dye molecule in Figure 1.9 was indeed still negative as the structure contained one cationic group and multiple anionic groups. Introduction of the cationic group should have acted to increase affinity of the dye for the fiber but the overall negative charge still acted to repel the dye molecule from the anionic cellulosic surface. No study of the dyeing characteristics or dyeing performance was conducted on this series of LS reactive dyes.

Hinks et al. developed and studied a series of vinylsulfone (VS) reactive dyes which carried overall net molecular charges ranging from -2 to +2. The study demonstrates “zero salt” fiber reactive dyes for cellulosic fibers via incorporation of cationic groups in lieu of anionic sulfonate water solubilizing ions, thereby producing a net positive charge on the dye.¹⁶ Cationically charged dyes, in combination with van der Waals forces and hydrogen bonding, should exhibit inherent substantivity towards negatively charged substrates, thus potentially eliminating the requirement for high salt levels. The dyes synthesized in the study all were of the general form seen in Figure 1.10.

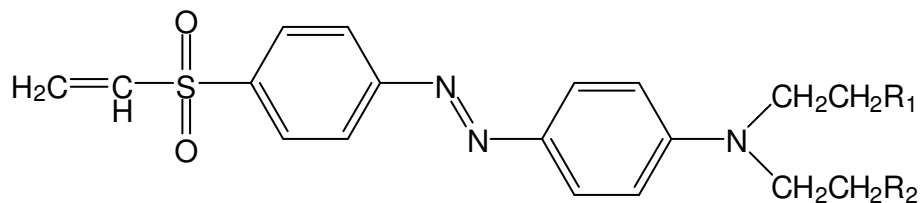


Figure 1.10 – General vinylsulfone dye structure developed by Hinks and coworkers where R_1 and R_2 are $\text{SO}_3(-)$, H or pyridinium(+) groups.¹⁶

The physical characteristics of the VS-based dyes in the study are summarized in Table 1.1. Dyeings were performed with all five dyes according to a standard exhaustive dyeing procedure for reactive dyes on cellulose with the exclusion of any electrolyte. The dyes termed VS4 and VS5 had a net positive charge. As a result, both of these dyes exhibited a higher affinity for the cotton substrate when compared to dyes VS1-VS3 by measurement of exhaustion of each dye onto the fiber, due to the attractive effect of the cationic sites on the dye molecules towards the anionic substrate. The study showed that the positively charged VS dyes had a high substantivity for cotton although the

washfastness and lightfastness properties for these dyes were somewhat marginal when compared to traditional reactive dyes. The former was attributed to a reduced fixation yield during the fixation step, and the latter was a result of the permanent cationic pyridinium group(s) in the structure.

Table 1.1 – Summary of physical characteristics of fiber reactive vinylsulfone dyes developed by Hinks and coworkers. (py+ = pyridinium chloride)¹⁶

Dye	R₁	R₂	Charge	Mol. Wt.
VS1	SO ₃ K	SO ₃ K	-2	559
VS2	OSO ₃ Na	H	-1	460
VS3	H	H	0	343
VS4	py+	H	1	456
VS5	py+	py+	2	569

Cotton Fiber Surface Modification

In addition to the development of new dyes to help reduce the salt demand in reactive dyeing, many researchers have focused on modifying the surface of cotton and other cellulose fibers to increase the affinity of traditional reactive dyes carrying multiple anionic solubilizing groups. Most of the studies involve the “cationization” of cotton which aims to incorporate positive charges along the cellulose chain. These cationic groups then serve as binding sites for the negatively charged dye molecules to interact before fixation takes place.

Hauser and Tabba investigated the reaction of glycidyltrimethylammonium chloride (GTMAC) with cellulose in an alkaline medium.¹⁷ The epoxy group of the cationic molecules will react with alcohol groups along the cellulose chain in an alkaline medium to form ethers, thus covalently bonding a quaternary ammonium group to the cellulose chain. The structure of the cationic reactant is shown in Figure 1.11. The cationized cotton was then dyed using traditional anionic dyes such as reactive, direct and acid. It was shown that the cationized cotton can be dyed without the use of electrolytes to give excellent color yields with a variety of reactive dyes. The color fastness of these dyeings was equal or superior to the color fastness of the same dyes on untreated cotton. The dyeing procedures for cationic cotton were shown to be shorter, use less water and chemical auxiliaries, and require less energy than the corresponding procedures for untreated cotton. One drawback to the technology is hydrolysis of the epoxy-based reactant under alkaline conditions. Depending on the reaction conditions, 20-50% of the epoxy groups initially formed will hydrolyze to inactive material.

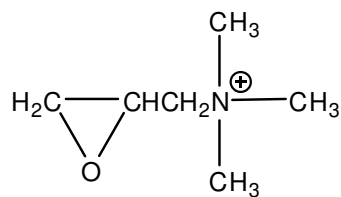


Figure 1.11 – Chemical structure of GTMAC—the cationic reactant used for fiber modification.

Another example of the direct cationization of cotton involves the application of a chitosan derivative which carries a positive charge. Lim and Hudson first developed the water-soluble chitosan derivative to impart antimicrobial properties to cotton substrates.¹⁸

A water-soluble chitosan derivative, *N*-[(2-hydroxy-3-trimethylammonium)-propyl]-chitosan chloride (HTCC) was prepared by reaction of chitosan with glycidyltrimethylammonium chloride (GTMAC). The HTCC was further modified by reacting with *N*-methylolacrylamide (NMA) to prepare the fiber reactive chitosan derivative, *O*-acrylamidomethyl-HTCC (NMA-HTCC). The structure of NMA-HTCC is shown in Figure 1.12.

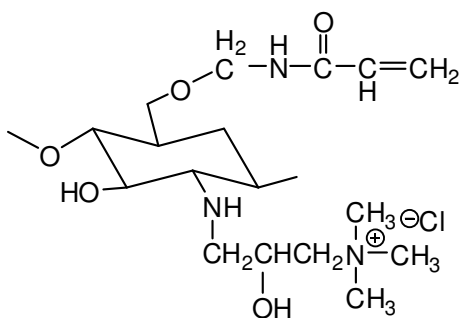


Figure 1.12 – Chemical structure of NMA-HTCC—the water-soluble chitosan derivative used to surface modify cotton.

In a separate study, Lim and Hudson applied NMA-HTCC to cotton fabric in an alkaline medium.¹⁹ Coupling takes place between the deprotonated hydroxyl group on the cellulose chain and the double bond of NMA-HTCC through Michael addition creating a durable cationic finish. The modified cotton was then dyed using direct dyes and traditional reactive dyes, CI Reactive Blue 21 and CI Reactive Orange 107, without the addition of electrolyte. Cotton treated with 1% NMA-HTCC produced a higher color yield without salt than did untreated cotton dyed in the presence of a large quantity of salt. In comparison with untreated cotton, the wash fastness of treated cotton after dyeing was superior for all dyes examined. On the other hand, the light fastness of dyes on

cotton treated with NMA-HTCC was inferior to that on untreated cotton. Synthesis of the chitosan derivative is quite costly, mainly due to the cost of the chitosan starting material, and therefore NMA-HTCC does not lend itself well to current industrial applications.

In another attempt to reduce the salt requirement for reactive dyeing by modifying the cotton surface, Blackburn and Burkinshaw developed a copolymer pre-treatment agent which contained not only cationic centers as previously discussed but also strong nucleophiles.²⁰ It is evident that the cationic entities were present to aid in the adsorption of anionic reactive dyes on the cotton surface while the nucleophilic groups allowed reactive dyeing to take place without the use of alkali. The exact structure of the pre-treatment agent was not disclosed; however, it was said to contain a plurality of cationic centers in the form of quaternary ammonium groups. The pre-treatment agent also contained free primary amino groups which acted as nucleophiles. The copolymer had a molecular weight in the range of 10,000 to 30,000 g/mol. Generally, the degree of cationicity was at least one cationic group per 500 g/mol with a maximum of one per 150 g/mol. The copolymer also contained at least one nucleophilic center per five monomer residues with an upper limit of one nucleophilic center per monomer residue. Since fixation took place at neutral pH, hydrolysis of the reactive dye was minimized due to the absence of alkali in the dyebath. Minimal washing was required, as the majority of the dye was fixed to the fiber. Dyeings conducted using the pre-treatment method had higher color strength values than the standard dyeings and wash fastness was similar to that for reactive dyes on untreated cotton.

1.3 MATERIALS AND METHODS

1.3.1 Background on Ionic Self-Assembly and Covalent Fixation

The current work is based on the principles of reactive-ionic chemistry. The idea of using electrostatic self-assembly followed by covalent fixation at elevated temperatures as macromolecular ion-coupling reactions was first proposed by Tezuka and Goethals more than twenty years ago.^{21, 22} Early work focused on creating macromolecular building blocks for the synthesis of precisely designed block and graft copolymers consisting of inherently incompatible segments.^{23, 24} The work was based on the synthesis of uniform-size poly(tetrahydrofuran) [poly(THF)] molecules having uniquely reactive end groups, namely moderately-strained cyclic onium salt groups. The cyclic onium salt groups were introduced either at a single chain end or at both chain ends through the reaction of the corresponding cyclic amines with the oxonium salt end group of a living poly(THF) chain. In the reaction scheme, the cyclic onium salt end group initially accompanied a counteranion with weak nucleophilic reactivity, such as triflate anion, which could be replaced during an ion-exchange reaction. Controlled conversion of the ionic bond to the covalent bond was achieved by an appropriate choice of cyclic onium salt group, a counteranion, and a reaction temperature to result in the selective formation of the coupling products in high yields. Covalent fixation was achieved via the ring-opening, ester-forming reaction caused by nucleophilic attack of a carboxylate anion on the cyclic onium salt group of the poly(THF) chain, either at ambient conditions or at an elevated temperature. A schematic of this reaction pathway is shown in Figure 1.13.

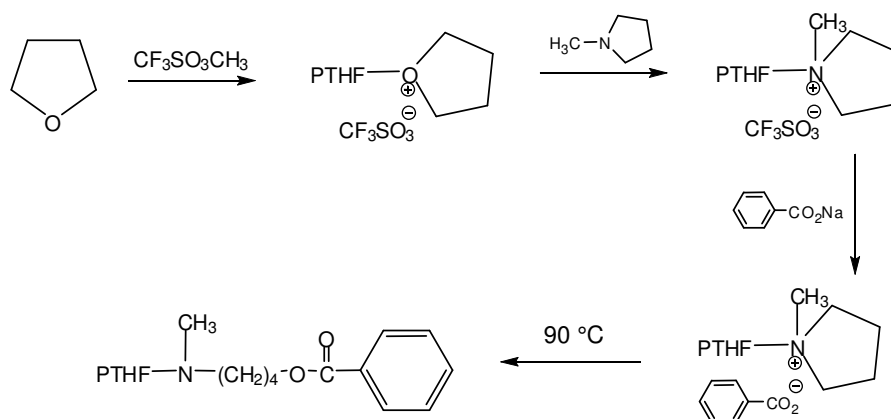


Figure 1.13 – Synthetic scheme used by Tezuka and coworkers for electrostatic self-assembly followed by covalent fixation of poly(THF) with an *N*-methylpyrrolidinium salt end group and sodium benzoate.²⁴

The same methodology was then used to couple poly(THF)²³⁻²⁸, poly(dimethylsiloxane)²⁹, polystyrene³⁰, and poly(oxyethylene)³¹ chains using several types of onium salt groups to a variety of mono-, di- and multi-functional carboxylates. Tezuka and coworkers have used this same pathway to explore the design of unusual polymer topologies and novel molecular architectures including: rings (cycles)³⁰⁻³⁴; star polymers³⁵⁻³⁸; catenanes³⁵⁻³⁸; and polyrotaxanes³⁹.

1.3.2 Cyclic Ammonium Reactions

Since the majority of reactive-ionic molecules are composed of cyclic ammonium ions or salts it is important to understand the different reactions these molecules can undergo. The scope of the reactions covered here will be limited to those involving exposure of the cyclic ammonium salt to a nucleophile, as is the case in the reactive-ionic

process. Gibbs and Marvel studied the conversion of cyclic ammonium salts through a ring-opening process to linear polymers more than seventy years ago.⁴⁰ In the 1940s, Kharasch and Fuchs investigated the conversion of quaternary pyrrolidinium salts to open-chain diamines upon reaction with a base.⁴¹ However, it is well known that ammonium ions are quite susceptible to Hofmann elimination in the presence of a strong base at elevated temperatures. The olefin-forming decomposition reaction involves β -elimination of a quaternary ammonium salt to an olefin, an alcohol and an amine. In the case of cyclic ammonium salts the products of Hofmann elimination include an unsaturated amine and an alcohol. An example of a cyclic ammonium molecule undergoing Hofmann elimination is shown in Figure 1.14. In a reactive-ionic system, Hofmann elimination is an undesirable side reaction because it denies coupling of the molecular ions.

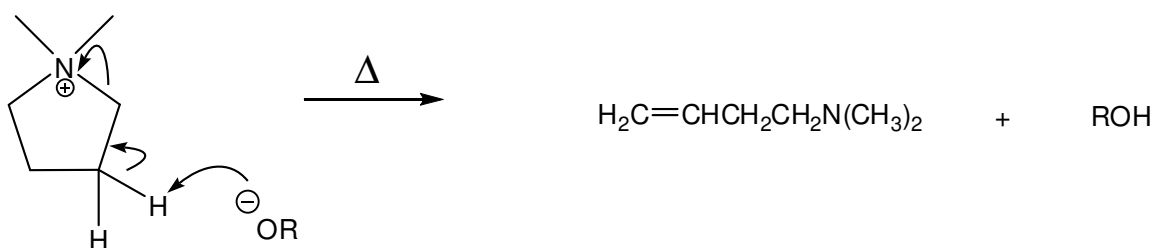


Figure 1.14 – A typical Hofmann elimination reaction involving the decomposition of a cyclic ammonium salt in the presence of base at elevated temperatures.

As previously mentioned, Hofmann elimination is not the only possible reaction between a cyclic quaternary ammonium salt and a nucleophile. Cope et al. showed that elimination is generally accompanied by nucleophilic substitution at the nitrogen-bonded saturated carbon.⁴² The reaction is a bimolecular process involving attack of the

nucleophile on an α ring carbon and an endocyclic C-N bond breaking which results in ring opening. An example of this endocyclic substitution reaction is shown in Figure 1.15.

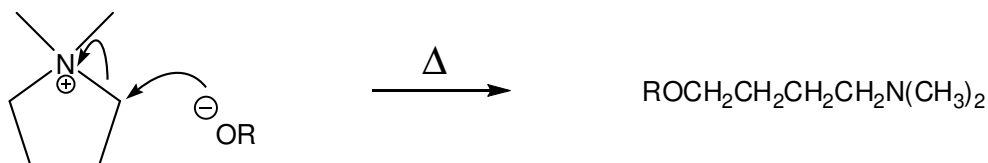


Figure 1.15 – A ring-opening nucleophilic substitution reaction between a cyclic ammonium ion and a nucleophile.

In addition to Hofmann elimination and the ring-opening nucleophilic substitution reaction a third possibility exists. An exocyclic demethylation reaction can also occur on *N,N*-dimethyl-substituted cyclic ammonium salts.⁴³ In the case that the removed group is not a methyl group, for example a phenyl group in a phenyl substituted ammonium ion, the reaction is termed substituent removal. However, for the purposes of this discussion, demethylation will be used regardless of the type of group removed. The reaction products include a cyclic amine and a substituted methyl ether. There is no ring-opening via this route and it is not beneficial to the reactive-ionic process because no coupling takes place. An example of this reaction is shown in Figure 1.16.

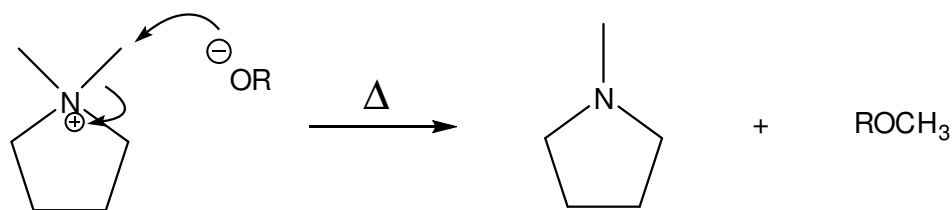


Figure 1.16 – An exocyclic nucleophilic substitution reaction involving the demethylation of an *N,N*-dimethyl-substituted cyclic ammonium salt.

In all there are three possible reactions that can take place between a cyclic ammonium salt and a nucleophile: (A) demethylation, (B) ring-opening nucleophilic substitution and (C) Hofmann elimination. Of these three processes, only process B provides a coupling route between the cyclic ammonium salt and the nucleophile. For this reason, the ring-opening nucleophilic substitution reaction is the desired reaction for a reactive-ionic system. An overview of the three processes is shown in Figure 1.17.

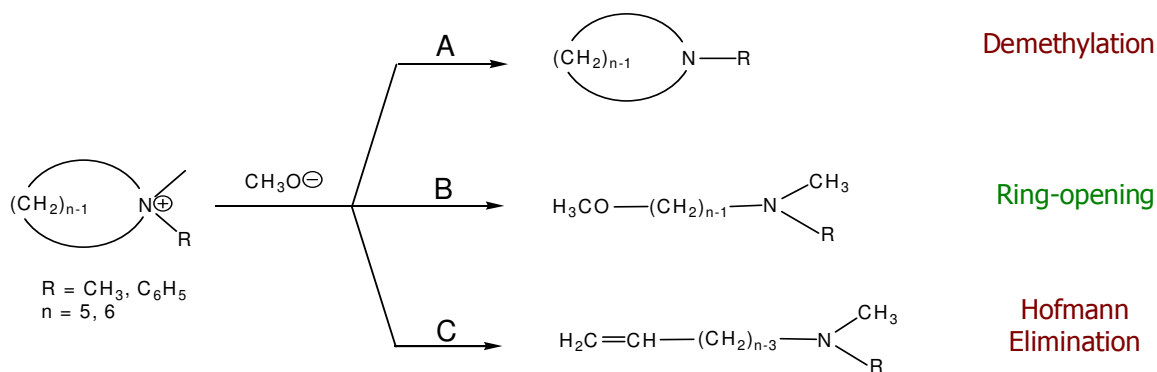


Figure 1.17 – Possible reactions of cyclic quaternary ammonium species in the presence of methoxide ion include demethylation, ring-opening and Hofmann elimination.

The distribution of products from the reaction of a cyclic ammonium salt with a nucleophile is dependant upon many factors. Illuminati and Lillocci studied the effect of ring size on the reaction rates and product distribution for the reaction of *N,N*-dimethyl cyclic ammonium ions with sodium methoxide in methanol. The early work showed that 5-membered rings are much more likely to react via a ring-opening mechanism compared to 6-membered rings which predominantly underwent demethylation.⁴³ The 5-membered cyclic ammonium reaction resulted in nearly 83% of reaction B, ring-opening substitution, whereas the 6-membered ring followed reaction A, demethylation, at 86% yield. This results was primarily attributed to relief of ring strain within the molecule. However, this is not the only consideration for differing reaction rates and product distribution. In later work, the researchers studied ring sizes varying from 5-16 atoms.⁴⁴ Larger rings over six atoms showed little correlation between ring strain and a propensity towards the ring-opening reaction, suggesting that molecular geometry also plays a role in determining the product distribution. For example, the 5-membered ring was more reactive in the ring-opening substitution reaction and less reactive in the ring-opening elimination reaction than expected from ring strain effects.

In a separate study, Cospito et al. found that adding methyl groups to the α,α' -carbons of the ring the product distribution favored the ring-opening elimination reaction.⁴⁵ The researchers also noted that cyclic ammonium 4-membered rings reacted quantitatively according to the ring-opening substitution reaction. The activation energy was so low for this reaction that it proceeded at ambient temperatures, attributed to the very high ring strain of 4-membered rings, 27.4 kcal/mol, compared to 5-membered rings which are considered moderately strained and have only 7.3 kcal/mol of ring strain.⁴⁶

Similar work concluded that once again ring strain relief is not the only driving force for ring-opening substitution of small rings containing 3-5 atoms. Di Vona et al. proposed that the ring-opening substitution reaction is aided by an “extra” driving force arising from a particular stereochemical situation in the transition state of the S_N2 reaction in the small rings which should make the approach of the nucleophile to the reaction center easier when the ring size is less than or equal to five.⁴⁷

Cerichelli and Luchetti studied the reactivity of *N*-methyl-*N*-phenylpyrrolidinium iodide and *N*-methyl-*N*-phenylpiperidinium iodide with sodium methoxide in methanol.⁴⁸ With these starting compounds, regardless of the reaction path followed, the product is an aniline derivative in which there is a mesomeric effect between the nitrogen lone pair and the aromatic ring. This conjugation influences the reaction rate and product distribution. The product of the *N*-methyl-*N*-phenylpiperidinium ion reaction showed negligible elimination and a preference (85% yield) for the ring-opening substitution reaction. The 6-membered piperidinium salt also showed negligible elimination, but the reaction followed demethylation (98% yield) due to a lack of ring strain. Figure 1.18 shows the product distribution for the reactions of *N*-methyl-*N*-phenylpyrrolidinium iodide and *N*-methyl-*N*-phenylpiperidinium iodide with sodium methoxide in methanol.

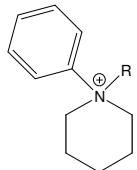
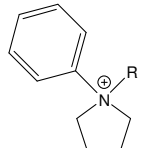
		% reaction				% reaction	
		90 °C	130 °C			90 °C	130 °C
	97	93	Demethylation	15	20		
	2	4	Ring-opening	85	80		
	1	3	Hofmann Elimination	0	0		
							

Figure 1.18 – Distribution of products from reactions of *N*-methyl-*N*-phenylpiperidinium (left) and *N*-methyl-*N*-phenylpyrrolidinium (right) with methoxide ion at temperatures of 90 °C and 130 °C.

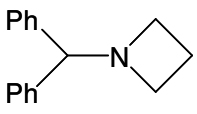
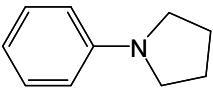
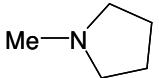

Oike and coworkers studied the ring-opening reaction of a 5-membered cyclic ammonium salt group at the end of a poly(THF) chain and the influence the counterion had on the reaction. The ring-opening reactivity was governed by the electronic characteristics of the substituent on the aromatic ring of the benzoate counterion. Electron donating groups tend to enhance the ring-opening reaction while electron withdrawing groups on the aromatic counterion hinder the reaction.⁴⁹

Another cyclic quaternary ammonium moiety that undergoes a ring-opening substitution reaction when exposed to a nucleophile at elevated temperatures is the 6-membered, bicyclic quinuclidinium ion. Lu et al. utilized this route in a zwitterionic polymerization of 1-[(4-carboxyphenyl)methyl]quinuclidinium hydroxide salt.⁵⁰ Polymerization proceeded as the terminal carboxylate from one molecule assembled with the quinuclidinium from a separate salt molecule and a ring-opening substitution reaction occurred at elevated temperatures. Number average molecular weights varying from 4000 to 17000 g/mol were achieved.

1.3.3 Cyclic Tertiary Amine Candidates for Formation of the Cyclic Ammonium Salt

From the discussion of possible reactions of cyclic ammonium compounds with nucleophiles it is evident that in order to promote the ring-opening substitution reaction the ring should possess a significant amount of ring strain. The 4-membered (azetidinium) and 5-membered (pyrrolidinium) rings are inherently strained and highly reactive towards the ring-opening substitution reaction. The bicyclic, 6-membered (quinuclidinium) ring also reacts with a preference towards the desired ring-opening route. Table 1.2 contains a list of commercially-available nucleophiles for incorporation into a reactive-ionic molecule. All of the structures in Table 1.2 are conducive to the ring-opening substitution reaction. Also included is the approximate temperature at which covalent fixation occurs. The temperature data were experimentally determined by Tezuka and Oike.³⁸

Table 1.2 – Possible nucleophiles for incorporation into a reactive-ionic molecule and the temperatures at which the ring-opening reaction takes place after formation of the corresponding quaternary ammonium group.

Structure	Name	Covalent conversion @
	1-(diphenylmethyl)-azetidine	~ 25 °C
	N-phenylpyrrolidine	~ 60 °C
	N-methylpyrrolidine	~ 90 °C
	quinuclidine	~ 100 °C

For a reactive-ionic molecule to be suitable for application to a fiber the covalent fixation temperature should be above ambient conditions. This permits the ion exchange reaction and the fixation reaction to be separate processes. The processes being separate allows for the migration and randomization of ionic molecules on the substrate surface which is important for even (“level”) coverage. For this reason, 1-(diphenylmethyl)-azetidinium is not a suitable candidate in this work.

The three remaining molecules all have expected covalent fixation temperatures above ambient conditions. Oike et al. showed, however, that a S_N2 process between the *N*-methyl pyrrolidinium salt group and carboxylate anions existed in which endocyclic demethylation occurred in parallel with the ring-opening substitution reaction.²⁵ As a result the overall covalent fixation yield was diminished. In order to maximize covalent fixation demethylation should be avoided. Demethylation was also prevalent in the reaction of *N*-methyl pyrrolidinium with a stronger nucleophile such as an alkoxide ion.⁴⁸ For these reasons, *N*-phenyl pyrrolidine and quinuclidine were chosen as the cyclic amines to be incorporated into the reactive-ionic structures in this study.

1.3.4 Suitable Substrates

Since the reactive ionic molecules are generally cationic, the substrate to which they are applied must contain anionic groups on the surface for ionic assembly to take place. More specifically, the surface should contain carboxylic acid groups or hydroxyl groups on the surface. These groups can be deprotonated with base in aqueous solution to form carboxylate and alkoxide ions, respectively.

The alkoxide ion is a much stronger nucleophile than the carboxylate, so strong that covalent fixation can take place immediately after formation of the ionic bond between substrate and reactive-ionic molecule, possibly at ambient temperatures. A route such as this fits in the realm of electrostatic assembly followed by covalent fixation, but the two events are not necessarily distinct processes. The carboxylate ion is a soft nucleophile compared to the alkoxide, and the ionic species are thus allowed to assemble during a charge transfer reaction and the ionic bonds remain stable at ambient temperatures. The covalent fixation step is then initiated at elevated temperatures. The same methodology was used by Tezuka and coworkers in an effort to produce molecules with novel architectures. In application to textiles, reshuffling of ionic species across the substrate surface is beneficial in the fact that it allows a method for obtaining even surface coverage of a finish or a level dyeing if using a reactive-ionic dye. If the ring-opening reaction occurs simultaneously with ionic bond formation, no method exists to reorganize surface coverage. The focus of this research will thus be to surface modify substrates containing carboxylic acid groups on the surface. Figure 1.19 details potential substrates for the reactive-ionic approach detailed above.

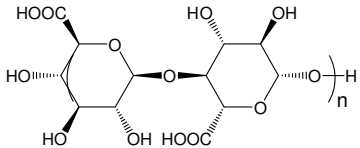
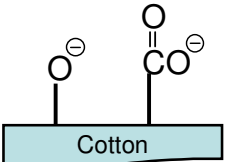
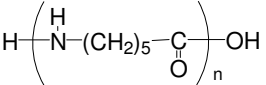
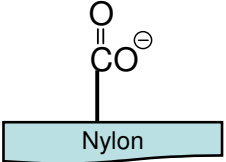
<p style="text-align: center; color: green;">Bleached Cotton</p>		<p>Carboxylate and alkoxide ions are formed under basic conditions at different pH values.</p>	
<p style="text-align: center; color: green;">Nylon</p>		<p>Acid chain ends form carboxylate ions under basic conditions.</p>	

Figure 1.19 – Potential substrates for reactive-ionic surface modification including the chain structure and a surface schematic of each detailing the necessary functional groups.

The most common bulk polymer that fits this requirement is nylon polyamide, which contains both carboxylic acid groups as well as amine groups present as polymer chain ends that are located both on the surface as well as throughout the amorphous regions of the bulk polymer. The carboxylic acid and amine groups are traditional ionic bonding sites for the dyeing of nylon with basic and acid dyes, respectively. Nylon is manufactured with an assortment of relative end group concentrations. Typical nylon contains approximately equal amounts of acid and amine chain ends. Deep-dyeable nylon contains a majority of amine end groups, while cationic-dyeable nylon contains predominantly acid end groups. Since carboxylic acid groups are of interest to this work, cationic-dyeable nylon would allow the highest level of surface modification by the reactive-ionic approach.

Another candidate for modification by the reactive-ionic technique is bleached cotton. Though raw cotton contains mostly a mixture of primary and secondary hydroxyl groups along the cellulose chain, bleached cotton contains a number of carboxyl groups

which were formed during the oxidative bleaching process. The content of these carboxylic acid groups is proportional to the extent to which the cotton has degraded during bleaching. Bleaching with sodium hypochlorite or hydrogen peroxide can increase the number of carboxyl groups in cellulose to upwards of 14 mmol/100g.⁵¹ A mildly alkaline bath (pH of about 8) will allow selective deprotonation of the carboxylic acid groups over deprotonation of the hydroxyl groups. Introducing the bleached cotton to a more alkaline solution (pH > 9) will cause deprotonation of both carboxyl and hydroxyl groups. Bleached cotton in a mildly alkaline bath will thus also serve as a suitable substrate for reactive-ionic surface modification.

1.3.5 Formation of the Quaternary Ammonium Group

Incorporation of the quaternary ammonium group into the structure of the reactive-ionic finish or reactive-ionic chromophore was accomplished by a nucleophilic substitution reaction. Tertiary amines carry enough nucleophilic character to displace a good leaving group at elevated temperatures to form quaternary ammonium salts. Mountrichas et al. reacted a poly(*p*-hydroxystyrene) which had been augmented with two *m*-dimethylamino groups per repeat unit with methyl iodide to form a polyelectrolyte which contained two cationic sites per monomeric unit.⁵² Using a similar reaction, Dizman and coworkers formed a quaternary ammonium compound by reaction of a methacrylate polymer containing alkyl chloride side chains with a dimethyl, tertiary amine in acetonitrile at reflux.⁵³ The resulting polymer was water-soluble and had antibacterial properties.

Cyclic tertiary amines tend to be less nucleophilic than their linear counterparts. As a result the nucleophilic substitution and subsequent displacement of the leaving group is more difficult. Therefore, a better leaving group than halides was used in the synthesis of the quaternary ammonium compounds in this study. The two leaving groups used were triflate for the reactive-ionic finishes and tosylate for the reactive-ionic chromophore. The leaving groups were incorporated into the structure by reaction of the corresponding alcohol with triflic anhydride and tosyl chloride, respectively.

1.4 SCOPE OF THE DISSERTATION

In keeping with the objectives outlined in Section 1.1, the present study was divided into five chapters. Chapter 2 covers the design, synthesis and characterization of the reactive-ionic alkyl (wax) finish. The starting material, a long-chain alcohol, was triflated in order to incorporate a better leaving group. The alkyl triflate was then reacted with a cyclic tertiary amine to form the cyclic quaternary ammonium salt. ^1H NMR was performed to confirm molecular structure and assess purity of each compound. A batch application method was developed and the reactive-ionic alkyl finish was successfully grafted to a glass slide. Contact angle measurements were conducted to assess the hydrophobicity of the modified surface.

Chapter 3 involves the design, synthesis and characterization of the reactive-ionic fluorinated finish. A perfluorinated alcohol with methylene spacer units was reacted with triflic anhydride to attach a better leaving group thus forming the corresponding triflate. The triflate was then reacted with a cyclic tertiary amine to form a perfluorinated cyclic ammonium compound. ^1H NMR spectroscopy was performed to confirm molecular

structure and assess purity of the reactive-ionic finish. A batch application method was developed and the reactive-ionic fluoro-finish was successfully grafted to a cationic-dyeable nylon carpet sample. The modified sample was put through a rigorous extraction process in an attempt to remove the finish. A water drop penetration test was performed to study the surface characteristics of the carpet samples.

Chapter 4 deals with the design, synthesis and characterization of the reactive-ionic, water-soluble chromophore. A commercially-available disperse dye containing an ethyl alcohol group was tosylated in order to provide a better leaving group for the next reaction. The tosylated disperse dye was then reacted with a bicyclic tertiary amine to form the reactive-ionic compound. ^1H NMR spectroscopy was performed to confirm molecular structure and assess purity of the reactive-ionic dye. Solubility and visible absorbance spectrophotometric studies were conducted to further characterize the behavior of the dye in solution. Dyeings were conducted on a variety of substrates including cotton, nylon, cationic-dyeable nylon, silk and others. Fastness studies were conducted on dyed samples in order to assess how well the covalent fixation reaction proceeded.

Chapter 5 provides a summary of the results obtained and some recommendations for future work involving reactive-ionic systems.

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CHAPTER 2

SYNTHESIS, CHARACTERIZATION AND APPLICATION OF A REACTIVE-IONIC ALKYL (WAX) FINISH

2.1 INTRODUCTION

Wax finishes have long been used to impart water-resistant properties to textile goods. In the 19th century fishermen impregnated cotton garments with waxes to make them non-wetting. Originally, tent material was also impregnated with waxes to prevent water leaking through the fabric and into the tent. The same is true for the first raincoats. Early application methods involved simply forcing a molten or liquefied wax into the fabric structure and allowing it to harden. Obviously, the hand, or feel, of the fabric is drastically altered.

More recently, aqueous wax dispersions have been developed to effectively treat the surface of garments and other textiles and provide a hydrophobic, non-wetting surface without affecting the feel of the fabric as much as earlier methods.^{1,2} However, these finishes are still temporary because they are held to the substrate via weak secondary forces and physical entrapment. The reactive-ionic wax finish developed in this work provides a permanent surface modification due to the formation of a covalent bond between finish and substrate.

2.1.1 Material Selection

The desired reactive-ionic alkyl finish should contain enough hydrocarbon character to impart water-repellent properties to the modified surface. However, since the wax finish was used as a model system to work out the chemistry for subsequent reactive-ionic molecules, the starting material needed to be a non-polymeric, relatively small organic molecule. This is somewhat of a break from common hydrocarbon-based water-repellent finishes for cotton which oftentimes are long-chain hydrocarbons that are physically adsorbed on the surface. The starting material must also be soluble in a polar, aprotic solvent, such as methylene chloride or chloroform, in order for the substitution reactions to proceed effectively. Another necessity for the starting material is the presence of a terminal hydroxyl group since this group will be involved in the first nucleophilic substitution reaction. For these reasons, 1-octadecanol (stearyl alcohol) was chosen as the surface-modifying component of the reactive-ionic wax finish. The structure of 1-octadecanol is shown in Figure 2.1. The eighteen carbon tail provides a substantial amount of hydrophobic character to the molecule and as a result should impart non-wetting properties to the surface that it modifies. Longer hydrocarbon tails result in solubility issues with the lower boiling point, non-polar, aprotic solvents.

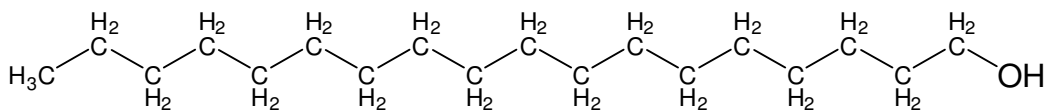


Figure 2.1 – The chemical structure of 1-octadecanol (stearyl alcohol)—the starting material for the reactive-ionic wax finish.

As previously mentioned in Chapter 1, *N*-phenyl pyrrolidine (NPP) and quinuclidine were chosen as the best possible candidates for the cyclic tertiary amines to be used in the present work. NPP was chosen over quinuclidine for incorporation into the reactive-ionic wax finish for several reasons, the first being that NPP has been used much more often in reactive-ionic work³⁻⁶ when compared to quinuclidine.⁷ Also, reactive-ionic molecules prepared from NPP exhibit a lower covalent fixation temperature than do molecules prepared from quinuclidine.⁸ Lastly, although both compounds are commercially available, NPP is nearly one fifth the cost of quinuclidine.

The precursor of the reactive-ionic wax finish is stearyl triflate. Considering that the triflate group is displaced in the formation of the quaternary ammonium ion, the reactive-ionic wax target molecule is *N*-octadecyl-*N*-phenyl pyrrolidinium triflate salt, the structure of which is shown in Figure 2.2.

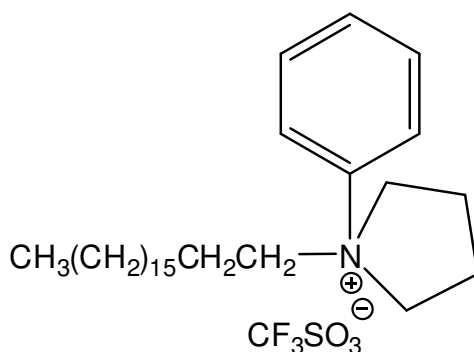


Figure 2.2 – The target chemical structure of the reactive-ionic wax finish—*N*-octadecyl-*N*-phenyl pyrrolidinium triflate salt.

2.1.2 *Synthetic Methods*

The synthetic scheme for the preparation of the reactive-ionic wax was designed as a two-step sequence. In the second step, incorporation of the cyclic tertiary amine to form the quaternary ammonium salt involves nucleophilic attack of the amine on the α -carbon of the precursor and subsequent displacement of a leaving group. A leaving group (X) is the atom or group of atoms displaced in a substitution or elimination reaction. A good leaving group should have a relatively weak and polarized C—X bond. After departure, X⁻ should be a very stable ion and if this ion can be effectively solvated then the leaving ability is further enhanced.⁹ In general, good leaving groups are large, possess low nucleophilicity and are more stable after departure. Some examples of good leaving groups include: tosylate [-OSO₂-C₆H₄(4-Me)], mesylate [-OSO₂-CH₃] and triflate [-OSO₂-CF₃], which are all derived from sulfonic acids.

The first attempt at synthesizing the reactive-ionic wax was based on the displacement of a tosylate group by *N*-phenyl pyrrolidine. However, the reaction did not proceed and the cyclic quaternary ammonium salt was not formed, even at temperatures exceeding 100 °C in toluene. Quinuclidine, on the other hand, shows better nucleophilic character due to the more accessible set of unpaired electrons on nitrogen. Watson showed that quinuclidine is capable of displacing the tosylate group in an S_N2 reaction at reflux in toluene.¹⁰ However, since the majority of previous reactive-ionic work focused on NPP-based ammonium salts, the decision was made to replace the tosylate group with a better leaving group rather than switching cyclic amines from NPP to quinuclidine. The tosylate group was subsequently replaced by the triflate group, a better leaving group.

The most common method of incorporating the triflate leaving group into a molecular structure is the reaction of trifluoromethanesulfonic (triflic) anhydride with a primary alcohol. Triflic anhydride is the acid anhydride of trifluoromethanesulfonic acid, and it is a particularly strong electrophile quite useful for introducing the triflate group.¹¹ Several groups have used triflic anhydride to incorporate the triflate leaving group into long chain primary alcohols. Heyes et al. reacted stearyl alcohol with triflic anhydride in methylene chloride (CH_2Cl_2) using free pyridine as a weak base and also as an acid scavenger. The reaction proceeded with 74% yield of stearyl triflate. The lower yield compared to the triflation of other long chain alcohols was attributed to the inherent low reactivity of stearyl alcohol.¹² Using a slightly different method, Ross et al. triflated stearyl alcohol with triflic anhydride in CH_2Cl_2 in the presence of poly(4-vinyl pyridine) (PVP). Once again, pyridine was used as a base and acid scavenger; however, rather than being free, the pyridine groups are attached to an insoluble polymer support. This helps to reduce alkylation of free pyridine and pushes the yield of alkyl triflates upwards of 90%.¹³

Stearyl alcohol is only sparingly soluble in methylene chloride at the low temperatures required for the reaction. Thus chloroform was chosen as the polar, aprotic solvent for the reaction medium since it is capable of dissolving the necessary amount of starting material. By using PVP in the system, not only was the overall yield improved, it also simplified the reaction workup because it was able to be easily removed from the product mixture by filtration.

As stated earlier, the second step in the synthetic scheme involves the formation of the cyclic quaternary ammonium salt by reaction of stearyl triflate with NPP.

Chloroform was chosen as the solvent for the reaction, once again because of its polar, aprotic nature and the fact that it effectively dissolves stearyl triflate. In adopting previous work by Foston,¹⁴ the first attempt to form the reactive-ionic wax involved running the reaction at reflux in chloroform (61 °C). The reaction was successful; however, at elevated temperatures NPP has a tendency to discolor and the reaction medium turned a dark brownish black. This problem was compounded by a more difficult work up. In an effort to remedy these problems, the reaction was allowed to proceed at room temperature for 48 hours. After isolation and characterization of the product it was determined that 48 hours and room temperature was a sufficient time and temperature for formation of the quaternary ammonium salt. Aminomethylated-polystyrene was added to the flask at the 48 hour mark to remove any unreacted alkyl triflate starting material through reaction and subsequent binding of the triflated material to the primary amines on the insoluble polymer chain.

2.2 EXPERIMENTAL SECTION

2.2.1 *Materials*

All reagents were used without further purification unless otherwise specified. 1-octadecanol (99%), poly(4-vinylpyridine) 2% cross-linked with divinylbenzene, (aminomethyl) polystyrene 200-400 mesh, extent of labeling: 1.0-2.0 mmol/g loading (2% cross-linked), trifluoromethanesulfonic anhydride (99+%), chloroform (anhydrous, >99%) were purchased from Aldrich Chemical Co. *N*-phenyl pyrrolidine (99%) was purchased from Alfa Aesar. Sodium bicarbonate (NaHCO₃), magnesium sulfate (MgSO₄, anhydrous), water (deionized, ultra-filtered), tetrahydrofuran (THF, 99%),

acetone (99%) and sodium hydroxide (pellets) were purchased from Fisher Scientific. Chloroform-*d* (CDCl₃) was purchased from Cambridge Isotope Laboratories, Inc. Glass slides (precleaned) were purchased from Fisher Scientific and rinsed with acetone prior to use.

2.2.2 Instrumentation

¹H NMR spectra were measured on a Bruker AMX 400 spectrometer in chloroform-*d* (CDCl₃) with concentrations of approximately 1 wt%. Melting points were measured with a Mel-Temp melting point apparatus at a heating rate of 5 °C/min.

Surface contact angle measurements were made using an AST Products Inc. Video Contact Angle (VCA) System with automatic syringe control (available drop sizes of 1 - 100 µL). The stage was lit by a Navitar light console. Contact angles were measured using WINVCA2500XE software.

2.2.3 Synthesis of Octadecyl Triflate (reactive-ionic precursor)

Poly(4-vinylpyridine) 2 % cross-linked with divinylbenzene (0.85 g, 7.77 mmol), which had been dried overnight in a vacuum oven at 40 °C, was added to a clean, dry three-neck, round-bottom flask containing a magnetic stir bar under positive nitrogen pressure. The flask was evacuated and then charged with anhydrous chloroform (20 mL) via cannula. The flask was back-filled with dry nitrogen gas and left under positive nitrogen pressure. Trifluoromethanesulfonic (triflic) anhydride (1.57 g, 5.55 mmol) was added to the flask via syringe over 2 minutes while stirring. The 1-octadecanol (1.00 g, 3.70 mmol) dissolved in 5 mL anhydrous chloroform was added to the flask dropwise via

syringe over a 10 minute period. The reaction was allowed to proceed for 1 hour at room temperature while stirring. Once the reaction was complete, the stir bar was removed, the contents of the flask were filtered and the solids washed with 5 mL of anhydrous chloroform. The organic filtrate was washed twice with a saturated, aqueous NaHCO₃ solution (5 mL). After each wash, the organic layer was removed by separatory funnel. The final organic layer was removed and dried over MgSO₄ and then filtered. The solvent was removed by rotary evaporation, the product cooled in a refrigerator and then dried overnight in a vacuum oven at 40 °C to yield octadecyl triflate as a waxy, white solid. Yield: 1.31 g (89%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 4.51 (t, 2H), 1.80 (p, 2H), 1.39 (p, 2H), 1.23 (broad multiplet, 28H), 0.86 (t, 3H).

2.2.4 Synthesis and Purification of Reactive-Ionic Alkyl Finish

Octadecyl triflate (1.30 g, 3.2 mmol) was added to a clean, dry three-neck, round-bottom flask containing a magnetic stir bar and equipped with a condensing column. The flask was evacuated then charged with anhydrous chloroform (20 mL). The flask was then back-filled with dry nitrogen gas. *N*-phenyl pyrrolidine (0.471 g, 3.2 mmol) was added to the flask via syringe. The reaction was allowed to proceed while stirring at room temperature for 48 hours. After 48 hours, aminomethyl polystyrene (0.16 g, 0.64 mmol) was added to the flask under positive nitrogen pressure. The contents were allowed to stir for an additional 1 hour at room temperature. The stirring bar was removed, the contents of the flask filtered and the solids washed with anhydrous chloroform (5 mL). The filtrate was collected and the solvent removed by rotary evaporation. The crude

product was a very pale, green solid which was dried in a vacuum oven at 40 °C for 24 hours.

The crude product was dissolved in a minimum amount of tetrahydrofuran and then precipitated into an excess of cold deionized water. The suspension was allowed to sit overnight in a refrigerator before it was filtered. The solids were collected and washed with cold deionized water. The purified product was a bright white, waxy solid which was dried in a vacuum oven at 40 °C for 24 hours. Yield: 1.61 g (91%). m.p. 114 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.59 (m, 5H), 4.27 (m, 2H), 4.11 (m, 2H), 3.81 (t, 2H), 2.38 (m, 2H), 2.10 (m, 2H), 1.22 (broad multiplet, 32H), 0.85 (t, 3H).

2.2.5 Application of Reactive-Ionic Alkyl Finish to a Glass Slide

A clean glass slide was placed into a 100 mL crystallizing dish containing an aqueous NaOH bath (pH=12). The dish was covered and then placed on an agitating stage for 30 minutes. The slide was then removed from the base bath and rinsed in a beaker containing deionized water to remove any residual hydroxide ions from the glass surface. The deprotonated glass slide was dried in a vacuum oven at 40 °C. The dry, deprotonated slide was then immersed in a crystallizing dish containing 50 mL of a solution of 0.1% (w/v) of the reactive-ionic alkyl finish in THF. The dish was covered and then placed on an agitating stage. After 3 hours, the slide was removed from the dish and placed in a vacuum oven at 80 °C for 4 hours. The slide was allowed to cool and then rinsed with fresh THF to remove any non-covalently bonded material. A separate glass slide was prepared in the same manner; however, the second slide was rinsed with

THF after application of the reactive-ionic wax but before the covalent fixation step of heating at 80 °C.

2.2.6 *Evaluation of Surface-Modified Glass Slide*

Contact angle measurements were collected for three different glass slide samples: an unmodified glass slide, a glass slide which had been surface-modified using the reactive-ionic alkyl finish and a glass slide which had been surface-modified but rinsed before the covalent fixation step. The contact angles of a 1 μ L drop of deionized water on the glass surface were measured at 5 different sites on each slide. The left and right contact angles were averaged and reported for each drop.

2.3 RESULTS AND DISCUSSION

2.3.1 *Synthesis and Characterization of Octadecyl Triflate (reactive-ionic precursor)*

The first step in the synthesis of the reactive-ionic wax finish was to provide a better leaving group to the alkyl chain than the hydroxyl group. This was accomplished by incorporating a triflate group via reaction of octadecyl (stearyl) alcohol with triflic anhydride to form octadecyl triflate. The general reaction scheme is depicted in Figure 2.3. The overall reaction yield was 1.31 g (89%) of a waxy, white solid after aqueous workup which is keeping with the approximately 90% yield stated in the literature for a similar primary alkyl triflation reaction.¹³

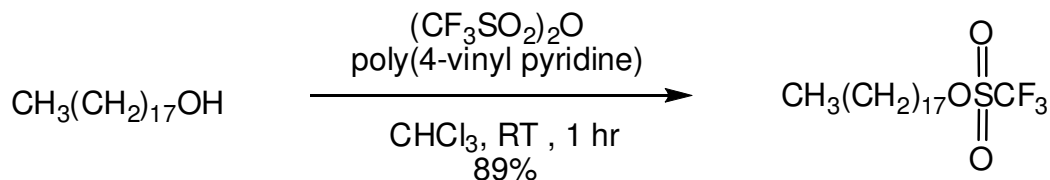


Figure 2.3 – General reaction scheme for the triflation of stearyl alcohol using triflic anhydride.

The crude product from the reaction was not purified any further after aqueous workup since the ^1H NMR spectrum showed little evidence of side products or contamination. The ^1H NMR spectrum of octadecyl triflate is shown in Figure 2.4. The peak assignments are labeled on the spectrum according to the corresponding protons in the chemical structure. The aliphatic protons labeled (a), (b) and (c) in Figure 2.4 are found at the same chemical shift as the starting material, expected since these protons are more than 2-3 carbon atoms away from the newly introduced group. The peak from the protons of the methylene group designated (d) in the spectrum shifted slightly downfield from 1.65 ppm in the starting material to 1.80 ppm in the product due to the proximity to the newly added trifluoromethanesulfonic ester group. The signature peak shift occurred for the protons adjacent to the triflate group, labeled (e) in Figure 2.4, from 3.5 ppm in 1-octadecanol to 4.51 ppm in the reactive-ionic precursor, octadecyl (stearyl) triflate. The ^1H NMR spectra of the starting materials are located in the Appendix.

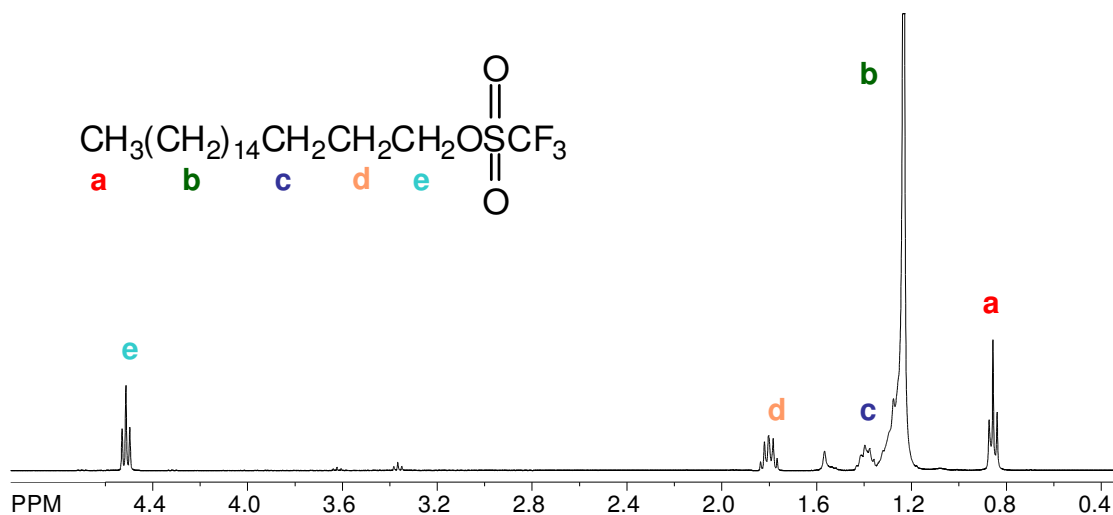


Figure 2.4 – ^1H NMR spectrum of the reactive-ionic alkyl finish precursor, stearyl triflate, with proton labels to identify location in the structure. (CDCl_3 solvent peak @ 7.24 ppm not shown)

2.3.2 *Synthesis and Characterization of Reactive-Ionic Alkyl (Wax) Finish*

The second step in the reaction sequence is to form the cyclic quaternary ammonium group by reaction of octadecyl triflate with *N*-phenyl pyrrolidine. The cyclic amine acts as a nucleophile to displace the triflate group in a nucleophilic substitution, $\text{S}_{\text{N}}2$, the reaction forming a cyclic quaternary ammonium group on the end of the alkyl chain. The general scheme is shown in Figure 2.5. The crude product from the first step was used without further purification in the second step.

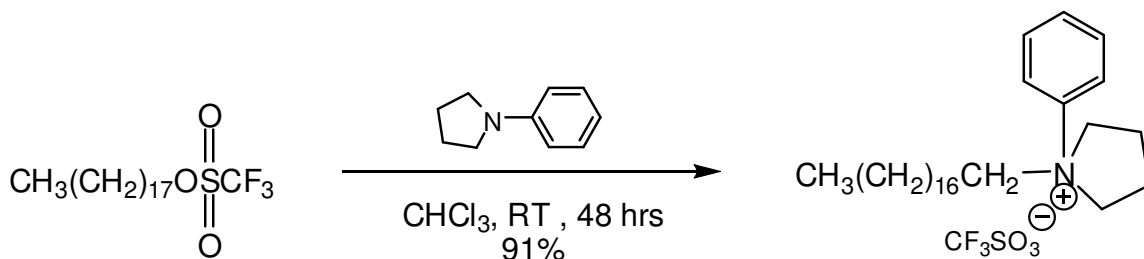


Figure 2.5 – General reaction scheme for the formation of the cyclic ammonium group by reaction of stearyl triflate with N-phenyl pyrrolidine.

Aminomethylated-PS (AM-PS) was added to the flask after 48 hours in order to remove any unreacted triflate material. The primary amines on AM-PS are much more reactive towards the alkyl triflates than the tertiary amine of NPP, thus covalently bonding the unreacted starting material to the insoluble polymer support. After 1 hour, the contents of the flask were filtered and the solvent removed by rotary evaporation. This afforded a very pale, white-green solid before purification due to residual NPP in the product. The crude product was fully soluble in THF but the pure product was insoluble in cold water. For this reason, the reactive-ionic wax was purified by repeated precipitation from THF into a water system. The purified product was recovered as a bright white, waxy solid in 91% yield.

The reaction was originally run at reflux; however, the flask contents after 48 hours were a greenish-black color while still in the solvent. Residual NPP in this system has a tendency to turn dark green upon heating or being left open to the atmosphere.

The ^1H NMR spectrum for the purified reactive-ionic alkyl (wax) finish is shown in Figure 2.6. The peak at 4.51 ppm, representing the protons on the methylene group

adjacent to the triflate in the starting material, is completely gone. This same group, labeled (c) in the figure below, now resides at 3.8 ppm which is characteristic for protons adjacent to a quaternerized nitrogen atom. The peaks from the structurally identical cyclic protons of NPP, (d) and (e), have split because the protons are magnetically inequivalent due to the tetrahedral bonding at nitrogen. The most obvious evidence for the formation of an NPP-based cyclic quaternary ammonium molecule is the clustering and downfield shift of the aromatic protons.³ The five phenyl protons, labeled (f) in Figure 2.6, are tightly centered around 7.59 ppm in the cyclic ammonium salt compared to peak locations of 6.6 ppm and 7.3 ppm in the starting material NPP.

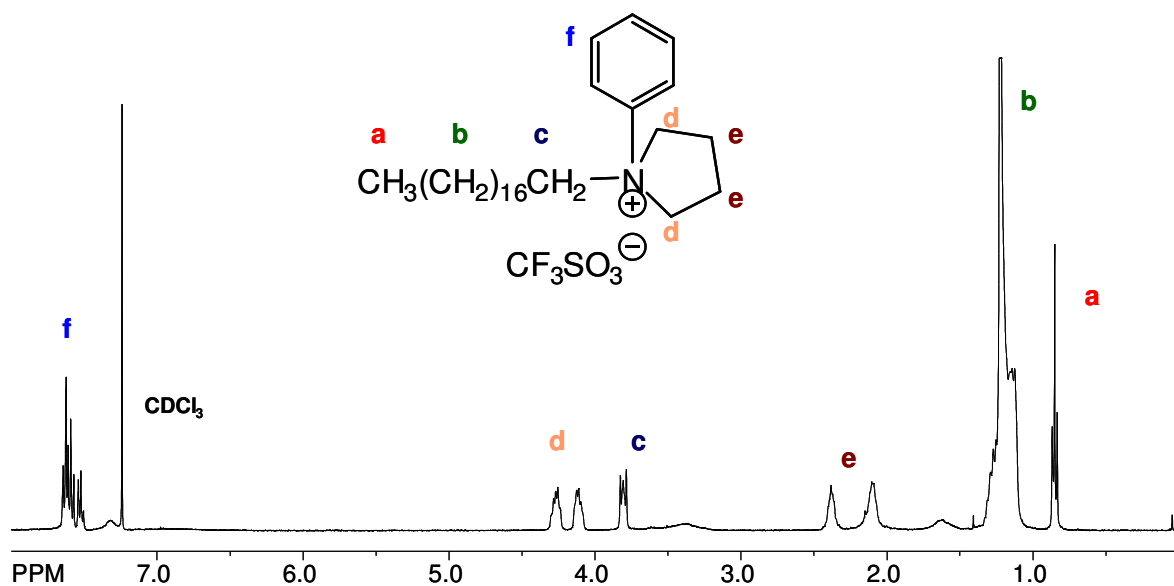


Figure 2.6 – ¹H NMR spectrum of the reactive-ionic alkyl finish with proton labels to identify corresponding location in the structure.

2.3.3 Application of Reactive-Ionic Alkyl (Wax) Finish to a Glass Slide

The first step in the application of the reactive-ionic wax finish involved the deprotonation of the silanol groups on the surface of the glass slide. The deprotonated slide was then rinsed in deionized water to remove any residual base. The slide was then placed in a 0.1% (w/v) solution of the reactive-ionic wax finish in THF. At this point, an ionic bond was formed between the reactive-ionic finish (cation) and the surface O⁻ (anion) via an ion exchange reaction. In this process, the triflate anion, originally part of the cyclic ammonium salt, is discharged and solvated by the THF solution. The slide was then removed from the processing bath and placed in a vacuum oven at 80 °C to induce the covalent fixation step. Upon removal from the vacuum oven the slide was rinsed with copious amounts of THF to remove any unfixed material. A schematic of the ring-opening, covalent fixation step is shown in Figure 2.7.

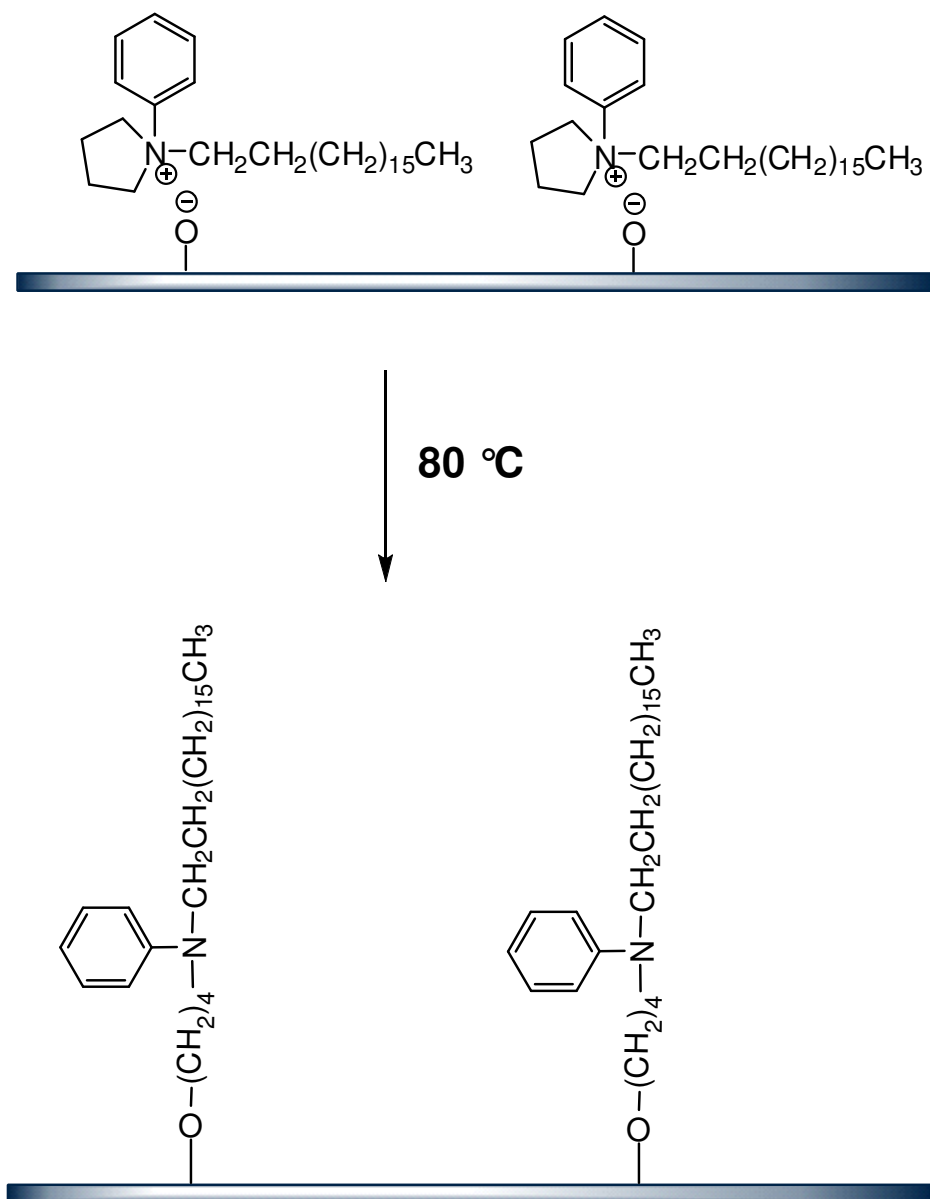


Figure 2.7 – Diagram depicting the ionic assembly of the reactive-ionic alkyl (wax) finish on a surface containing deprotonated hydroxyl groups and subsequent covalent fixation at 80 °C.

2.3.4 *Evaluation of the Surface-Modified Glass Slide*

To assess the physical characteristics of the surface-modified glass slide, contact angle measurements were performed using deionized water drops. Three different samples were tested: a precleaned slide which had not been treated, a slide treated with the reactive-ionic wax and covalently fixed at 80 °C, and a slide that had been immersed in the reactive-ionic wax bath but not heated to induce covalent fixation. All three slides were rinsed with THF and dried before testing. Five drops were placed at random locations on each slide and the resulting static contact angles were measured. The contact angles for all three slides are compiled in Table 2.1 below.

Table 2.1 – Measured contact angles of 1 μ L drops of deionized water on glass slides which had been (A) precleaned with no treatment, (B) treated with reactive-ionic wax finish then covalently fixed at 80 °C and (C) treated with reactive-ionic wax with no covalent fixation.

Static Contact Angle (degrees)			
	A	B	C
Drop	No Treatment	RI-wax 80 °C Fixation	RI-wax No Fixation
1	24.0	55.1	20.8
2	23.9	63.4	17.8
3	11.6	71.1	25.9
4	16.5	66.6	20.8
5	17.4	58.7	24.0
AVG	18.7	63.0	21.9

The average contact angle for the untreated glass slide was 18.7°. This value was expected since glass surfaces are notoriously hydrophilic as a result of the high number of potential hydrogen bonding sites on the silicon oxide surface. The average contact angle for the treated and fixed sample was dramatically higher, 63.0°, indicating that the surface modification was successful. The fact that the finish did not rinse off with THF is evidence that the covalent fixation step indeed occurred. This is further supported by the fact that the average contact angle for the sample which had been treated with the reactive-ionic wax but not covalently fixed returned almost to the value of the untreated sample. Video captures of a 1 μL drop of deionized water sitting on the surface of various slides are shown in Figures 2.8-2.10.

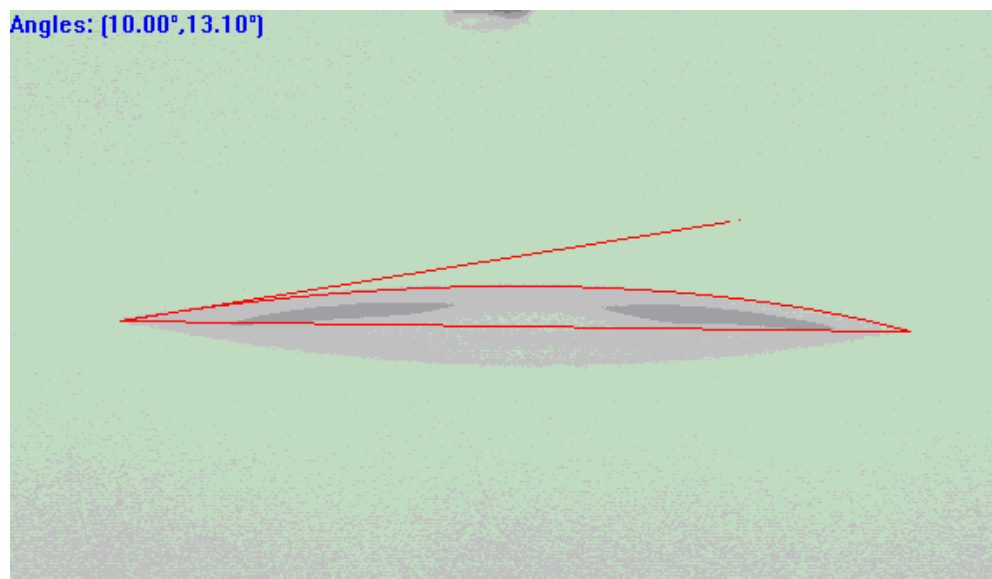


Figure 2.8 – Video capture of a 1 μL drop of deionized water sitting on the surface of an untreated, clean glass slide.

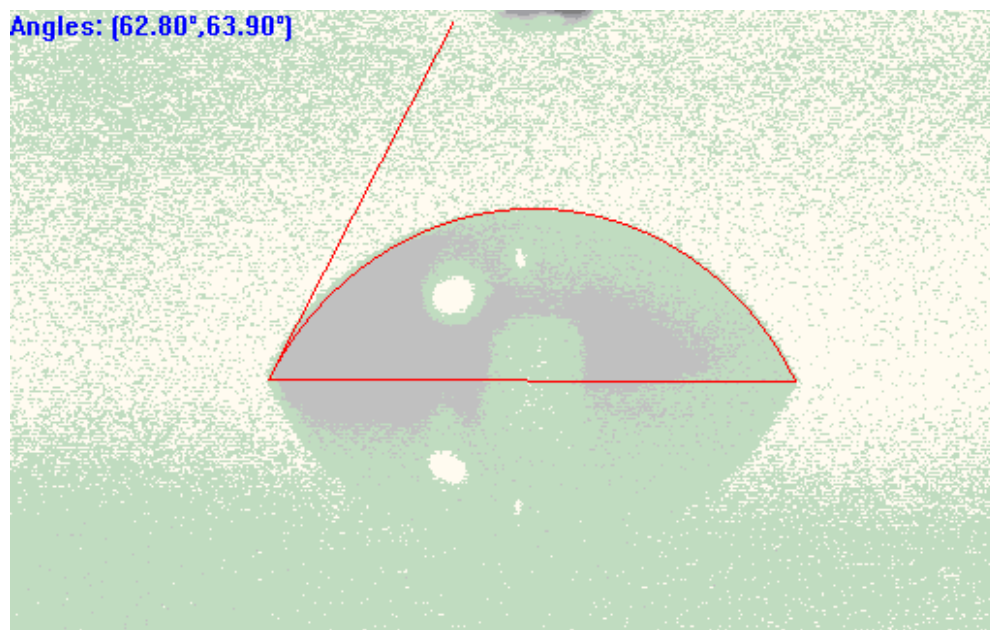


Figure 2.9 – Video capture of a 1 μL drop of deionized water sitting on the surface of a glass slide which had been treated with the reactive-ionic wax finish and covalently fixed at 80 °C.

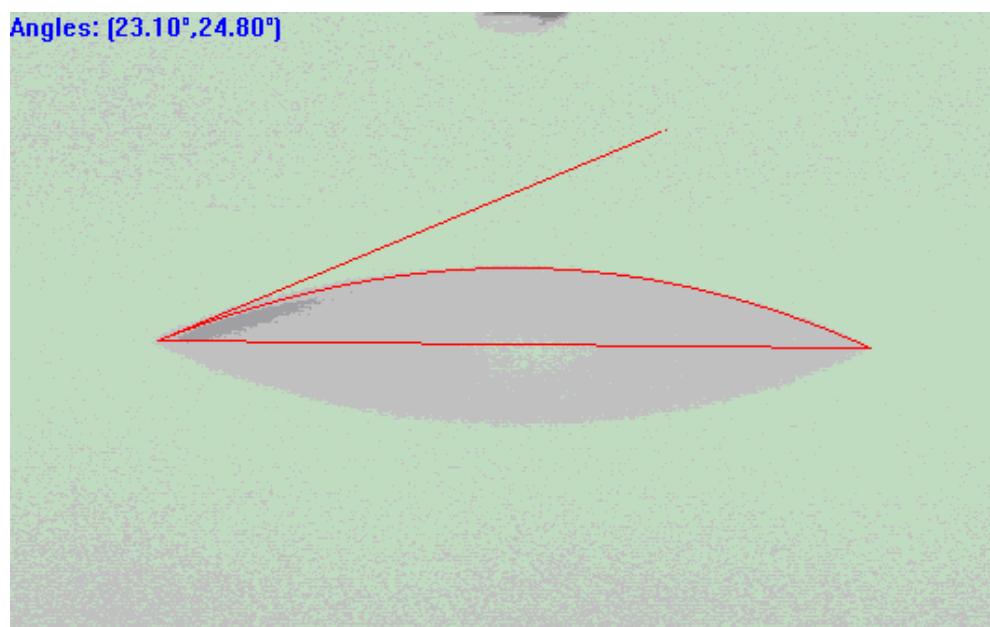


Figure 2.10 – Video capture of a 1 μL drop of deionized water sitting on the surface of a glass slide which had been treated with the reactive-ionic wax finish but rinsed with THF before the covalent fixation step.

2.4 CONCLUSIONS

A reactive-ionic alkyl (wax) finish was prepared by triflation of octadecanol (stearyl alcohol) and subsequent substitution with *N*-phenyl pyrrolidine via a S_N2 reaction. The resulting quaternary ammonium compound was purified by precipitation from THF into water and then characterized by ¹H NMR spectroscopy. The reactive-ionic wax was then successfully applied to a deprotonated glass slide by ionic assembly of the cationic finish followed by covalent fixation at 80 °C. The surface was characterized by measuring contact angles. An increase in average contact angle of nearly 45° was seen after application of the reactive-ionic wax. The finish was indeed permanent, as a slide which was treated with the reactive-ionic finish but not covalently fixed and then rinsed with solvent exhibited contact angles close to that of an untreated slide.

2.5 REFERENCES

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CHAPTER 3

SYNTHESIS, CHARACTERIZATION AND APPLICATION OF A REACTIVE-IONIC FLUORINATED FINISH

3.1 INTRODUCTION

For nearly six decades researchers have recognized that fluorochemicals produce surfaces with low surface energies.¹ These fluorochemicals act to increase the contact angles between high surface tension liquids, like water, and the exposed interface thereby making the surfaces more hydrophobic. Fluorochemicals protect fibers from foreign materials such as water and oil. The surface energy of nylon, normally around 43 dynes/cm, is reduced by about 50% with the application of a fluorocarbon.² The lower surface energy prevents the fiber from wetting out and thus reduces contamination from dissolved or suspended species. For these reasons, fluorochemical finishes have been used extensively in textiles as non-wetting and anti-stain agents.

As early as 1957 several different fluorochemicals were applied to cotton fabric to obtain oil- and water-repellent surfaces. These early finishes included chromium coordination complexes of saturated perfluoromonocarboxylic acids and polymers of fluoroalkyl esters of acrylic acid.³ In the mid 1960s, various fluorinated alcohols, with the carbon chain containing the fluorine atom ranging in length from C₃ to C₁₁, were synthesized and reacted with methyl methacrylate to prepare a fluoroacrylate monomer. After emulsion polymerization, the latex was applied in a pad-type process and after

drying the impregnated fabrics were repellent to both oil and water.⁴ This work progressed into the late 1980s where similar molecules were used in conjunction with rewetting agents to create anti-staining finishes for olefins, polyamides, polyesters, acrylics and wool.⁵

Fluorinated cationic compounds have also been manufactured as additives to impart soil resistance to textiles. The majority of these cationic compounds include a quaternary ammonium group bonded in some way to fluorocarbon moieties ranging in length from 3-6 carbon atoms.^{6,7} Fluorochemicals containing epoxy groups were developed which could bond directly to cellulosic materials thus imparting a permanent non-wetting surface.⁸ Another class of stain-resistant compounds was proposed by Matsuo et al. consisting of tertiary amines containing long arms substituted with both alkyl and perfluoroalkyl groups.⁹

Fluorochemicals have been used for decades as anti-stain treatments for nylon, particularly in the carpet industry. Scotchgard™ from 3M is an example of a fluorinated spray application finish that has been in use as a fabric protector since the mid 1950s. DuPont introduced Stainmaster® carpet in 1986—nylon carpeting which had been sprayed with a Teflon® finish application. Both of these products provided excellent resistance to oil- and water-borne contaminants; however, in 1999 the EPA began an investigation into the class of chemicals used in Scotchgard. The key ingredients and breakdown products in these temporary fluorinated finishes, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), have been found to compromise the immune system of mammals and are now global pollutants due to release of the fluorochemical from the substrate to which they are applied into the environment. The new formulation

from 3M employs the use of perfluorobutane sulfonate (PFBS) as the key ingredient which has the benefit of shorter half life in humans than PFOS, a little over one month in the former compared to 5.4 years in the latter.¹⁰

A reactive-ionic fluorinated finish should drastically reduce the impact of the fluorochemical on the environment due to the covalent bond between finish and fiber. Compared to the traditional ionic finishes of the past few decades, a reactive-ionic finish should have dramatically improved durability due to its permanent nature.

3.1.1 Material Selection

The desired reactive-ionic fluorinated finish should contain enough fluorocarbon character to impart water-repellent and anti-stain properties to the modified surface. Solubility requirements of the starting material, for subsequent synthesis of the reactive-ionic finish, dictate that the molecule should contain no more than eight fluorinated carbon atoms. For the purpose of this work, the molecule must also possess a terminal, primary hydroxyl group for incorporation of the triflate leaving group in the first synthetic step. A methylene spacer unit between the fluorinated portion of the molecule and the polar hydroxyl head is required to insulate the withdrawing effect of the fluorine atoms and to allow the subsequent reactions to proceed correctly. The most promising candidates that fit these requirements were 1H,1H-perfluoro-1-octanol [$\text{CF}_3(\text{CF}_2)_6\text{CH}_2\text{OH}$] and 1H,1H,2H,2H-perfluoro-1-octanol [$\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2\text{OH}$]. The only difference between the two molecules is the presence of one methylene spacer unit in the former while there are two methylene groups in the latter molecule. Both molecules are soluble in dichloromethane and have been triflated in the literature.¹¹⁻¹³

Since 1H,1H-perfluoro-1-octanol has more fluorine character it was chosen as the original starting material for synthesis of the reactive-ionic fluorine finish. However, it was found during the course of the reactive-ionic finish synthetic sequence that once the triflate group is incorporated into the structure the molecule is unreactive towards the cyclic, tertiary amine used in the second step of the reaction. Thus, 1H,1H,2H,2H-perfluoro-1-octanol, the compound containing two methylene spacer groups and shown in Figure 3.1, was the successful starting material for the synthesis of the reactive-ionic fluorinated finish. 1H,1H,2H,2H-perfluoro-1-decanol was also commercially available but not soluble in low BP, polar, aprotic solvents such as dichloromethane that were desired in this work .

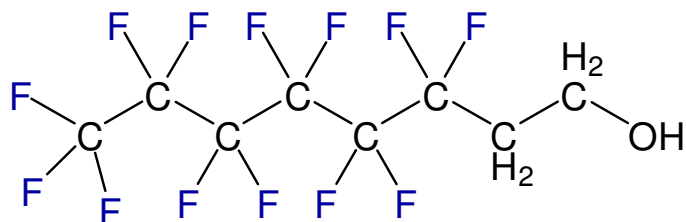


Figure 3.1 – The chemical structure of 1H,1H,2H,2H-perfluoro-1-octanol—the starting material for the reactive-ionic fluorinated finish.

NPP was chosen as the cyclic, tertiary amine to be incorporated into the reactive-ionic structure for formation of the quaternary ammonium ion. NPP has sufficient reactivity to displace the triflate group of an alkyl triflate, as was evident in the synthesis of the reactive-ionic wax finish in Chapter 2. NPP was chosen as a reactant over

quinuclidine due to the lower covalent fixation temperature of the resulting reactive-ionic molecule and for cost reasons.

Considering that the triflate group is displaced in the formation of the quaternary ammonium ion, the reactive-ionic fluorinated finish target molecule is *N*-phenyl-*N*-(1H,1H,2H,2H-perfluoro-1-octyl)-pyrrolidinium triflate salt. The structure is shown in Figure 3.2.

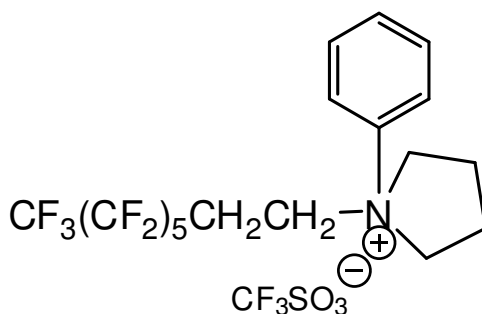


Figure 3.2 – The target chemical structure of the reactive-ionic fluoro-finish— *N*-phenyl-*N*-(1H,1H,2H,2H-perfluoro-1-octyl)-pyrrolidinium triflate salt.

3.1.2 Synthetic Methods

The synthetic scheme for the preparation of the reactive-ionic fluoro-finish is similar to the scheme used for the synthesis of the reactive-ionic wax. The two-step process involves incorporation of a triflate leaving group into the structure of the fluorinated alcohol followed by substitution of NPP and displacement of the triflate group to form the quaternary ammonium ion and thus the reactive-ionic finish.

As previously stated in Chapter 2, the most common method of incorporating the triflate leaving group into a molecular structure is the reaction of triflic anhydride with a

primary alcohol. The first attempt at forming the perfluorinated alkyl triflate was conducted using a method identical to that used for the preparation of the reactive-ionic wax molecule. Triflic anhydride was reacted with the primary perfluorinated alcohol starting material using poly(4-vinyl pyridine) (PVP) as a polymer-supported base and acid scavenger. The reaction, however, proceeded with minimal yield of the perfluorinated alkyl triflate, around 20%. The yield was too low and this particular reaction was abandoned. Rabai and coworkers published a reaction in which free pyridine was used in the triflation of 1H,1H-perfluoro-1-octanol with yields of the triflate in excess of 90%.¹³ This method was successfully adopted until it was found that 1H,1H-perfluoro-1-octyl triflate was unreactive in the subsequent S_N2 substitution reaction with NPP. This was attributed to the presence of a single methylene spacer unit between the fluorinated carbons and the triflate group. Briza et al. were able to form the triflate from 1H,1H,2H,2H-perfluoro-1-octanol in 91% yield via reaction with triflic anhydride using pyridine in a dichloromethane and dioxane co-solvent system.¹¹ Koshti et al. formed the same fluorinated alkyl triflate by reaction of 1H,1H,2H,2H-perfluoro-1-octanol with triflic anhydride using triethylamine as the base in a CH₂Cl₂ solvent system with yields around 80%.¹² The method used to form the fluorinated alkyl triflate, reactive-ionic fluoro-finish precursor, in this work is a combination of the procedures adopted from Briza and Koshti, in which free pyridine is used as the base in a CH₂Cl₂ system.

Following the procedure developed for formation of the reactive-ionic wax in Chapter 2, the fluorinated alkyl triflate was reacted with NPP in a polar, aprotic solvent. The reactive-ionic wax molecule was formed by reaction of the alkyl triflate with NPP in chloroform at ambient temperatures; however, this temperature was not sufficient for

formation of the reactive-ionic fluoro-finish. Following previous work by Foston,¹⁴ the second step of the scheme was conducted at reflux in chloroform (61 °C). The higher temperature afforded the system with enough energy to allow substitution of the perfluorinated alkyl triflate by NPP. Once again, in an effort to reduce the workup and purification steps, aminomethylated-polystyrene (AM-PS) was added at the end of the reaction to remove any unreacted triflate starting material. The resulting crude product contained only the target chemical and residual NPP.

3.2 EXPERIMENTAL SECTION

3.2.1 *Materials*

All reagents were used without further purification unless otherwise specified. 1H,1H,2H,2H-perfluoro-1-octanol was purchased from Synquest Labs. Trifluoromethanesulfonic (triflic) anhydride (99+%), (aminomethyl) polystyrene 200-400 mesh, extent of labeling: 1.0-2.0 mmol/g loading (2% cross-linked), carbon tetrachloride (CCl₄, 99%), chloroform (CHCl₃, anhydrous, >99%) and dichloromethane (CH₂Cl₂, anhydrous, >99.9%) were purchased from Aldrich Chemical Co. *N*-phenyl pyrrolidine (99%) was purchased from Alfa Aesar. Pyridine (anhydrous) was purchased from ACROS Organics. Hydrochloric acid (HCl), sodium bicarbonate (NaHCO₃), magnesium sulfate (MgSO₄, anhydrous), water (deionized, ultra-filtered), tetrahydrofuran (THF, 99%), acetone (99%) and sodium hydroxide (pellets) were purchased from Fisher Scientific. Chloroform-*d* (CDCl₃) was purchased from Cambridge Isotope Laboratories, Inc. Cationic-dyeable nylon carpet was tufted in-house at Georgia Tech using fiber supplied by DuPont.

3.2.2 Instrumentation

¹H NMR spectra were measured on a Bruker AMX 400 spectrometer in chloroform-*d* (CDCl₃) with concentrations of approximately 1 wt%. Melting points were measured with a Mel-Temp melting point apparatus and confirmed by differential scanning calorimetry (DSC) analysis on a Seiko 220 DSC with a heating rate of 10 °C/min in a N₂ environment.

3.2.3 Synthesis of 1H,1H,2H,2H-Perfluoro-1-Octyl Triflate (Precursor)

1H,1H,2H,2H-perfluoro-1-octanol (2.00 g, 5.5 mmol) was added to a clean, dry flask containing a magnetic stir bar under positive nitrogen pressure. The flask was evacuated and then charged with anhydrous dichloromethane (25 mL) via cannula. The flask was back-filled with dry nitrogen gas and placed in an ice bath at ~ 5 °C and left under positive nitrogen pressure. Pyridine (0.52 g, 6.6 mmol) was added to flask via syringe. Next, trifluoromethanesulfonic (triflic) anhydride (1.86 g, 6.6 mmol) was added to the flask via syringe over 10 minutes while stirring. The reaction was allowed to proceed in the ice bath for 1 hour at 5 °C while stirring. The ice bath was removed and contents of the flask were allowed to stir for an additional hour at room temperature. Once the reaction was completed, the stir bar was removed and the contents of the flask were washed with 2 M aqueous HCl (10 mL), ice water (10 mL) and finally a saturated, aqueous NaHCO₃ solution (10 mL). After each wash, the organic layer was removed by separatory funnel. The final organic layer was removed and dried over MgSO₄ and then filtered. The solvent was removed by rotary evaporation which gave the product as a

pale yellow liquid. The product was dried overnight in a vacuum oven at 40 °C. Yield: 1.89 g (81%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 4.77 (t, 2H), 2.66 (m, 2H).

3.2.4 Synthesis and Purification of Reactive-Ionic Fluorinated Finish

1H,1H,2H,2H-perfluoro-1-octyl triflate (1.90 g, 3.8 mmol) was added to a clean, dry flask containing a magnetic stir bar and equipped with a condensing column. The flask was evacuated then charged with anhydrous chloroform (20 mL). The flask was then back-filled with nitrogen gas. *N*-phenyl pyrrolidine (0.56 g, 3.8 mmol) was added to the flask via syringe. The flask was then immersed in an oil bath which had been heated to 65 °C. The reaction was allowed to proceed for 48 hours at reflux. After 48 hours, aminomethyl polystyrene (0.19 g, 0.76 mmol) was added to the flask under positive nitrogen pressure. The contents were allowed to stir for an additional 1 hour at room temperature. The stirring bar was removed, the contents of the flask filtered and the solids washed with anhydrous chloroform (5 mL). The filtrate was collected and the solvent removed by rotary evaporation. This afforded a light green solid as the crude product. The crude product was then purified by precipitation from a minimum amount of dichloromethane into an excess of cold carbon tetrachloride. The precipitate was collected by filtration and then washed with cold carbon tetrachloride. The purified product, a white solid, was dried overnight in a vacuum oven at 40 °C. Yield: 2.16 g (88%). m.p. 132-133 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.76 (d, 2H), 7.65 (t, 2H), 7.29 (t, H), 4.35 (m, 4H), 4.30 (m, 2H), 2.42 (m, 2H), 2.26 (m, 2H), 2.03 (m, 2H).

3.2.5 Application of Reactive-Ionic Fluorinated Finish to Cationic-Dyeable Nylon Carpet

A cationic-dyeable nylon carpet sample measuring approximately 1" x 1" (0.98 g) was placed in a crystallizing dish containing an aqueous NaOH bath (pH=10). The dish was covered and then placed on an agitating stage for 30 minutes. The carpet sample was then removed from the base bath and rinsed in a beaker containing deionized water to remove any residual hydroxide ions from the nylon surface. The deprotonated sample was dried in a vacuum oven at 40 °C. The dry, deprotonated nylon carpet sample was then immersed in a crystallizing dish containing 50 mL of a solution of 0.1% (w/v) of the reactive-ionic fluorinated finish in a 3:2 mixture of THF and deionized water. The dish was covered and then placed on an agitating stage. After 3 hours, the carpet was removed from the dish and placed in a vacuum oven at 80 °C for 4 hours. The sample was allowed to cool and then rinsed with fresh THF to remove any non-covalently bonded material. The sample was then dried overnight in a vacuum oven at 40 °C.

3.2.6 Evaluation of Surface-Modified Carpet Sample

After application of the reactive-ionic fluorinated finish to the cationic-dyeable nylon carpet the sample was subjected to a water drop penetration test. A 1% solution of Direct Red 80 dye in deionized water was prepared to be used as the drop medium. This was done to provide contrast between the water drop and the colorless nylon carpet sample. Drops of the colored solution (approximately 50 µL) were placed with a dropper from a height of 1 cm onto the surface of the modified carpet sample and observed. Observations were made and photos taken at time intervals of 1, 10 and 60 minutes after identical manner.

A nylon carpet sample surface-modified with the reactive-ionic fluorinated finish was also subjected to a stain-resistance test based on AATCC Test Method 175-2003. The carpet specimen was immersed 1 cm in double strength cherry-flavored Kool-Aid[®] at 60 °C for 60 seconds, rinsed in cold water for 30 seconds and dried at 60 °C. An unmodified sample was also tested. The specimens were observed for wetting and/or wicking and residual staining was assessed after drying.

3.3 RESULTS AND DISCUSSION

3.3.1 Synthesis and Characterization of 1H,1H,2H,2H-Perfluoro-1-Octyl Triflate (Precursor)

The first step in the synthesis of the reactive-ionic fluorinated finish was to provide a better leaving group to the perfluorinated alkyl chain than the hydroxyl group. This was accomplished by incorporating a triflate group via reaction of 1H,1H,2H,2H-perfluoro-1-octanol with triflic anhydride to form 1H,1H,2H,2H-perfluoro-1-octyl triflate. The general reaction scheme is depicted in Figure 3.3. The overall reaction yield was 1.89 g (81%) of a pale yellow, oily liquid after aqueous workup. The 81% yield of the first reaction was similar to the yields achieved by Briza¹¹ and Koshti¹² in similar reactions involving the triflation of 1H,1H,2H,2H-perfluorinated alcohols.

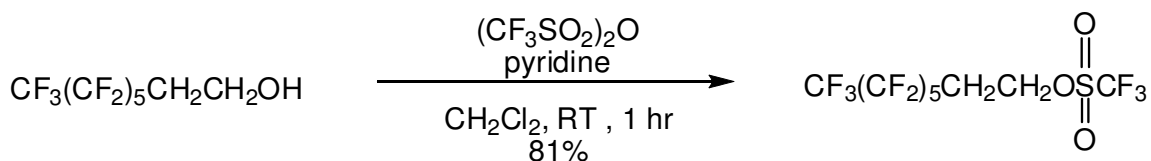


Figure 3.3 – General reaction scheme for the triflation of 1H,1H,2H,2H-perfluoro-1-octanol using triflic anhydride.

The crude product from the reaction was not purified any further after aqueous workup since the ^1H NMR spectrum showed little evidence of side products or contamination. The ^1H NMR spectrum of 1H,1H,2H,2H-perfluoro-1-octyl triflate is shown in Figure 3.4. The peak assignments are labeled on the spectrum according to the corresponding protons in the chemical structure. Due to fluorination of six carbon atoms in both the starting material and the isolated product of the first reaction there are only four protons available to be measured by ^1H NMR. This is a sufficient number of protons because of their location within the molecule. Both sets of protons are within the field of influence of the newly added triflate group. Comparison of the peak locations for these two sets of protons from both the starting material and product provided the necessary evidence for chemical structure determination. The peak from the protons of the methylene group designated (a) in the spectrum shifted slightly downfield from 2.37 ppm in the starting material to 2.66 ppm in the product due to proximity to the newly added trifluoromethanesulfonic ester group. The signature peak shift occurred for the protons adjacent to the triflate group, labeled (b) in Figure 3.4, from 3.97 ppm in the starting material, 1H,1H,2H,2H-perfluoro-1-octanol, to 4.77 ppm in the reactive-ionic precursor, 1H,1H,2H,2H-perfluoro-1-octyl triflate. The chemical shift of each peak corresponds exactly to data from literature references for similar molecules.¹¹⁻¹³ The ^1H NMR spectra of the starting materials are located in the Appendix.

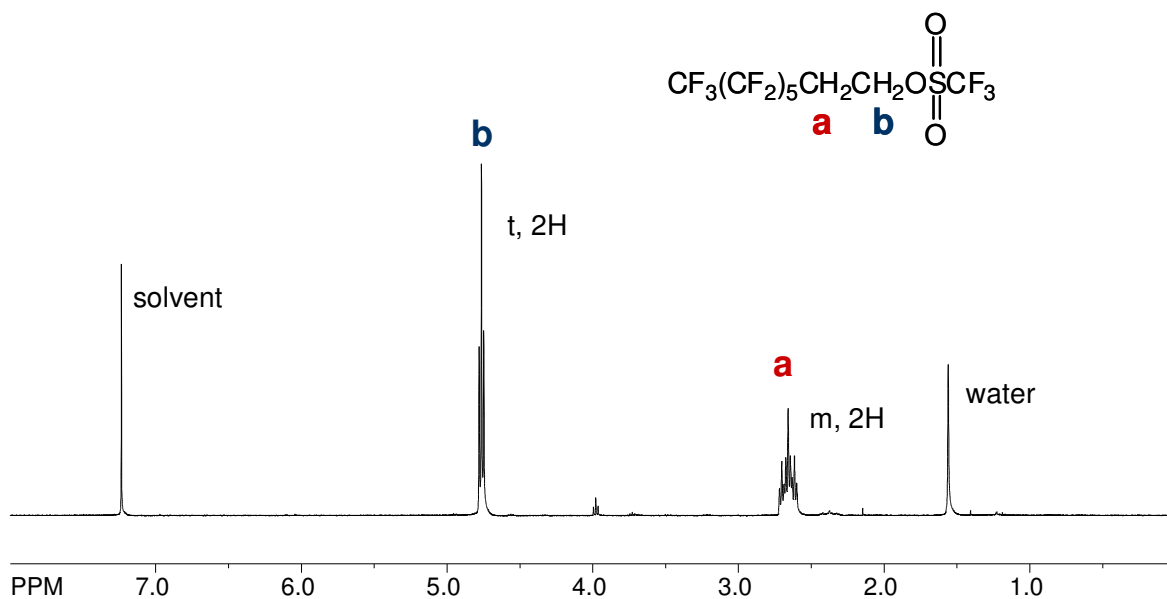


Figure 3.4 – ^1H NMR spectrum of the reactive-ionic fluorinated finish precursor, 1H,1H,2H,2H-perfluoro-1-octyl triflate, with proton labels to identify location in the structure.

3.3.2 *Synthesis and Characterization of Reactive-Ionic Fluorinated Finish*

The second step in the reaction sequence is to form the cyclic quaternary ammonium group by reaction of 1H,1H,2H,2H-perfluoro-1-octyl triflate with *N*-phenyl pyrrolidine. The cyclic amine acts as a nucleophile to displace the triflate group in a nucleophilic substitution, $\text{S}_{\text{N}}2$, reaction thus forming a cyclic quaternary ammonium group on the end of the perfluorinated alkyl chain. The general scheme for the second reaction is shown in Figure 3.5. The crude product from the first reaction was used without further purification in the second step.

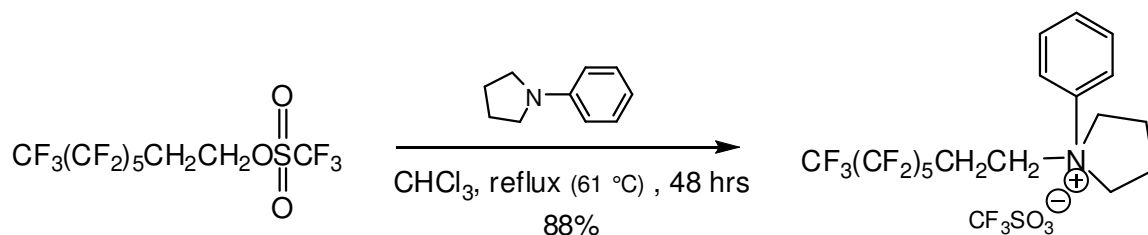


Figure 3.5 – General reaction scheme for the formation of the cyclic ammonium group by reaction of 1H,1H,2H,2H-perfluoro-1-octyl triflate with N-phenyl pyrrolidine.

Aminomethylated-PS was added to the flask after 48 hours in order to remove any unreacted triflate material. The primary amines on AM-PS are much more reactive towards the perfluorinated alkyl triflates than the tertiary amine of NPP, thereby covalently binding the unreacted starting material to the insoluble polymer support. After 1 hour, the contents of the flask were filtered and the solvent removed by rotary evaporation. This afforded a light green, waxy solid before purification due to residual NPP in the product. The crude product was fully soluble in dichloromethane. The reactive-ionic target compound was insoluble in carbon tetrachloride, whereas only residual starting material, NPP, was soluble in carbon tetrachloride. For this reason, the reactive-ionic fluorinated finish was purified by repeated precipitation from CH_2Cl_2 into CCl_4 . The purified product was recovered as a bright white, waxy solid in 88% yield.

The ^1H NMR spectrum of the purified RI-F finish is shown in Figure 3.6. The first item of importance in the spectrum is the absence of the peak at 4.77 ppm representing the protons on the methylene group adjacent to the triflate in the starting material. This confirms that there is no unreacted triflate starting material remaining in the purified product which is expected since AM-PS was used to remove the unreacted

material. This same group, labeled (c) in the figure below, now overlaps with peaks from the protons of the α -ring carbons labeled (e) at approximately 4.2 ppm. The peaks from the protons of the β -ring carbons, labeled (d), are split due to conformational effects and reside at 2.0 and 2.4 ppm. As with other reactive-ionic products, the protons of the α -ring carbons, labeled (e), are not always split.¹⁴ The most compelling evidence that the quaternary ammonium molecule was formed is the clustering and downfield shift of the aromatic protons from NPP which is a well known characteristic of reactive-ionic molecules of this type.¹⁵ The five phenyl protons, labeled (a) in Figure 3.6, are tightly centered around 7.6 ppm in the cyclic ammonium salt compared to peak locations of 6.6 ppm and 7.3 ppm in the starting material NPP.

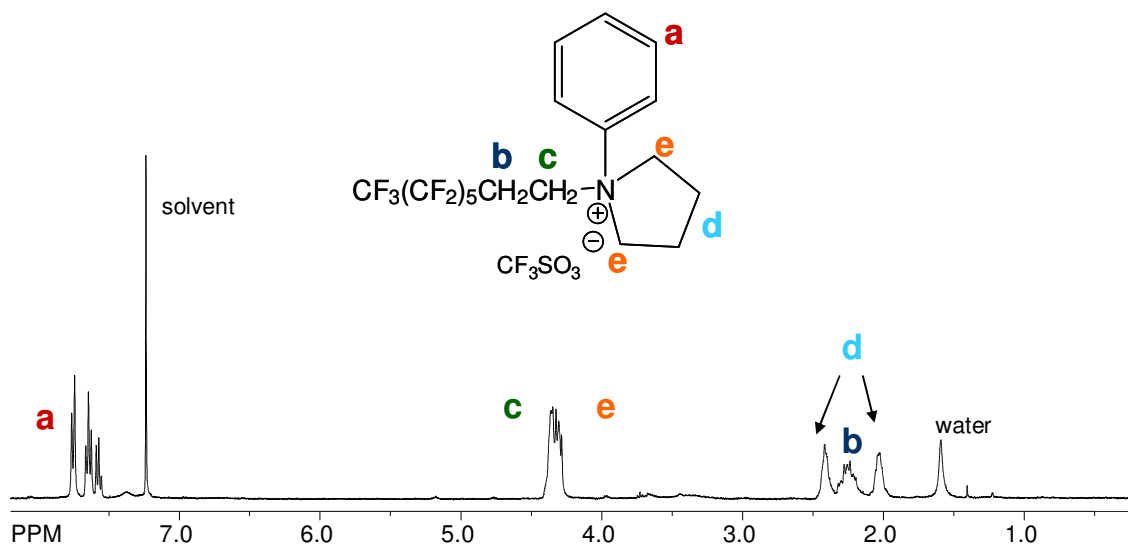


Figure 3.6 – ¹H NMR spectrum of the reactive-ionic fluorinated finish with proton labels to identify corresponding location in the structure.

3.3.3 *Application of Reactive-Ionic Fluoro-finish to Cationic-Dyeable Nylon Carpet*

The first step in the application of the reactive-ionic fluorinated finish involved the deprotonation of the acid chain ends of the cationic-dyeable nylon to form carboxylate anions. The cationic-dyeable nylon carpet sample was placed in an aqueous NaOH bath at a pH of 10. The deprotonated nylon carpet sample was rinsed in deionized water to remove any residual base and then dried in a vacuum oven at 40 °C. The carpet sample was then placed in a 0.1% (w/v) solution of the RI fluorinated finish in a 3 parts THF to 2 parts deionized water system. Although the reactive-ionic fluorinated finish is soluble in pure THF, DI water was added to the solution to reduce the solubility of the RI molecule. The 3:2 ratio of THF to water is nearly the highest water content allowed before precipitation of the RI molecule from the solution. At this point, through an ion-exchange reaction, ionic bonds are formed between the reactive-ionic finish (cations) and the carboxylate groups (anions) of the cationic-dyeable nylon. In this process, the triflate anion, originally part of the cyclic ammonium salt, is discharged and solvated by the co-solvent system. After allowing three hours, for the ion-exchange reaction at ambient temperature, the sample was removed from the processing bath, rinsed with DI water and then placed in a vacuum oven at 80 °C to initiate the covalent fixation step. Upon removal from the vacuum oven the sample was rinsed with copious amounts of THF to remove any unfixed material. A schematic of the ring-opening, covalent fixation step of the RI-F finish on a nylon surface is shown in Figure 3.7.

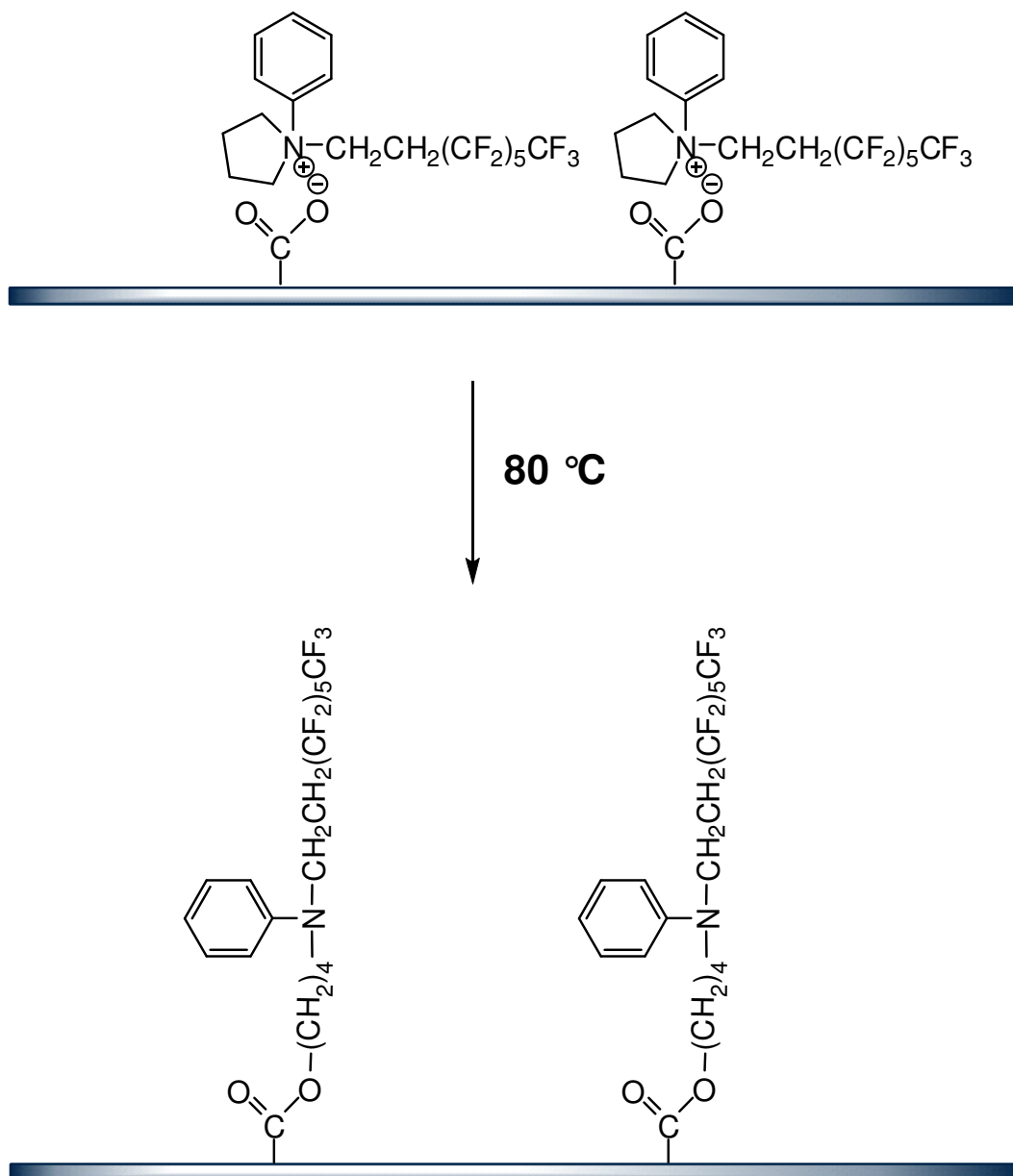


Figure 3.7 – Diagram depicting the ionic assembly of the reactive-ionic fluorinated finish on a nylon surface containing carboxylate groups and subsequent covalent fixation at 80 °C.

3.3.4 *Evaluation of the RI-F Surface-Modified Carpet*

The first assessment of the surface-modified, cationic-dyeable nylon carpet involved a water drop penetration test to evaluate the surface hydrophobicity. Application of the RI-F finish to the rough carpet fibers should act to create a highly hydrophobic surface which repels water droplets and prevents the droplets from penetrating down into the fiber tufts. Direct Red 80 dye was added to DI water in order to provide color contrast between the water droplet and the fiber surface. Three different samples were tested: a cationic-dyeable nylon carpet sample which had not been treated, a carpet sample treated with the RI-F finish and covalently fixed at 80 °C and a carpet sample that had been immersed in the RI-F bath but not heated to induce covalent fixation. All three samples were subsequently rinsed with THF and dried before testing.

The only sample that showed water-repellent properties was the RI-F surface-modified carpet. A drop placed on the carpet surface did not penetrate the top of the fiber tufts and remained in place for over two hours. Upon sitting overnight, the water in the drop evaporated leaving a crusty dye residue on top of the carpet fibers. Digital photos of a water drop containing red dye sitting atop the RI-F surface-modified carpet fibers are shown in Figures 3.8 and 3.9. The surface was in fact so hydrophobic that the water drop could be rolled around on top of the tufts by manipulating the horizontal plane of the sample. The drop was then removed by placing an absorbent paper towel on the carpet surface after which the fibers showed no evidence of having been in contact with a red dye. The nylon fiber surfaces appeared bright white with no traces of red dye. Evidence that a covalent bond was formed between the RI-F finish and the nylon carpet exists in the fact that the finish could not be removed by repeated THF extractions.



Figure 3.8 – Photo of a drop of DI water containing Direct Red 80 dye sitting atop a cationic-dyeable nylon carpet sample which had been surface-modified with the reactive-ionic fluorinated finish. (Elapsed time = 1 minute)



Figure 3.9 – Close-up of the same drop sitting on the RI-F surface-modified carpet sample. (Elapsed time = 60 minutes)

The results of the water drop penetration test on the untreated and unfixed carpet samples were dramatically different from those with the RI-F modified sample. The surface of the cationic-dyeable fibers which were treated with the RI-F finish and then extracted with solvent before fixation offered no resistance to water penetration, absorbing the water drops almost instantaneously. A covalent bond was obviously not formed during ionic assembly of the unfixed sample since the RI-F material was removed by rinsing with THF. An untreated carpet sample had similar results. The time for water penetration was less than one second for both sample types. A digital photograph of an untreated cationic-dyeable nylon which had been tested with a water drop containing red dye is shown in Figure 3.10.



Figure 3.10 – Photo of a drop of DI water containing Direct Red 80 dye which has penetrated the tufts of an untreated cationic-dyeable carpet sample. (Elapsed time = < 1 minute)

In order to further assess the surface properties of the RI-F-modified cationic-dyeable nylon carpet, a stain-resistance test loosely based on AATCC Test Method 175-2003 was performed. The AATCC test method applies to acid dye resistance of regular-dyeable nylon treated with a combination of stainbocker (ionomer) and fluoroalkyl finishes. A modified and an unmodified sample were both immersed 1 cm into double-strength cherry Kool-Aid[®] at 60 °C for 1 minute. The samples were then removed, rinsed with cold water for 30 seconds and dried at 60 °C. The samples, after testing, are shown in Figure 3.11.



Figure 3.11 – Cationic-dyeable carpet samples subjected to stain-resistance test. Immersed 1 cm from bottom of sample which relates is about 2 rows of tufts. (LEFT): Unmodified sample (RIGHT): RI-F-modified sample

When placed in the bath the fibers of the unmodified sample instantly colored and the liquid began wicking up through the tufts above the level of the liquid. Upon rinsing, a good portion of the dye solution was removed and some staining occurred—both above and below the immersion line. Staining was minimized by the fact that cationic-dyeable nylon was used. The limited number of amine end groups in cationic-dyeable nylon relates to fewer binding sites for acid food dyes—the colored component of Kool-Aid[®] mix. Regular nylon fibers stain a deep pink color when subjected to the test. The RI-F-modified sample showed little evidence of wetting and absolutely no wicking of the liquid when placed in the dyebath. Upon rinsing the modified sample, all of the dye liquor was rinsed away and there was a very small amount of staining that occurred below the immersion line. The results of this test indicate that the RI-F treatment imparts a high degree of acid dye stain-resistance to nylon fibers.

3.4 CONCLUSIONS

A RI fluorinated finish was prepared by triflation of 1H,1H,2H,2H-perfluoro-1-octanol and subsequent substitution with *N*-phenyl pyrrolidine via a S_N2 reaction. The resulting quaternary ammonium compound was purified by precipitation from dichloromethane into carbon tetrachloride and then characterized by ¹H NMR spectroscopy. The reactive-ionic fluorinated finish was then successfully applied to a cationic-dyeable nylon carpet sample by ionic assembly of the cationic finish with the carboxylate groups of the nylon fibers followed by covalent fixation at 80 °C. The surface was characterized by being subjected to a water drop penetration test. The nylon fiber surface went from completely wetting in the untreated sample to a highly

hydrophobic surface capable of repelling a water drop and preventing penetration of tufts in the sample treated with RI-F. The finish was indeed permanent because the finish could not be removed from the treated sample by rinsing with THF, whereas, the sample that was treated with RI-F, left unfixed and then rinsed with THF exhibited surface behavior similar to that of the untreated sample. The stain-resistance tests indicate that the RI-F treatment deters acid food dye staining of nylon by creating a surface that resists wetting and wicking.

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CHAPTER 4

SYNTHESIS, CHARACTERIZATION AND APPLICATION OF A REACTIVE-IONIC CHROMOPHORE (DYE)

4.1 INTRODUCTION

To overcome some of the processing limitations and environmental problems associated with traditional reactive dyeing, a reactive-ionic chromophore (dye) has been prepared. Traditional reactive dyes have a relatively-low affinity for cellulose due to the fact that both the dye and the substrate in water carry negative charges. To overcome this electro-kinetic potential, copious amounts of salt are added to traditional reactive dyebaths to increase the ionic strength of the solution, thus aiding exhaustion of the dye onto the fiber. As a consequence of having to overcome the electrical double layer and problems associated with dye hydrolysis due to dyeing in basic conditions, reactive dyebath exhaustion is low. This is not only cost ineffective but also creates a large amount of chemical waste, in the form of unused dye and salt, which must be removed from the effluent to avoid the environmental concerns of discharging into the fresh water supply.

The reactive-ionic dye prepared in this chapter overcomes these limitations by utilizing complementary ionic interactions between the positively-charged dye molecule and the negatively-charged surface to create a driving force for the dye to leave the processing bath and adsorb on the fiber. Conversion of the ionic bond to a covalent bond

at elevated temperatures creates a permanent link between dye and fiber resulting in the superior wash fastness attributed to traditional reactive dyes.

4.1.1 Material Selection

The search for the starting material for the reactive-ionic dye synthesis was crucial to the success of the project. There were two important criteria that the successful compound must have met to be chosen. The final reactive-ionic dye should be water soluble; however, the starting material should contain no ionic water-solubilizing groups like sodium sulfonates, which might interfere with the synthesis or pose a problem later by creating a zwitterionic product. The synthetic plan included nucleophilic substitution reactions, thus the starting material needed to contain a reactive group, preferably a hydroxyl group, which was not part of the conjugated, aromatic system of the chromophore. To make the subsequent synthesis as simple as possible, the starting material should contain only the single reactive group, not a multitude.

To reduce the number of synthetic steps in RI-dye synthesis, the decision was made to choose the starting material from a commercially-available textile dye or pigment. The first requirement of the starting material, the absence of anionic solubilizing groups, quickly removes several entire dye classes from the list of possible candidates. Acid, direct and reactive dyes inevitably contain numerous sodium sulfonate groups to impart water solubility. Vat dyes in their oxidized state are generally large, bulky, water-insoluble molecules that would be very difficult to make water soluble through the incorporation of a single cationic center. Disperse dyes and solvent dyes represent the dye classes which offer the most promising candidates for use as starting

materials in the reactive-ionic dye synthesis. Both dye classes are made up of relatively small azo- or anthraquinone-type chromophores with simple molecular structures, and they possess no charged groups such as sulfonates.

An exhaustive search of dye structures in the Colour Index¹ led to the selection of a subset of dyes that matched the required criteria. The best possible candidates were all monoazo dyes of the arylamine variety (Colour Index Numbers 11000-11230) including both disperse and solvent dyes. Some of the possible candidates included the following: C.I. Disperse Orange 5; C.I. Disperse Red 1; C.I. Disperse Red 13; C.I. Disperse Violet 12; C.I. Solvent Yellow 58; and C.I. Disperse Red 19. The common structural feature among all of the above dyes was the presence of one or two ethanol groups substituted onto an aryl nitrogen atom. This provided a reactive hydroxyl group isolated from the aromatic system by several methylene groups. The best possible choice for the starting material was C.I. Disperse Red 1, 4-[N-(2-hydroxyethyl)-N-ethylamino]-4'-nitroazobenzene, shown in Figure 4.1. The structure of DR1 is quite simple, containing only a nitro substituent on the azo chromophore. This group has an ionic resonance structure which will help aid water solubility but should not interfere with the synthetic scheme. In addition to having a simple structure and containing the preferred reactive group, DR1 is readily available from several commercial suppliers.

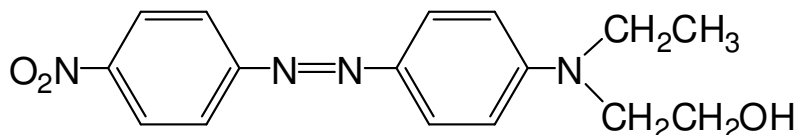


Figure 4.1 – The chemical structure of C.I. Disperse Red 1 dye—the starting material for the reactive-ionic chromophore.

In keeping with the procedure used to prepare the RI-wax finish and the RI-F finish, the original plan was to incorporate a triflate leaving group on DR1 via reaction with triflic anhydride. However, due to multiple nucleophilic groups within the DR1 structure and the extremely high reactivity of triflic anhydride, a series of side products were formed during the reaction. For this reason, the triflation of DR1 using triflic anhydride was abandoned.

Several groups have incorporated the tosylate leaving group into the structure of DR1 for subsequent nucleophilic substitution reactions.²⁻⁵ Although the tosylate group is not as good of a leaving group as the triflate group, it has been shown that tosylate can be displaced by quinuclidine in an S_N2 reaction at elevated temperatures.⁶ Thus, quinuclidine was chosen as the cyclic tertiary amine starting material for subsequent formation of the cyclic ammonium salt of DR1 since, as was concluded earlier in this work, NPP is not capable of displacing the tosylate group. Thus, the target compound for the reactive-ionic dye is the quinuclidinium tosylate salt of DR1. The structure of which is shown in Figure 4.2.

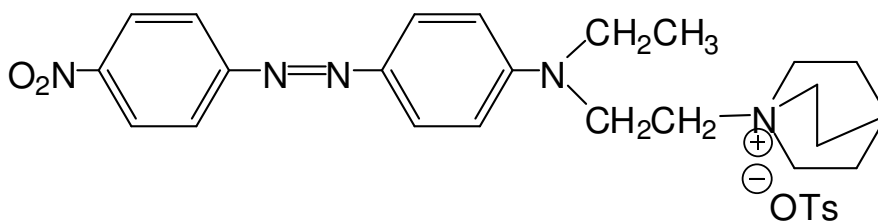


Figure 4.2 – The target chemical structure of the reactive ionic dye—a quinuclidinium tosylate salt of C.I. Disperse Red 1.

4.1.2 *Synthetic Methods*

The synthetic procedure for the preparation of the reactive-ionic dye is a two-step sequence in which DR1 is first tosylated and then reacted with quinuclidine to form the quaternary ammonium salt of DR1. As previously mentioned, several groups have tosylated DR1 to add a leaving group that can be displaced via nucleophilic substitution in a later step. Allcock and coworkers tosylated DR1 via reaction of DR1 with tosyl chloride in pure pyridine. The reaction proceeded to form DR1-tosylate (DR1-OTs) in 47.8% yield.² Hohle³ and Woo⁵ also published procedures for the tosylation of DR1 using similar reaction conditions to Allcock but with different workups; however, the yields were similarly low, 47% and 50% respectively. A different procedure for the tosylation of DR1 was published by Liu et al. in which DR1 was reacted with tosyl chloride using triethylamine as base in dichloromethane. The polar, aprotic solvent helped to increase yields of DR1-OTs up to 85%.⁴ A slightly different procedure for the tosylation of DR 1 was adopted from that of Liu et al. for the purpose of this work.

Quinuclidine has seldom been used as a nucleophile to form quaternary ammonium groups; however, it has been done. Robiette et al. reacted quinuclidine with substituted benzyl chlorides to form aryl-stabilized ammonium ylides.⁷ Bhat and Maitra formed cationic bile salts via reaction of iododeoxycholine with numerous tertiary amines including quinuclidine.⁸ The reactions involved displacement of an iodide ion during the formation of the cationic group. The reaction with quinuclidine proceeded at reflux in acetonitrile to 70% yield after purification. Considering tosylate is a better leaving group than iodide, formation of the RI-dye via reaction of DR1-OTs with quinuclidine was considered viable. In fact, Watson formed a quinuclidine-

functionalized polystyrene molecule by reaction of α,ω -ditosyl-PS with quinuclidine at 90 °C in toluene with 83% yield.⁶ A procedure similar to that used by Watson was adopted for the formation of the RI-dye from DR1-OTs and quinuclidine.

4.2 EXPERIMENTAL SECTION

4.2.1 *Materials*

All reagents were used without further purification unless otherwise specified. C.I. Disperse Red 1 (50% dye content) was purchased from MP Biomedical. Acetonitrile (CH₃CN, anhydrous) and *p*-toluenesulfonyl chloride (tosyl chloride, TsCl) were purchased from ACROS Organics. TsCl was dried in a vacuum oven at 40 °C for 24 hours prior to use. Triethylamine (Et₃N), dichloromethane (CH₂Cl₂, anhydrous, 99.9%), methyl sulfoxide-*d*₆ (DMSO-*d*₆) and quinuclidine (97%) were purchased from Aldrich Chemical Co. Hydrochloric acid (HCl), sodium bicarbonate (NaHCO₃), magnesium sulfate (MgSO₄, anhydrous), methyl sulfoxide (DMSO, 99%), water (deionized, ultra-filtered), tetrahydrofuran (THF, 99%) and sodium hydroxide (pellets) were purchased from Fisher Scientific. Chloroform-*d* (CDCl₃) was purchased from Cambridge Isotope Laboratories, Inc. Nylon 6,6 film was graciously supplied by DuPont Canada. Cellophane film was purchased from Fisher Scientific. Woven nylon 6 fabric, bleached cotton print cloth, woven silk fabric and multi-fiber test fabric were purchased from TestFabrics Inc. Regular-dyeable nylon and cationic-dyeable nylon carpet yarns were supplied by the E.I. DuPont Co.

4.2.2 Instrumentation

¹H NMR spectra were measured on a Bruker AMX 400 spectrometer in methyl sulfoxide-*d*₆ (DMSO-*d*₆) and chloroform-*d* (CDCl₃) with concentrations of approximately 1 wt%. Melting points were measured with a Mel-Temp melting point apparatus at a heating rate of 5 °C/min and confirmed by DSC analysis on a SEIKO 220 DSC instrument with a heating rate of 10 °C/min in a N₂ environment. Spectrophotometric analysis was performed using a ThermoSpectronic Genesys 20 UV/vis spectrophotometer with sample concentrations of 50 ppm in DMSO.

Reflectance measurements were made on a HunterLab Ultrascan XE reflectance spectrophotometer running HunterLab EasyMatchQC software with D65 light source and 10° standard observer. CIE *L*, *a*, *b*, *dE* values and spectral K/S data were automatically calculated by the software. K/S values are reported at the wavelength of minimum reflectance.

4.2.3 Purification of C.I. Disperse Red 1

Pure C.I. Disperse Red 1 was obtained by purification of 50% Disperse Red 1.² The impure material was dissolved in hot dichloromethane and the insoluble components were filtered off. The solvent was removed by rotary evaporation, and the solids were collected to yield dark red crystals of pure DR1. The crystals were dried in a vacuum oven at 40 °C for 24 h. Yield: (49%); m.p. 160-162 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.30 (d, 2H), 7.88 (m, 4H), 6.79 (d, 2H), 3.88 (t, 2H), 3.60 (t, 2H), 3.52 (q, 2H), 1.23 (t, 3H)

4.2.4 *Synthesis of Disperse Red 1-Tosylate*

Purified C.I. Disperse Red 1 (0.99 g, 3.2 mmol) and tosyl chloride (0.60 g, 3.2 mmol) were added to a clean, dry, three-neck, round-bottom flask containing a magnetic stir bar under positive nitrogen pressure. The flask was maintained at a temperature of 0 to 5 °C in an ice bath. The flask was evacuated and then charged with anhydrous dichloromethane (25 mL) via cannula. The flask was back-filled with dry nitrogen gas and left under positive nitrogen pressure. Triethylamine (0.35 g, 3.5 mmol) was added via syringe over 2 minutes while stirring. The reaction was allowed to proceed for 1 hour at which point the ice bath was removed and the contents of the flask were allowed to stir at room temperature for an additional 3 hours. Once the reaction was completed, the stir bar was removed and the contents of the flask were washed with ice water (10 mL), 2 M aqueous HCl (10 mL), ice water (10 mL) and finally a saturated, aqueous NaHCO₃ solution (10 mL). After each wash, the organic layer was removed by separatory funnel. The final organic layer was removed and dried over MgSO₄ and then filtered. The solvent was removed by rotary evaporation to yield DR1-tosylate as a dark red powder. Yield: 1.25 g (85%). m.p. 137-148 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 8.33 (d, 2H), 7.92 (d, 2H), 7.84 (d, 2H), 7.73 (d, 2H), 7.27 (d, 2H), 6.63 (d, 2H), 4.22 (t, 2H), 3.71 (t, 2H), 3.44 (q, 2H), 2.39 (s, 3H), 1.19 (t, 3H)

4.2.5 *Synthesis of Reactive-Ionic Chromophore (Dye)*

DR1-tosylate (0.90 g, 1.9 mmol) and quinuclidine (0.25 g, 2.3 mmol) were added to a clean, dry, three-neck, round-bottom flask containing a magnetic stir bar and equipped with a condensing column. The flask was evacuated then charged with

anhydrous acetonitrile (20 mL). The flask was then back-filled with nitrogen gas and lowered into an oil bath. The reaction was allowed to proceed at reflux (81 °C) for 18 hours. After 18 hours, the flask was removed from the oil bath and condensing column, and then sealed. The flask was chilled in a refrigerator for 3 hours. The contents were filtered and the precipitate washed with cold acetonitrile and collected. The bright red powder was dried in a vacuum oven at 40 °C for 24 hours. Yield: 0.81 g (73%); m.p. 233-234 °C; ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) = 8.37 (d, 2H), 7.95 (d, 2H), 7.87 (d, 2H), 7.47 (d, 2H), 7.09 (d, 2H), 6.92 (d, 2H), 3.87 (t, 2H), 3.53 (m, 8H), 3.33 (m, 2H), 2.26 (s, 3H), 2.08 (m, 1H), 1.88 (m, 6H), 1.16 (t, 3H)

4.2.6 Application of Reactive-Ionic Chromophore (Dye) to Cellophane Film

Cellophane film (2 cm x 2 cm) was placed in an aqueous NaOH bath (pH = 13). The film was allowed to stir in the base bath for 15 minutes before being removed and transferred directly to a beaker containing THF. After 2 minutes in THF, the film was removed and placed in a bath containing a 50:50 by volume mixture of THF:water with a reactive-ionic dye concentration of 0.3% (w/v). The film was allowed to stir in the dye bath for 10 minutes at room temperature. The cellophane film was then removed and rinsed with a small amount of THF:water to remove any non-adsorbed dye. The film was then placed in an oven at 120 °C for 10 minutes. One half of the film was subjected to a 15 minute boil in water and a 15 minute boil in THF. The same procedure was then repeated using pure DR1 and the reactive-ionic precursor DR1-tosylate.

4.2.7 Application of Reactive-Ionic Chromophore (Dye) to Nylon 6,6 Film

Nylon film (2 cm x 2 cm) was placed in an aqueous NaOH bath (pH = 10). The film was allowed to stir in the base bath for 15 minutes before being removed and transferred directly to a beaker containing THF. After 2 minutes in THF, the film was removed and placed in a bath containing a 90:10 by volume water:THF mixture with a reactive-ionic dye concentration of 0.3% (w/v). The nylon film was allowed to stir in the dye bath for 10 minutes at room temperature. The film was then removed and rinsed with a small amount of THF:water to remove any non-adsorbed dye. The film was then placed in an oven at 120 °C for 10 minutes. One half of the film was subjected to a 15 minute boil in water and a 15 minute boil in THF. The same procedure was repeated with a dye bath temperature of 60 °C.

4.2.8 Application of Reactive-Ionic Chromophore (Dye) to Cationic- and Regular-Dyeable Nylon Carpet Yarns

A 20-inch length of cationic-dyeable nylon carpet yarn (0.16 g) and a similar 20-inch length of regular-dyeable nylon carpet yarn (0.16 g) were placed in an aqueous NaOH bath (pH=9.5) and allowed to stir for 15 minutes. The yarns were removed and rinsed in a beaker of deionized water for 5 minutes to remove any residual base. The yarns were then placed in separate beakers containing 50 mL each of a 10% owf solution of RI-dye in distilled water. A stirring bar was added and the beakers covered. The yarns were allowed to stir overnight at room temperature. After 18 hours, the yarns were removed and rinsed well with warm tap water. The samples were then blotted dry with paper towels and placed in an oven at 120 °C for 15 minutes.

4.2.9 Application of RI-Dye to Multi-Fiber Test Fabric

Two multi-fiber fabric test strips (total weight 4 g) were placed in a dyebath containing 100 mL of DI water (liquor ratio = 25:1), 1% owf RI-dye and NaOH to a pH of 9. The dyebath was heated to 80 °C and held for 30 minutes with frequent stirring. At the end of the dyeing both strips were removed from the bath and rinsed thoroughly with warm tap water. Both strips were dried overnight at 40 °C in a vacuum oven. One strip was then placed in an oven at 120 °C for 1 hour to initiate the ring-opening, covalent fixation step.

4.2.10 Application of Reactive-Ionic Chromophore (Dye) to Nylon Fabric

A woven nylon fabric sample (1.01 g) was placed in an aqueous NaOH bath (pH=8.5) and allowed to stir for 15 minutes. The sample was removed and rinsed in a beaker of deionized water for 5 minutes to remove any residual base. The fabric was then placed in a beaker containing 40 mL of a 1% owf solution of RI-dye in distilled water. The bath was heated to 80 °C and held for 30 minutes while stirring. The sample was removed from the bath, rinsed well with warm tap water and blotted dry with paper towels. The sample was then placed in an oven at 120 °C for 30 minutes.

A separate nylon fabric sample (0.98 g) was placed in 40 mL of distilled water containing 1% owf of the reactive-ionic dye. The bath was heated to 80 °C and a 0.1 M NaOH solution in distilled water was added dropwise until the pH reached 8.5. The bath was held at 80 °C for 45 minutes while stirring. The sample was removed from the bath, rinsed well with warm tap water and blotted dry with paper towels. The sample was then placed in an oven at 120 °C for 30 minutes.

4.2.11 Application of Reactive-Ionic Chromophore (Dye) to Bleached Cotton Fabric

A bleached, desized fabric swatch of cotton print cloth (0.34 g) was placed in a beaker containing 20 mL of an aqueous bath containing the chemicals listed under Dyebath 1 in Table 4.1 below with the exception of NaOH. The bath was then heated to 80 °C and a 0.1 M NaOH solution in distilled water was added dropwise until the pH listed in Table 4.1 was reached. The bath was held at 80 °C for 45 minutes while stirring. The sample was removed from the bath, rinsed well with warm tap water and blotted dry with paper towels. The sample was then placed in an oven at 120 °C for 30 minutes. The same procedure was used to dye similar swatches (0.34 g) of the bleached cotton print cloth using Dyebaths 2-4.

Table 4.1 – Chemical composition of dyebaths used to dye bleached cotton print cloth using reactive-ionic dye.

Dyebath	1	2	3	4
NaOH (pH)	9.5	9.5	11.5	9.5
RI-Dye (% owf)	1	1	1	2
NaCl (g/L)	0	40	0	0

4.2.12 Application of RI-Dye to Silk Fabric

A sample of woven silk fabric (1 g) was placed in an aqueous NaOH bath (pH = 9) and stirred for 15 minutes at room temperature. The deprotonated sample was removed from the base bath and rinsed for 3 minutes in an excess of deionized water to remove any residual base. The sample was then placed in 50 mL of DI water containing 1% owf of the reactive-ionic dye. The dyebath was heated to 80 °C and held for 30

minutes while stirring. The dyed silk sample was then removed from the dyebath, rinsed well with warm tap water and allowed to air dry overnight. One half of the sample was then heated in an oven at 120 °C for 30 minutes to initiate covalent fixation. The process was repeated with a RI-dye concentration of 2% owf.

4.3 RESULTS AND DISCUSSION

4.3.1 Purification of C.I. Disperse Red 1 Dye

C.I. Disperse Red 1 (DR1) dye is commercially-available in two different forms: 50% dye content and 95% dye content. The balance of ingredients is made up of lignin sulfonates, which are used to help disperse the non-soluble dyes. Therefore, purification of the as-received dye was inevitable since pure starting material is required for the first synthetic step towards the reactive-ionic dye. The price of the 95% dye was much higher than that of the 50% dye mixture. Thus, considering that the purification step is straightforward and relatively inexpensive, C.I. Disperse Red 1 with 50% dye content was purchased and used in this work.

Purification of DR1 involved dissolving the as-received dye mixture in hot dichloromethane, filtration of the suspended solids and subsequent evaporation of the solvent to yield dark, red crystals of DR1. The next step in the procedure, as described by Allcock and coworkers,² was to recrystallize the crude product from a 95% ethanol solution. After recrystallizing the crude product using the filtration technique, the ¹H NMR spectra of the crude product and the recrystallized product were compared. The spectra were essentially identical; therefore, it was concluded that the recrystallization step in the published purification procedure could be abandoned for the purposes of this

work. The ^1H NMR spectrum and labeled chemical structure of purified Disperse Red 1 is shown in Figure 4.3.

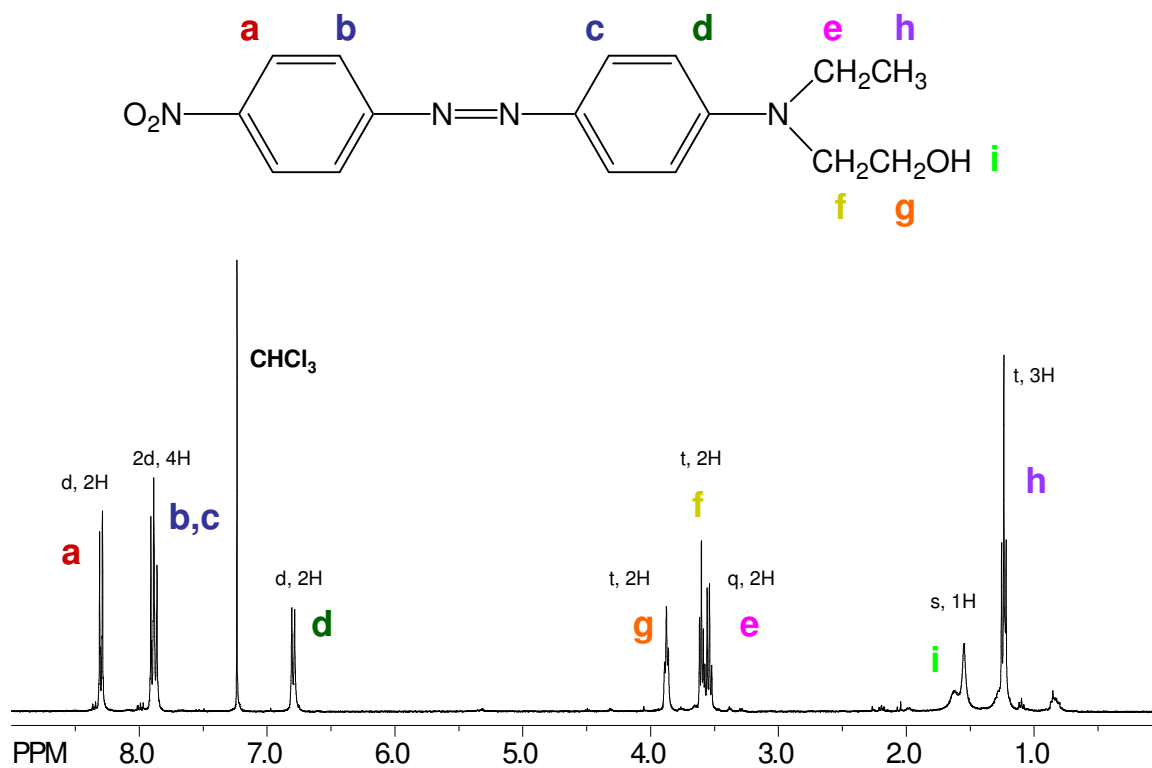


Figure 4.3 – ^1H NMR spectrum of purified C.I. Disperse Red 1 dye with peaks labeled to corresponding protons in chemical structure.

4.3.2 *Synthesis and Characterization of DR1-tosylate (reactive-ionic precursor)*

The first step in the synthesis of the reactive-ionic dye molecule was to incorporate a better leaving group than the hydroxyl group into the chemical structure. As previously mentioned, the initial attempt was to triflate DR1 via reaction with triflic anhydride. The high reactivity of triflic anhydride posed serious problems with this reaction because of the other nucleophilic groups within DR1. DR1 contains a nitro group and a tertiary amine both of which are reactive towards triflic anhydride. As a

result, several side reactions ensued. For this reason, triflation of DR1 with triflic anhydride was abandoned. Although the tosylate group is not as good of a leaving group as triflate and can not be displaced by NPP to form the quaternary ammonium group, tosylate can be displaced in the second substitution reaction by quinuclidine at elevated temperatures.⁶ The ¹H NMR spectrum of quinuclidine is located in the Appendix.

The tosylation of DR1 was accomplished via reaction of purified DR 1 with tosyl chloride (TsCl) using triethylamine (Et₃N) as a base in dichloromethane. The reaction proceeded for four hours at room temperature to form Disperse Red 1 tosylate (DR1-OTs) in 85% yield. This yield is similar to that published by Liu et al. in their work on electro-optical materials.⁴ Aqueous workup removed residual TsCl and triethylamine, as well as the ammonium salts formed during the reaction. The crude product was in the form of dark, red crystals having a melting point of 137-138 °C. The general reaction scheme for the tosylation of DR1 is shown in Figure 4.4.

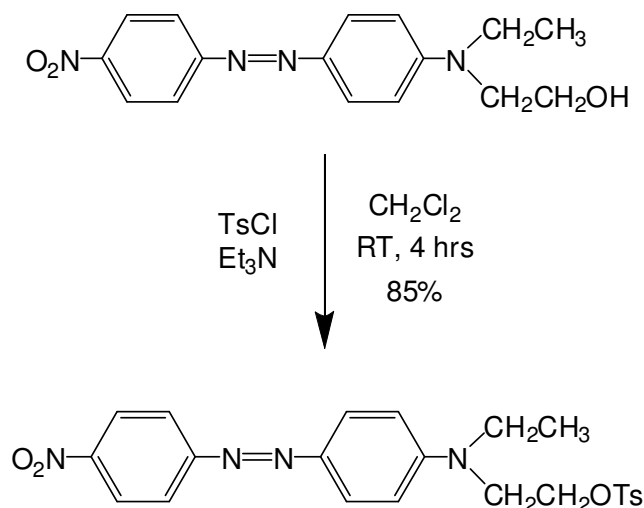


Figure 4.4 – General reaction scheme for the tosylation of Disperse Red 1 using tosyl chloride.

The crude product from the first reaction was not purified any further since the ^1H NMR spectrum showed little contamination and the measured melting range of the crude product was in line with published data. The ^1H NMR spectrum of DR1-tosylate is shown in Figure 4.5. The peak assignments are labeled on the spectrum according to the corresponding protons in the chemical structure. Peak intensity integrals relate directly to the number of protons in the structure. The peak due to the protons of the methylene group, once adjacent to the hydroxyl group in the starting material and now adjacent to the tosylate group in the product and labeled (h) in Figure 4.5, shifted downfield from 3.88 ppm in DR1 to 4.22 in DR1-OTs. The singlet peak from the three protons of the methyl group which is part of the tosyl group, labeled (k), appears at 2.39 ppm. The other protons from the tosyl group, which are part of the phenyl ring and labeled (i) and (j), appear in the aromatic proton region of the spectrum at 7.73 ppm and 7.27 ppm respectively. The chemical shift of each peak corresponds exactly to data from literature references for DR1-OTs.³ The small doublet peak located at approximately 6.8 ppm is due to residual DR1 starting material in the product. The presence of a small amount of DR1 in the crude product is inconsequential because DR1 is not reactive towards quinuclidine in the subsequent synthetic step.

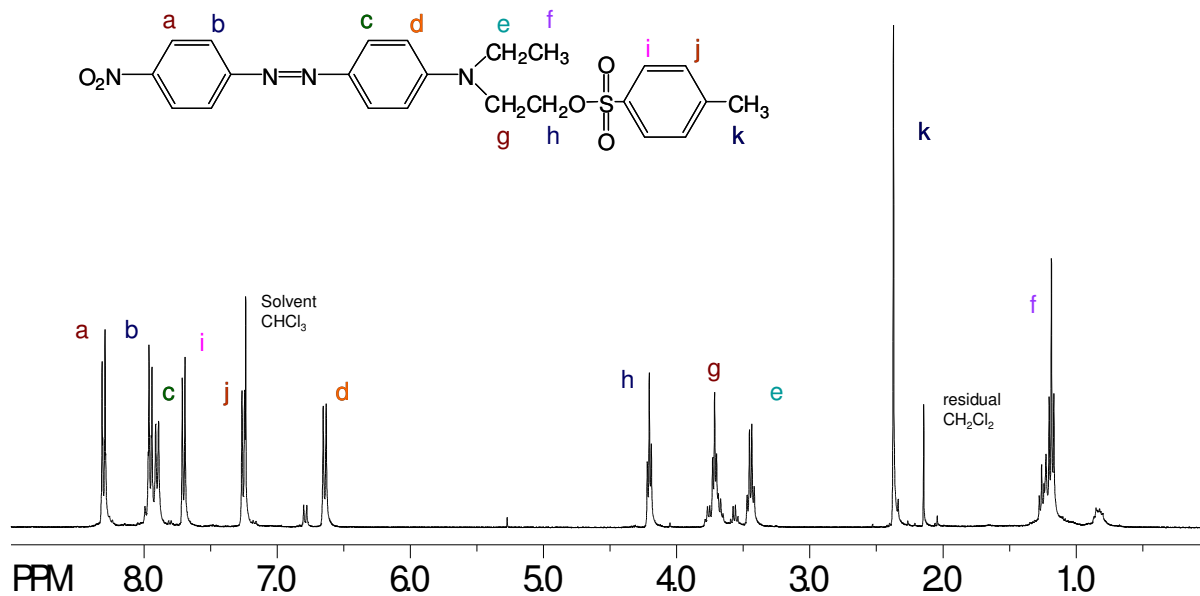


Figure 4.5 – ¹H NMR spectrum of the reactive-ionic dye precursor, DR1-tosylate, with peak labels to identify proton location within chemical structure.

4.3.3 Synthesis and Characterization of Reactive-Ionic Dye

The second step in the reaction sequence involved formation of the reactive-ionic dye via reaction of Disperse Red 1 tosylate with quinuclidine. The bicyclic amine acted as a nucleophile to displace the tosylate group in a nucleophilic substitution, S_N2 reaction, thus forming the cyclic quaternary ammonium group bridged to the chromophore. The general scheme for the reaction is shown in Figure 4.6. The crude product from the first step was used without further purification as the starting material in the second reaction.

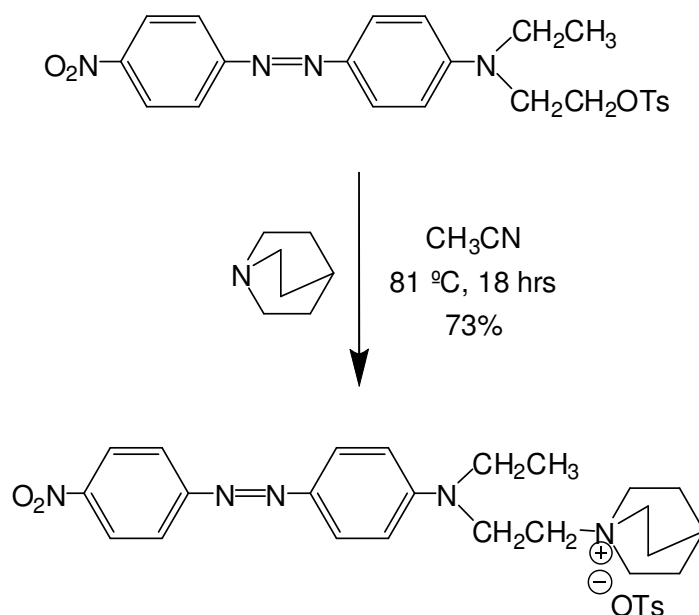


Figure 4.6 – General reaction scheme for the preparation of the reactive-ionic dye by reaction of DR1-tosylate with quinuclidine.

Acetonitrile was used as the solvent for the reaction since it was a good choice for the formation of ionic products and it had a high enough boiling point (81 °C) to initiate the substitution reaction. The reaction was allowed to proceed for 18 hours at reflux. The main advantage of using acetonitrile in this system is that the ionic product precipitates from solution upon formation, thus eliminating the need for aqueous workup and further purification of the crude product. The pure product, reactive-ionic dye, was recovered by filtration as a bright, red solid in 73% yield.

The ^1H NMR spectrum of the reactive-ionic dye molecule is shown in Figure 4.7. DMSO- d_6 was used as the solvent for NMR measurements because the reactive-ionic dye is not soluble in chloroform or any other lower boiling point, polar solvents with the exception of THF which has overlapping peaks. Due to its hygroscopic nature, DMSO

normally contains a small portion of residual water, and as a result, there is a strong water peak located at 3.34 ppm in addition to the DMSO peak at 2.50 ppm. A notable feature of the spectrum is the extremely flat baseline and the absence of any side peaks arising from contaminants or residual starting material. This is evidence of the high purity of the reactive-ionic product.

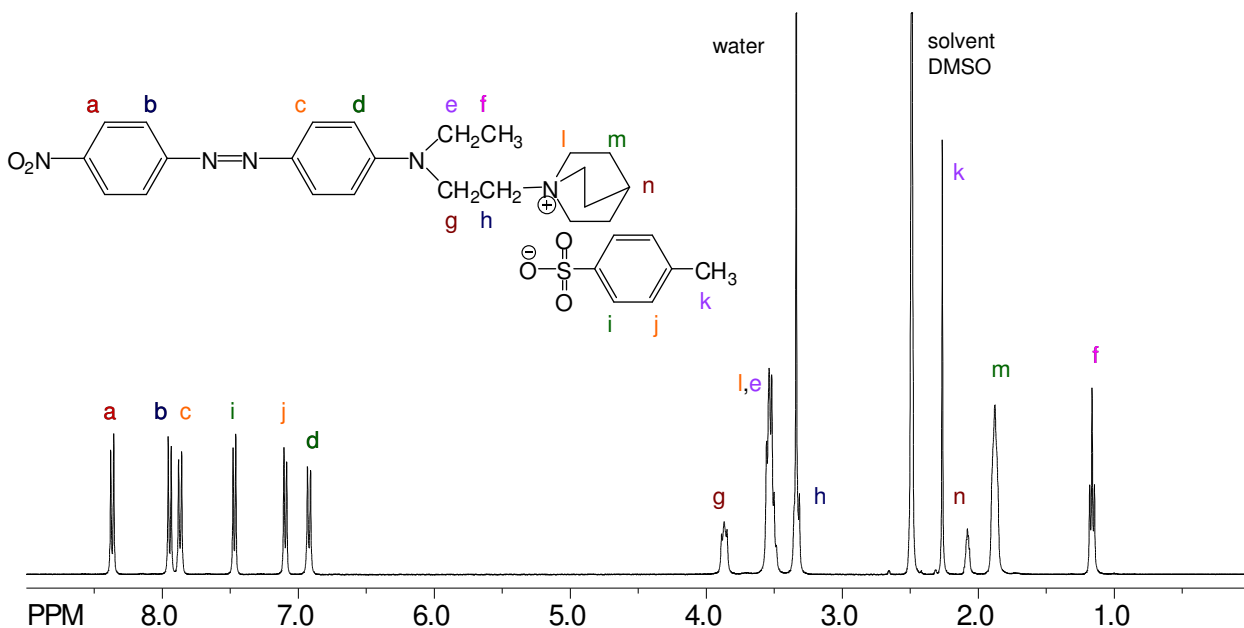


Figure 4.7 – ^1H NMR spectrum of the reactive-ionic dye with peak labels to identify proton location within the chemical structure.

One of the more prominent peak location changes is the shift of the peak due to the methylene protons adjacent to the tosylate group in DR1-OTs to the newly substituted quaternary ammonium group in the RI-dye, labeled (h) in Figure 4.7, corresponding to an upfield shift from 4.22 ppm to 3.32 ppm. Most of the aromatic proton peak locations were similar in both the starting material and the product with the exception of the peak

due to the set of phenyl protons located closest to the tertiary nitrogen bridge, (d), which shifted from 6.6 ppm in DR1-OTs to 6.9 ppm in the RI-dye. As was the case with the RI-wax and RI-F finishes, aromatic protons located within a few atoms of the quaternary ammonium exhibit a strong downfield shift due to the formation of an ionic charge and the same is true here. Further evidence of the formation of the ammonium salt is the perfect match in peak integrations between protons from both starting materials—quinuclidine and DR1-OTs including the newly formed tosylate counterion.

To the naked eye, pure DR1 crystals appear dark red with blue undertones. The RI-dye crystals are a much lighter, brighter shade of red with a hint of orange. The two materials can be seen in Figure 4.8.



Figure 4.8 – Photos of purified DR1 solids (LEFT), RI-dye solids (CENTER) and RI-dye crystals (RIGHT)

Due to the difference in appearance of the two materials, visible light absorbance measurements were made on solutions of both of these dyes in a common solvent, DMSO. The results of the absorbance measurements are shown on the graph in Figure 4.9. The wavelength of maximum absorbance, λ_{max} , of Disperse Red 1 at 50 ppm in DMSO is 520 nm. The λ_{max} for a similar solution of the RI-dye shifted approximately 40

nm towards the blue region to 480 nm. In fact, the entire absorbance spectrum for the RI-dye appears to have shifted towards the blue region. An increase in absorbance in the blue region translates to an increase in transmittance in the yellow region, which confirms the more orange appearance of the RI-dye when compared to DR1.

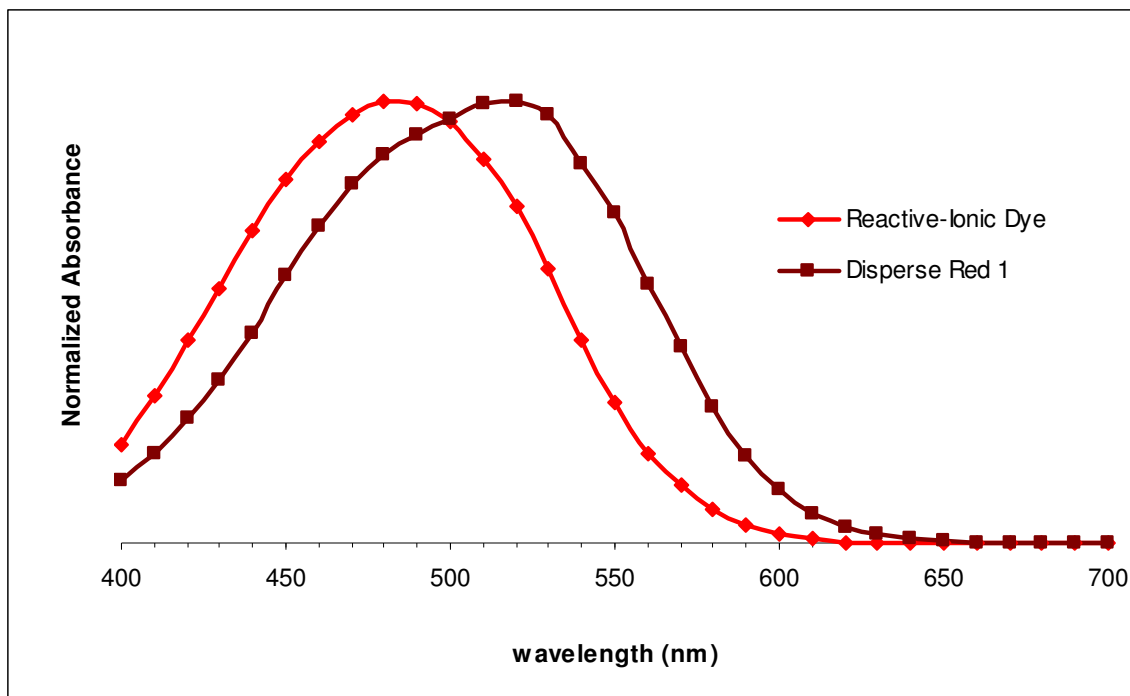


Figure 4.9 – Visible light absorbance measurements as a function of wavelength for 50 ppm solutions of Disperse Red 1 and RI-dye in DMSO. The points were measured and the lines were added to aid the eye.

Solubility characteristics of the RI-dye are of importance because the dye needs to be in solution for proper ionic assembly of the chromophore to an anionic substrate via the ion-exchange reaction. Since the RI-dye molecule contains ionic groups it would suggest that the molecule is soluble in polar solvents. The two best solvents found for the RI-dye, among common solvents, were DMSO and THF. The RI-dye was readily soluble

in both solvents at room temperature at levels up to 10 mg/mL which were the highest measured due to a limited amount of RI-dye. Due to the inherent high boiling point of DMSO, it is not a very good solvent to be used in processing since it is difficult to remove via air- or vacuum-drying. THF is a much better candidate due to its lower boiling point; however, the use of organic solvents in processing leads to issues with health and environmental safety.

The RI-dye molecule was designed to be partially water soluble. DR1, while not being highly soluble in water, contains a nitro group in the chemical structure which makes it at least somewhat soluble in water due to the ionic resonance structure of the nitro group. Incorporating a formal ionic charge into the structure of the RI-dye was projected to increase water solubility. The RI-dye does indeed exhibit limited solubility in water with no other chemical auxiliaries present like dispersing agents. In fact, the RI-dye is soluble in distilled water at levels approaching 0.5 mg/mL at room temperature. This value can be increased at higher temperatures. Even though the RI-dye is not readily water soluble like most textile dyes which contain numerous sodium sulfonate groups to aid solubility, it can still be effective in wet processing because as RI-dye is exhausted from the bath onto the substrate the effective amount of material in solution will be replenished by non-dissolved material present in the system. Therefore, as long as there is a driving force for dissolved dye to leave the bath and assemble on the substrate, e.g. ionic interactions, then the dye needs not be fully dissolved at the start of processing for proper buildup of the chromophore on the substrate to take place. In other words, a large concentration gradient is not required for proper dyeing in this system.

4.3.4 *Application of RI-Dye to Cellophane Film*

To quickly assess the dyeing characteristics of the RI-dye and to serve as a proof of concept for the RI process with chromophores, cellophane and nylon films were chosen as the first substrates onto which the RI-dye would be applied. Working with films removes many of the processing variables attributed to the dyeing of fibers and, to a higher degree, fabrics.

A batch processing sequence was developed in order to sequentially deprotonate the hydroxyl groups of the cellophane film, rinse away any residual base, adsorb the RI-dye on the substrate through ionic interactions and finally create a permanent bond between the two via covalent fixation at elevated temperatures. First, the films were placed in an aqueous NaOH bath with a pH of 13 for 15 minutes to deprotonate the cellulose chain. The films were then removed and rinsed with THF to remove any residual base. The films were then placed in a bath containing a 50:50 (v/v) mixture of THF and water with a reactive-ionic dye concentration of 0.3% (w/v). The films were allowed to stir at room temperature for 10 minutes. The samples were then removed from the processing bath and rinsed quickly with water to remove any non-adsorbed material. The dyed films were then placed in an oven for 10 minutes at 120 °C to initiate covalent fixation. A similar procedure was followed for dyeing cellophane films with both the original starting material, DR1, and the reactive-ionic precursor, DR1-OTs. The dyed samples can be seen in Figure 4.10. The sample which had been dyed with the RI-dye, labeled (a), was a deep red color with excellent levelness. The two samples which were dyed with DR1 and DR1-OTs, labeled (c) and (d) respectively, showed no signs of dyeing and only a minimal amount of staining. In order to assess the permanence of the

bonds between the RI-dye and cellophane film, a RI-dyed specimen was subjected to a 15 minute boil in water followed by a 15 minute boil in THF. The extracted sample, labeled (b) in Figure 4.10, displayed a small amount of color loss compared to the unextracted sample. This can be attributed to the removal of unfixed dye from the cellophane film.

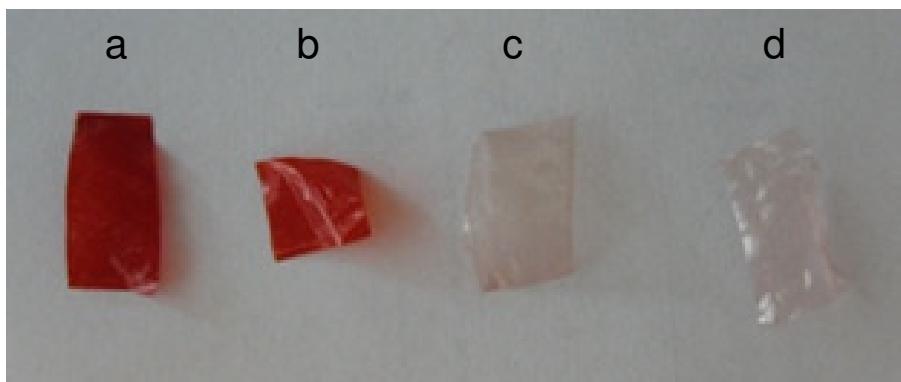


Figure 4.10 – (a) Cellophane film dyed by reactive-ionic dye. (b) Cellophane film dyed by reactive-ionic dye after boiling in water and then THF. (c) Cellophane film dyed by DR1. (d) Cellophane film dyed by DR1-OTs.

4.3.5 Application of RI-Dye to Nylon 6,6 Film

After confirmation that the RI process was effective on the hydroxyl-containing cellophane film, nylon 6,6 film was dyed to assess the effectiveness of the RI-dye on a carboxyl-containing substrate. A step-wise batch procedure, similar to that of the cellophane application, was used to dye the nylon films. The samples were placed in an aqueous NaOH bath, this time with a pH of 10 since the carboxylic acid protons of nylon are more easily removed than the hydroxyl protons of cellulose. Subsequent rinsing, ionic assembly in a THF:water mixture at room temperature and covalent fixation in an oven at 120 °C afforded dyed a nylon film sample that was a dark orange color with

excellent levelness. Finally, the sample was extracted with water and THF in order to remove any unfixed material. The entire process was repeated; however, this time the dyebath temperature was held at 60 °C. The sample dyed at 60 °C was a much deeper red than the sample dyed at room temperature. Extracted samples from both dyeings are shown in Figure 4.11.

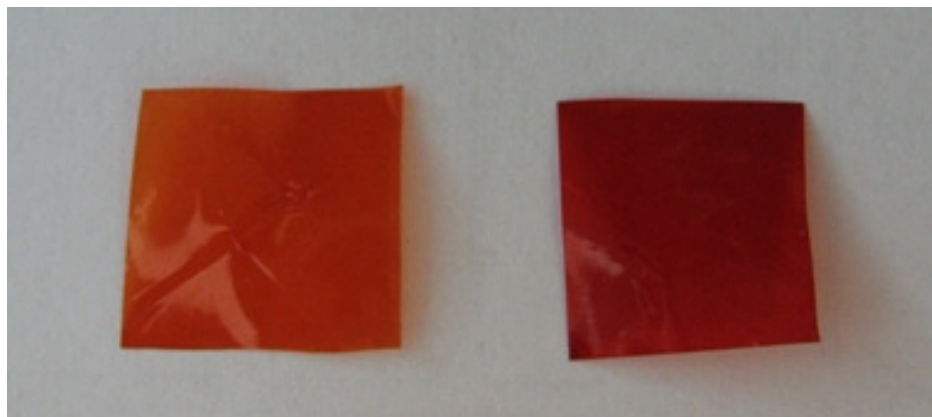


Figure 4.11 – (LEFT) Nylon 6,6 film dyed by reactive-ionic dye at room temperature. (RIGHT) Nylon 6,6 film dyed by reactive-ionic dye at 60 °C. After dyeing, the samples were extracted for 15 minutes in THF at the boil.

The results from the dyeing of cellophane film and nylon 6,6 film with RI-dye by the described procedure confirm that the RI process is effective for the dyeing of cellulose and polyamides. The proposed mechanism for ionic assembly and covalent fixation of the RI-dye to a nylon surface is depicted in Figure 4.12. Upon activation by elevated temperatures, the electrons from the carboxylate anion attack the α -carbon of the cyclic ammonium group causing a ring-opening reaction which covalently bonds the RI-dye to the nylon substrate.

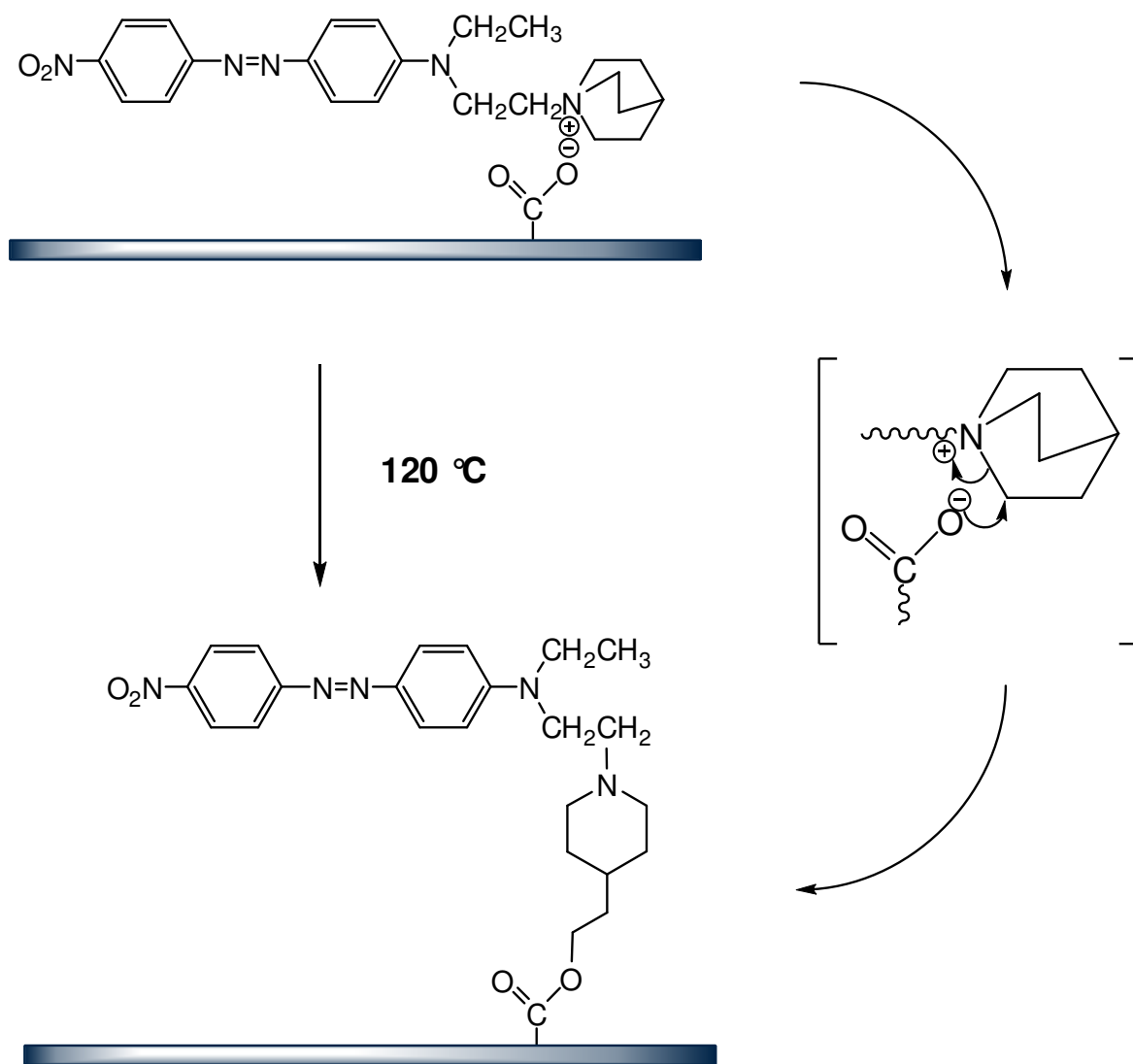


Figure 4.12 – Diagram depicting the ionic assembly of the reactive-ionic dye on nylon containing carboxylate groups and subsequent fixation at 120 °C.

4.3.6 *Application of RI-Dye to Cationic- and Regular-Dyeable Nylon Carpet Yarns*

Up to this point in the research, it had been proposed that the RI-dye assembles on the surface of nylon via ionic interactions between the cationic cyclic ammonium group of the RI-dye and the anionic carboxylate groups of nylon. Another logical possibility exists where the amine end groups of nylon, acting as nucleophiles, attack the cyclic ammonium group thus causing the ring to open and fixation occur. In an effort to clarify the method by which the RI-dye assembles, two different types of nylon carpet yarns were dyed with the RI-dye. One type of nylon yarn was regular dyeable nylon in which the end groups of the polymer chain have a nearly equivalent number of carboxylic acid groups and amine groups. The other type of nylon carpet yarn used was cationic-dyeable nylon in which the majority of chain ends are of the carboxylic acid variety. Therefore, according to RI theory, the cationic-dyeable nylon yarns should dye to a deeper shade than the regular nylon yarns with all other dyeing parameters equal.

A sample of each type of yarn was deprotonated in an aqueous NaOH bath (pH = 9.5) and then placed in separate beakers containing 50 mL each of a 10% owf solution of RI-dye in distilled water. The samples were allowed to sit overnight in the dyebaths at room temperature. At the end of the dyeing, the yarns were removed, rinsed well with warm tap water and then placed in an oven at 120 °C for 15 minutes. The samples are shown in Figure 4.13. Indeed, the cationic-dyeable carpet yarn dyed to a much deeper red than did the regular nylon yarn. This work confirms that the RI-dye adsorbs on nylon and reacts with carboxylate groups present, not the amine groups, and that an increase in the number of available dye sites increases the permissible depth of shade.

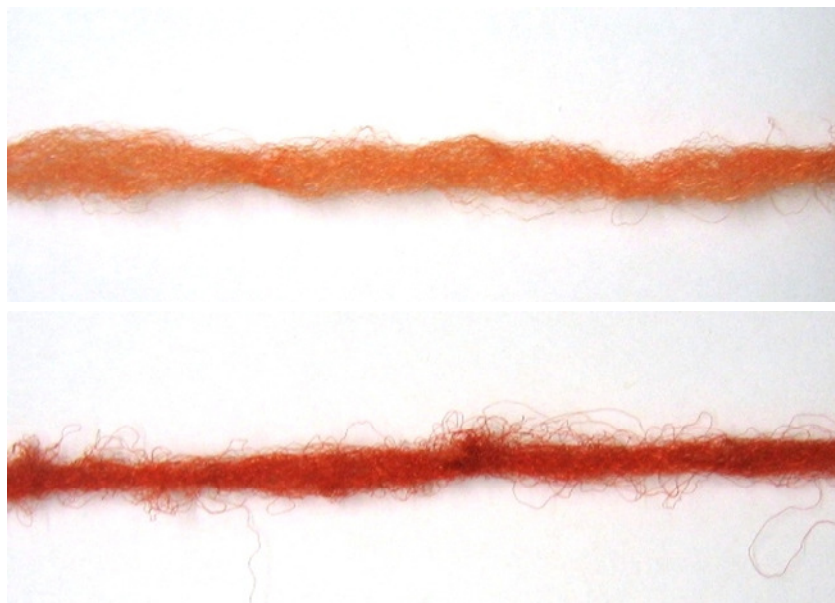


Figure 4.13 – (TOP) Regular-dyeable nylon carpet yarn dyed with RI-dye at 25 °C.
(BOTTOM) Cationic-dyeable nylon carpet yarn dyed with RI-dye at 25 °C.

4.3.7 Application of RI-Dye to Multi-Fiber Test Strip

In an effort to determine the different types of fibers that can be dyed using the reactive-ionic process, a multi-fiber test fabric was dyed with RI-dye. The test fabric contained the following types of fiber: cellulose acetate, modacrylic, cellulose triacetate, cotton, acrylic (Creslan 61), polyester, cationic-dyeable polyester, nylon 6,6, acrylic (Orlon 75), silk, polypropylene, rayon and wool. The multi-fiber strip was placed in a bath with a liquor ratio of 25:1, RI-dye concentration of 1% owf and a pH of 9 with NaOH. The sample was dyed for 30 minutes at 80 °C, removed from the dyebath, rinsed thoroughly with warm tap water and blotted dry with paper towels. The RI-dyed multi-fiber strip is shown in Figure 4.14.



Figure 4.14 – A multi-fiber fabric test strip dyed with 1% owf RI-Dye at 80 °C for 30 minutes.

The fibers that showed the highest affinity for the RI-dye were the polyamides—nylon, silk and wool. This is indicative of the high number of carboxyl groups found within the fiber structure of these polyamides. The RI-dye also had good affinity for the acrylics. This result was not surprising since most acrylics are normally dyed with cationic dyes. Commercial acrylic fibers contain acidic dye sites, presumably sulfonic acid groups, which result from the redox catalysts, potassium persulfate and sodium bisulfite, used in the polymerization.⁹ Therefore, the RI-dye performs as a normal basic

dye when applied to acrylics as it is only being held by ionic interactions. Another example of a fiber that is dyed by the RI-dye in a strictly ionic process is cationic-dyeable polyester. Cationic-polyester (Dacron 64) is polymerized with sodium sulfonate containing comonomers which imparts dyeability with cationic dyes. The sodium sulfonate groups can carry a formal negative charge in solution which bond ionically with the RI-dye; however, the groups do not possess enough nucleophilic character to initiate the ring-opening reaction.

One surprising feature of the RI-dyed multi-fiber strip is the minimal coverage on the cotton portion. One possibility for the low levels of adsorption is the lower pH of 9 used in the processing step. A higher pH would deprotonate more of the hydroxyl groups thus creating more potential dye sites.

As expected, the RI-dye was ineffective at dyeing both polyester and polypropylene fibers. Neither of these fiber types have functional groups present in the structure that would create a driving force for the adsorption of RI-dye.

4.3.8 Application of RI-Dye to Nylon Fabric

For the application of RI-dye to nylon fabric a procedure was developed that models traditional batch exhaustion dyeing methods. Dyebath preparation began with the addition of RI-dye (1% owf) to distilled water. Once the dye was partially dissolved the fabric sample was placed in the bath and the bath was heated to 80 °C while stirring. At this point a 0.1 M solution of NaOH in distilled water was added dropwise until the pH of the bath reached 8.5. The dyebath was held at 80 °C for 45 minutes while stirring. The sample was then removed from the bath, rinsed well with warm tap water and placed in

an oven at 120 °C for 45 minutes to fix the dye on the fiber. A schematic of the dyeing process is shown in Figure 4.15.

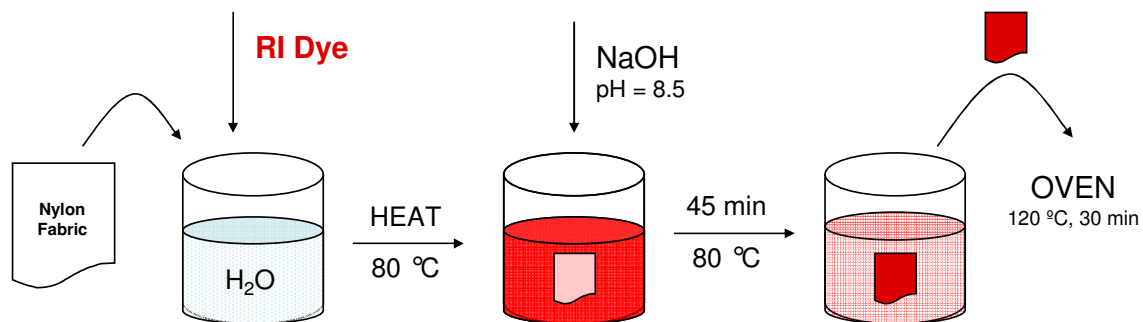


Figure 4.15 – Schematic of the dyeing method developed for application of RI-dye to nylon fabric.

Upon removal from the processing bath the nylon fabric samples were a deep, bright orange. The samples exhibited excellent levelness properties. This level dyeing behavior was expected due to the reshuffling of ionic species during the ion-exchange process. Upon rinsing with warm water, a small amount of dye was rinsed from the fabric until the rinse water became clear. Upon blotting dry with paper towels, no significant dye transfer occurred between sample and paper towel indicating that the samples had been well rinsed. After the covalent fixation step, 120 °C for 30 minutes, the samples appeared a bit lighter in shade due to being completely dry. One of the dyed nylon samples was then placed in an extraction bath of THF at the boil for 15 minutes to remove any non-covalently bonded material. At the end of the 15 minute extraction, the THF bath had a minimal amount of pale orange color indicating that a small portion of the dye was removed during the process. The extracted sample was then removed from the bath and allowed to air dry overnight. The nylon fabrics before and after extraction

were both a bright orange color with great levelness. After the extracted sample was dry it was visually compared to the unextracted sample. The results of the visual assessment concluded that the depths of shade were almost identical, indicating that a negligible amount of dye was lost in the extraction process and confirming that the RI process indeed resulted in a permanent covalent bond between dye and fiber. The RI dyed nylon fabric samples are shown in Figure 4.16.

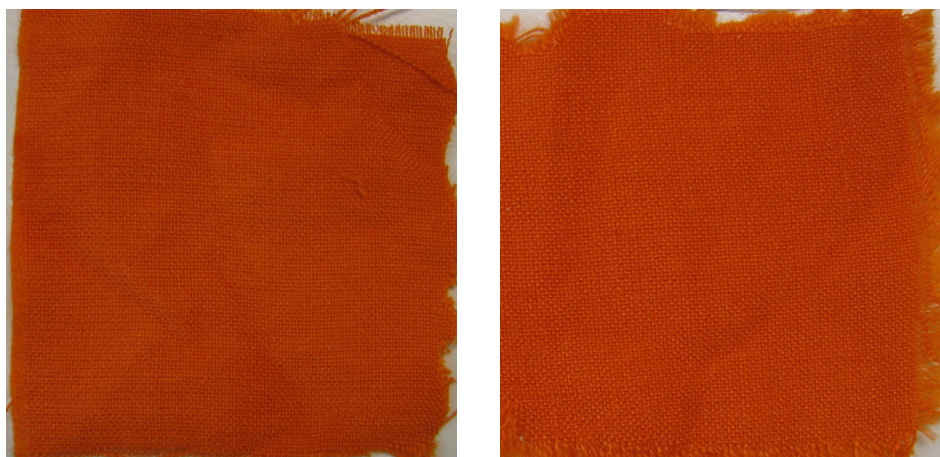


Figure 4.16 – Nylon fabrics dyed with 1% owf RI-Dye at 80 °C for 45 minutes followed by covalent fixation at 120 °C. (LEFT): No post-dye extraction (RIGHT): 15 minutes extraction in THF

To further investigate the dyeing results of the RI-dye on nylon fabric, reflectance measurements were made on the dyed fabrics using a reflectance spectrophotometer. CIE L , a , b measurements were made on both the unextracted and extracted nylon fabrics and the CIE dE value calculated. The reflectance measurement results are shown in Table 4.2. The overall color difference between the two samples was calculated to be $dE = 1.72$. Generally, dE values less than 2 are considered acceptable for shade matching.

The higher *L* value for the extracted samples correlates to a sample with less color. These measurements further confirm the visual assessment that little color loss took place during the THF extraction.

Table 4.2 – Reflectance measurement data (*L*, *a*, *b*, *dE* values) of nylon fabrics dyed with RI-dye.

Sample	L	a	b	dE
unextracted	50.08	50.22	45.35	---
extracted with THF	50.70	48.63	45.13	1.72
Δ	-0.62	1.59	0.22	---

K/S values were also measured for the RI dyed nylon fabrics. K/S values are a function of the spectral reflectance at a given wavelength and are defined as the ratio between light absorption (K) and scattering (S) characteristics of the sample, and are often used to describe the color strength of a dye-substrate system. The K/S values were 15.1 and 14.2 for the unextracted and extracted samples, respectively. Thus, the color strength of the sample decreased approximately 6% after extraction with THF. This loss in color strength is attributed to the removal of unfixed, unreacted dye on the surface of the fibers during the extraction process.

4.3.9 *Application of RI-Dye to Bleached Cotton Fabric*

For the application of RI-dye to bleached cotton fabric a procedure similar to that developed for the dyeing of nylon fabric was used. Dyebath preparation began with the addition of RI-dye and NaCl (if necessary) to distilled water. Once the dye was partially dissolved the fabric sample was placed in the bath and the bath was heated to 80 °C while stirring. At this point, a 0.1 M solution of NaOH in distilled water was added dropwise until the pH of the bath reached the desired value (9.5 or 11.5). The dyebath was held at 80 °C for 45 minutes while stirring. The sample was then removed from the bath, rinsed well with warm tap water and placed in an oven at 120 °C for 45 minutes to fix the dye on the fiber. A schematic of the dyeing process is shown in Figure 4.17.

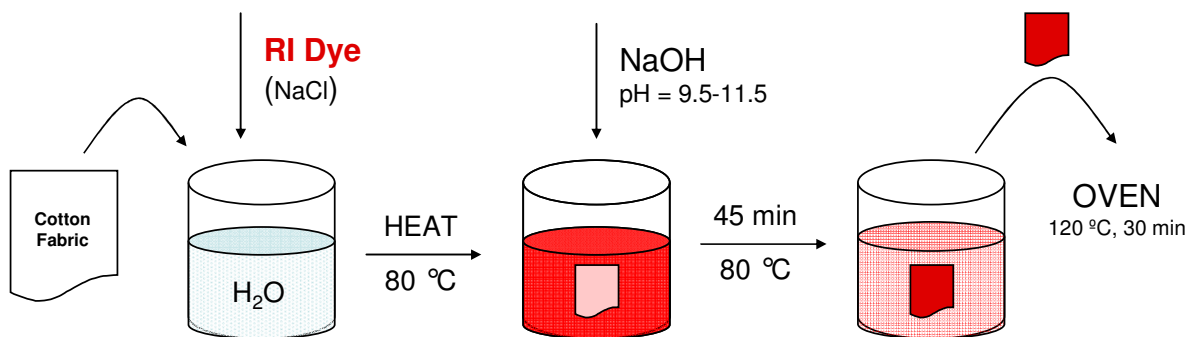


Figure 4.17 – Schematic of the dyeing method developed for application of RI-dye to cotton fabric.

Upon removal from the dyebath the samples were a light orange, almost peach-like color. Samples from the dyeings at 1% owf and pH of 9.5 are shown in Figure 4.18. Visually there was little difference between any of the samples, regardless of dye concentration, pH or salt loading.



Figure 4.18 – Bleached cotton fabrics dyed with 1% owf RI-Dye at 80 °C for 45 minutes. (LEFT): No NaCl added to dyebath. (RIGHT): 40 g/L NaCl added to dyebath.

The main goal of the cotton dyeings was to determine if the addition of NaCl was beneficial to the exhaustion of RI-dye onto the fiber, as is the case with conventional reactive dyeing. CIE L , a , b , dE measurements were made on two of the 1% owf dyed samples fabrics, one with salt added and one without. The reflectance measurement results are shown in Table 4.3. The samples have a color difference value of 1.67 which is below 2 and represents a matched color sample.

The sample which was dyed in the presence of salt actually has an L value that is higher than the sample dyed without salt indicating that the sample is lighter, thus less dye was transferred during the dyeing process that contained salt. This contradicts traditional reactive dyeing theory but is consistent with the effect on the dyeing of ionic substrates with oppositely charged ionic dyes, where salts are used as retarding agents to slow the dyeing rate. K/S values were measured for each sample and are shown in Table 4.4. The sample dyed without salt had a K/S value of 2.9 while the sample dyed with salt

had a color strength value of 2.8 as calculated at the wavelength of minimum reflectance ($\lambda = 480$ nm). Once again, this is evidence that not only is salt not required during the RI-dyeing of cotton, it may act to hinder the dyeing rate.

Table 4.3 – Reflectance measurement data (*L*, *a*, *b*, *dE* values) of bleached cotton fabrics dyed with 1% owf RI-dye both with and without salt added during the dyeing processes.

Sample	<i>L</i>	<i>a</i>	<i>b</i>	<i>dE</i>
No Salt	62.53	34.72	29.64	---
40 g/L NaCl	63.67	34.49	28.44	1.67
Δ	-1.14	0.23	1.20	---

K/S values were also calculated for the other samples to determine the effect of pH and dye concentration on color strength. The K/S values are shown in Table 4.4. Increasing the pH of the processing bath resulted in increased color strength as seen by the K/S values of the samples from Dyebaths 1 and 3. The K/S value increased by approximately 14% as a result of increasing the pH of the dyebath from 9.5 to 11.5. This can be attributed to the formation of more dye sites due to increased deprotonation of the cotton substrates.

Table 4.4 – K/S values of RI-dyed samples along with chemical composition of dyebaths used to dye bleached cotton print cloth.

Dyebath	1	2	3	4
NaOH (pH)	9.5	9.5	11.5	9.5
RI-Dye (% owf)	1	1	1	2
NaCl (g/L)	0	40	0	0
K/S	2.9	2.8	3.3	4.1

Comparison of the K/S values from Dyebaths 1 and 4 in Table 4.4 gives insight into the effect of increased dye concentration on color strength. The K/S value for the 2% owf sample was 4.1 while the K/S value of the 1% owf sample was calculated to be 2.9. If within the linear portion of the dyeing isotherm, color strength is directly proportional to dye concentration, thus the 2% K/S value should be approximately twice that of the 1% value. The difference in theoretical and experimental value is most likely the result of a lack of activated dye sites in the more concentrated dyeing. Increasing the pH of the dyebath should result in more available dye sites and thus a deeper permissible shade.

4.3.10 Application of RI-Dye to Silk Fabric

The RI-dye was applied to silk in a batch method similar to that developed for the nylon films. Silk fabric samples were placed in an aqueous NaOH bath (pH = 9) for 15 minutes in order to deprotonate the carboxylic acid groups. The samples were then rinsed in DI water and placed in dyebaths with RI-dye concentrations of 1% and 2% owf. The samples were allowed to stir in the dyebath for 30 minutes at 80 °C. After removal from the dyebath the samples were rinsed well with warm water, blotted dry with paper towels and placed in an oven at 120 °C for 20 minutes to initiate covalent fixation. The samples dyed a deep orange/red color with very good levelness. The samples are shown in Figure 4.19.

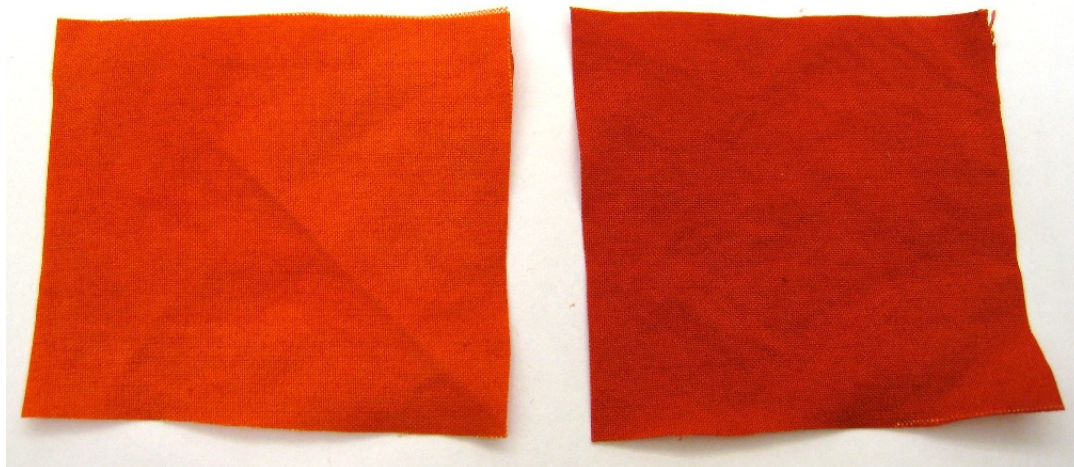


Figure 4.19 – Silk fabrics dyed with RI-Dye at 80 °C for 30 minutes. (LEFT): 1% owf (RIGHT): 2% owf

K/S values were calculated for each sample. The values are reported at the wavelength of minimum reflectance ($\lambda = 470$ nm). The K/S value of the 1% sample was found to be 16.7 while the K/S value of the 2% sample was 24.0. K/S theory states that there is a direct relationship between concentration and color strength; therefore, the value of the 2% sample should be twice the value of the 1% sample. The deviation could be due to a lack of available dye sites during dyeing at the higher concentration.

In the dyeing of textiles, exhaustion is a relative measure of the amount of dye that leaves the processing bath and adsorbs onto the fiber. Exhaustion can be calculated by measuring the ratio of the concentration of dye on the fiber after dyeing compared to the concentration of dye in the original dyebath. Since the absorbance of light for a particular dye is directly proportional to the concentration of that dye in solution, percent exhaustion can be calculated from absorbance measurements of the dyebath before and after dyeing. The initial dyebath for the dyeing of silk at 1% owf, after appropriate dilution, corresponded to an absorbance of 1.646 at 480 nm. The final dyebath, after

appropriate dilution, had an absorbance reading of 0.037 at 480 nm. Thus, the percent exhaustion for this system was calculated to be 97.8%. The physical assessment of the dyebath after dyeing confirms the exhaustion value, as the dyebath changed from deep orange to almost clear during the 30 minute dyeing process. The fact that most of the dye leaves the dyebath does not conclude that all of the dye covalently bonds to the fiber. Some dye is lost during the rinsing step before fixation, in addition to the dye lost in the extraction step. However, the high level of dyebath exhaustion of the RI-dye on polyamides is a very beneficial aspect of the technology. More material adsorbing on the fiber corresponds to less material that is being discharged from the processing bath. In essence, high exhaustion relates to savings in the form of waste reduction, beneficial not only for financial reasons but for environmental aspects as well.

4.4 CONCLUSIONS

A reactive-ionic chromophore (dye) was prepared by tosylation of the commercially-available disperse dye C.I. Disperse Red 1 and subsequent substitution of the tosylated product with quinuclidine via a S_N2 reaction. The resulting quaternary ammonium salt was highly pure after synthesis and required no purification, other than the filtering of solids, due to precipitation from the reaction medium. The RI-dye was characterized using 1H NMR and visible light absorbance spectroscopy. The wavelength of maximum absorbance for the RI-dye was found to be 480 nm. The RI-dye was successfully applied to cellophane and nylon 6,6 films, nylon styling carpet yarns, a multi-fiber test fabric and nylon, bleached cotton and silk fabrics. As expected, the RI-dye showed affinity for polyamides, cellulose and acrylics due to ionic bond formation

between complementary charges. The bond between the reacted RI-dye and hydroxyl- or carboxylate-containing fibers was indeed permanent as the extraction of a RI-dyed nylon sample resulted in a color strength loss of only 6%, as described by K/S values, and a CIE dE value of less than 2. The addition of copious amounts of salt to aid in exhaustion of these dyes on cotton was not necessary as it is in traditional reactive dyeing. This is due to the interaction of complementary charges on the dye and substrate. The RI-dye is indeed a high exhaustion dye on silk as the percent exhaustion of a 1% owf dyeing of silk was calculated to be nearly 98% via visible light absorbance measurements.

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CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

5.1 CONCLUSIONS

The major findings of the present work are summarized below.

- A reactive-ionic alkyl (wax) finish was prepared using a two-step sequence. In the first step, 1-octadecanol was triflated via reaction with triflic anhydride. The reaction yielded octadecyl triflate in 89% yield. Octadecyl triflate was then reacted with *N*-phenyl pyrrolidine to form the alkyl-functionalized, cyclic ammonium triflate salt. The reactive-ionic product was then purified by repeated precipitation from THF into water, resulting in 91% yield. The reaction product and purity were characterized by ^1H NMR.
- The reactive-ionic wax finish was adsorbed on the surface of a deprotonated glass slide from a THF solution via ionic assembly of complementary charges between chemical and substrate. In a second step, the ionic bond was converted to a covalent bond by heating the sample at 80 °C for 4 hours. The bond conversion is the result of a thermally-induced, ring-opening reaction in which the electrons

from the anion on the substrate attack the carbon α to nitrogen in the ring of the RI wax.

- To characterize the RI-wax-modified glass surface, several glass slide samples was subjected to water contact angle measurements. A clean glass slide exhibited an average static contact angle of 18.7°; the surface-modified glass slide, after rinsing with THF, had an average contact angle of 63.0°; the control slide, in which the surface was rinsed with THF after ionic assembly but before covalent fixation, had an average contact angle of 21.9°. These contact angles proved that the RI process does indeed apply a permanent, covalently-bonded wax finish.
- A reactive-ionic fluorinated finish was prepared in a two-step sequence. In the first reaction, 1H,1H,2H,2H-perfluoro-1-octanol was triflated via reaction with triflic anhydride. The reaction yielded 1H,1H,2H,2H-perfluoro-1-octyl triflate in 81% yield. The triflate was then reacted with *N*-phenyl pyrrolidine to form the perfluoro-functionalized, cyclic ammonium triflate salt. The reactive-ionic product was then purified by repeated precipitation from CH₂Cl₂ into CCl₄, resulting in 88% yield. The reaction product and purity were characterized by ¹H NMR.
- The reactive-ionic fluorinated finish was adsorbed on the surface of a deprotonated, cationic-dyeable nylon carpet sample from a solution of RI-fluorinated finish in THF and water. The ionic bond was then converted to a

covalent bond by heating the sample at 80 °C for 4 hours. The sample was then extracted in boiling THF to remove any unfixed material.

- The RI-F-modified, cationic-dyeable nylon carpet sample was subjected to a water drop penetration test to assess the hydrophobicity of the modified surface. Drops of DI water containing red dye were placed on the surface of the modified samples. The surface was completely non-wetting as the drop sat on top of the carpet tufts and rolled around when the sample was moved. The drop persisted on the surface for over 2 hours. The RI-F-modified nylon carpet sample was subjected to a stain-resistance test. A modified and an unmodified sample were each immersed 1 cm in a double-strength cherry Kool-Aid[®] solution at 60 °C for 1 minute. The unmodified sample wicked the liquid up the tufts and was moderately stained up to 4 cm from the bottom. The surface-modified sample was non-wetting, did not wick any liquid and was very lightly stained below the immersion line.
- A reactive-ionic chromophore (dye) was prepared in a two-step sequence. In the first reaction, C.I. Disperse Red 1 was tosylated via reaction with tosyl chloride. The reaction yielded DR1-tosylate in 85% yield. DR1-tosylate was then reacted with quinuclidine to form the DR1-functionalized, cyclic ammonium tosylate salt. The extremely pure reactive-ionic product was recovered from the reaction medium by filtration, resulting in 91% yield. The reaction product and purity were characterized by ¹H NMR.

- The light absorbance characteristics of the RI-dye were measured and found to have shifted 40 nm towards the blue region, from a λ_{max} of 520 nm for DR1 to a λ_{max} of 480 nm for the RI-dye.
- As a proof of concept, the RI-dye was successfully applied to both cellophane and nylon 6,6 films and tested for permanency. The covalent fixation step, 120 °C for 30 minutes, was indeed successful as very little dye was removed during the extraction process.
- A dyeing method was developed for the application of RI-dye to hydroxyl- and carboxyl-containing substrates. The RI-dye was applied to nylon, bleached cotton and silk fabrics. K/S values for 1% owf dyeings were calculated for all three substrates at the wavelength of minimum reflectance (470 nm). The K/S values for nylon, bleached cotton and silk were 15.1, 2.9 and 16.7, respectively, indicating that the RI-dye resulted in a much lower color strength on cotton.
- The RI-dyed nylon fabric was extracted with THF at the boil. The K/S values indicated a loss in color strength of approximately 6% due to the extraction. This was attributed to removal of unfixed dye and leads to the conclusion that a covalent bond was formed between the RI-dye and the substrate.
- Bleached cotton samples were subjected to 1% owf RI-dyeings with and without the addition of NaCl as an auxiliary to aid exhaustion. K/S values were found to

be 2.9 without the addition of salt and 2.8 with salt added. Thus the addition of electrolyte did not aid in the exhaustion of RI-dye onto the cotton fiber.

- Percent exhaustion was calculated for the 1% owf dyeing of silk with RI-dye using spectrophotometric absorbance measurements. The initial dyebath correlated to an absorbance of 1.646 at λ_{max} . The final dyebath had an absorbance of 0.037. The percent exhaustion for this system was calculated to be ~ 98%.
- The reactive-ionic process provides a novel method for the high yield add-on and permanent surface-modification and coloration of fibers and films via ionic assembly followed by covalent fixation.

5.2 RECOMMENDATIONS FOR FUTURE WORK

- Design and synthesize a tertiary set of reactive-ionic dyes to cover a broader range of the color spectrum. Perform dyeings of suitable substrates, monitor the dyeing rates and construct adsorption isotherms for all three dyes.
- Synthesize a RI-F finish that contains more fluorinated character for use as an anti-wetting agent for cotton. The successful reaction design will call for a different solvent system than that used in the current work.
- Synthesize polymeric and block polymeric RI molecules for use as surface-modification agents.

- Incorporate multiple RI groups into the structure of a single RI-dye molecule to help increase water solubility and affinity for cellulosic materials.
- Explore the possible incorporation of the more reactive, four-membered cyclic ammonium group into RI molecules intended for cellulose in an attempt to increase coverage. One drawback may be reduced levelness due to the lower covalent fixation temperature.
- Conduct x-ray photoelectron spectroscopy (XPS) measurements on the RI-modified surfaces to further characterize surface composition and coverage.
- Investigate the use of the RI process to enable crosslinking of multi-layers formed by layer-by-layer (LBL) deposition of charged species. More specifically, focus on the use of polyamideamine-epichlorohydrin (PAE) resins in conjunction with polyacrylic acid (PAA) to form “crosslink-on-demand” multi-layers. PAE has been used extensively in the paper industry for years as a wet-strength additive.¹⁻³

The structure of PAE resin is shown in Figure 5.1.

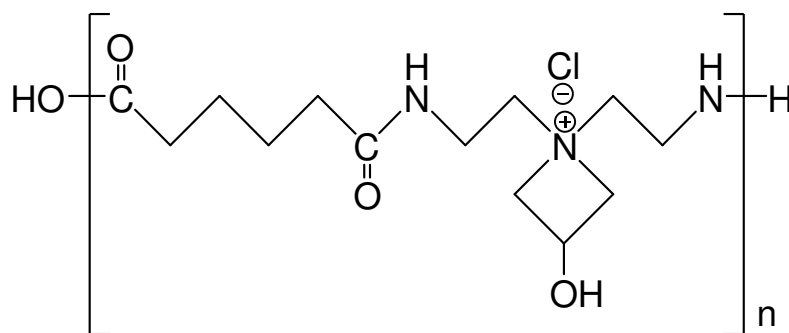


Figure 5.1 – The chemical structure of polyamideamine-epichlorohydrin (PAE) resin.

Obokata and coworkers have recently discovered the mechanism to be ionic bond formation between the 3-hydroxy-azetidinium groups of PAE and the carboxylate groups of wood pulp followed by a ring-opening reaction which converts the ionic bond to a covalent bond at elevated temperatures.^{2,3} A schematic of the overall process is shown in Figure 5.2.

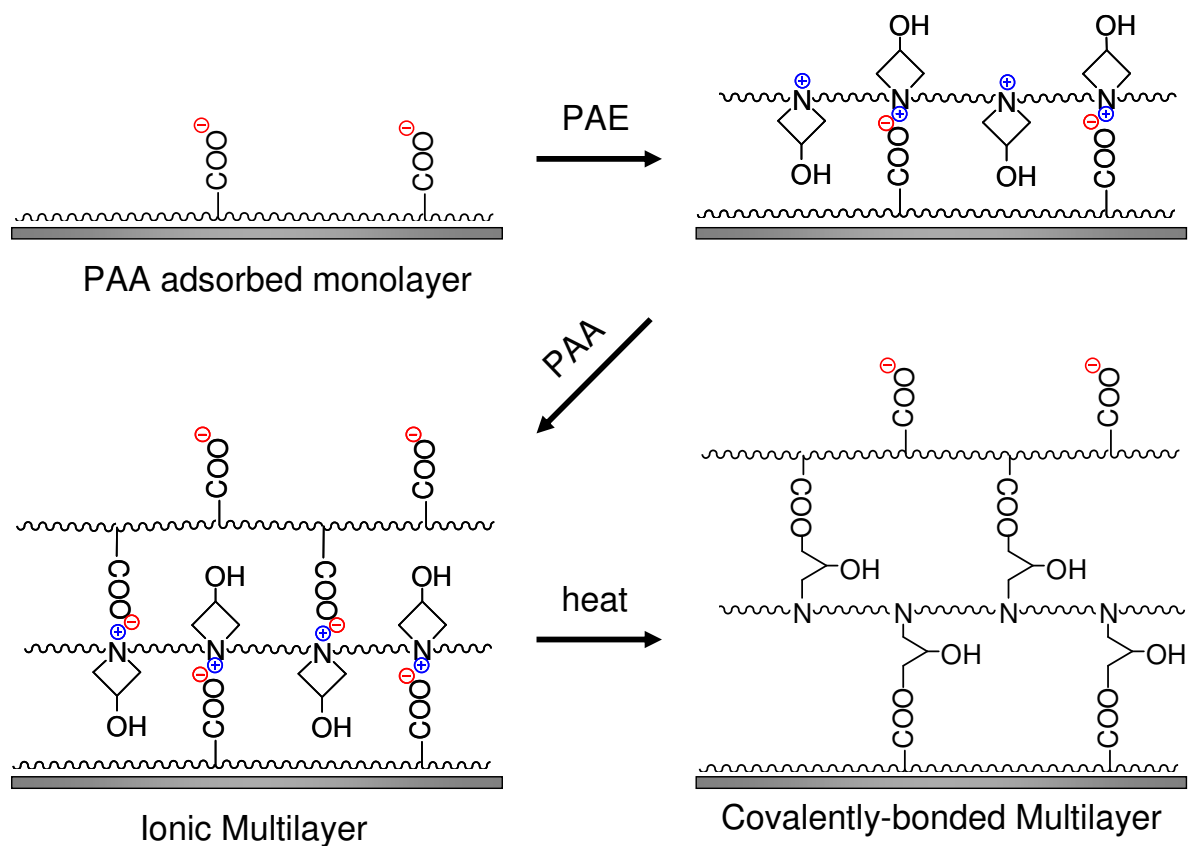


Figure 5.2 – A schematic of the proposed use of reactive-ionic technology in LBL assembly of cationic PAE and anionic PAA polymers followed by covalent crosslinking at elevated temperatures.

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APPENDIX

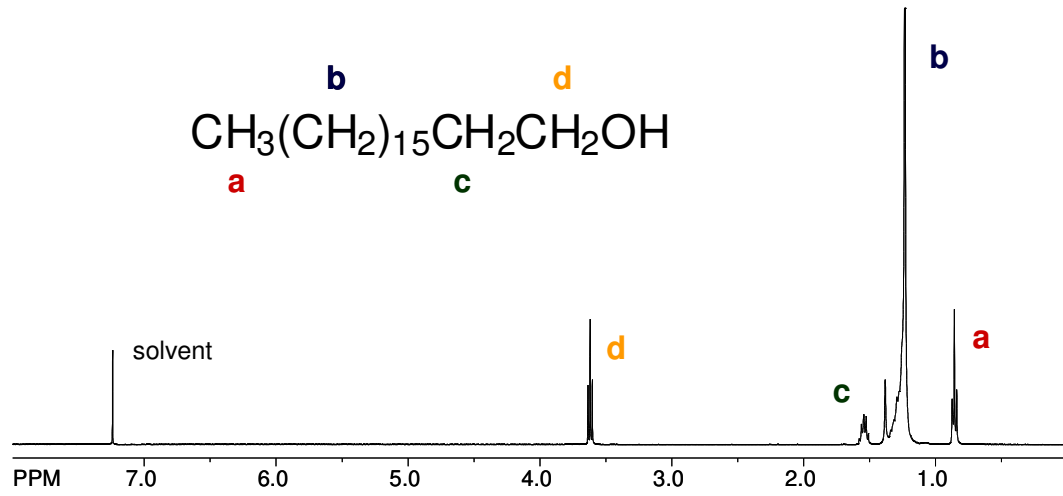


Figure A-1. ^1H NMR spectrum of 1-octadecanol

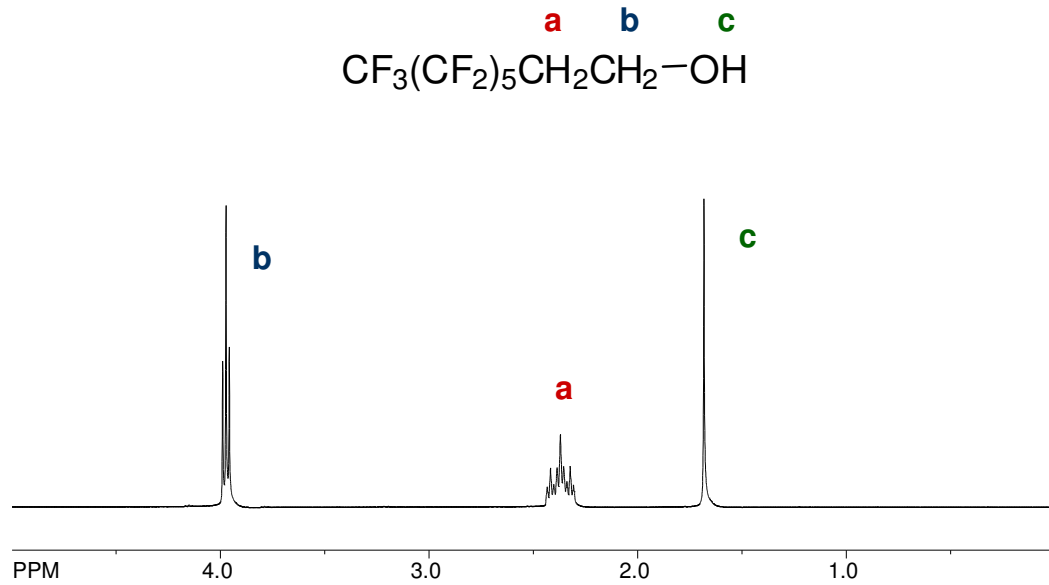


Figure A-2. ^1H NMR spectrum of 1H,1H,2H,2H-perfluoro-1-octanol

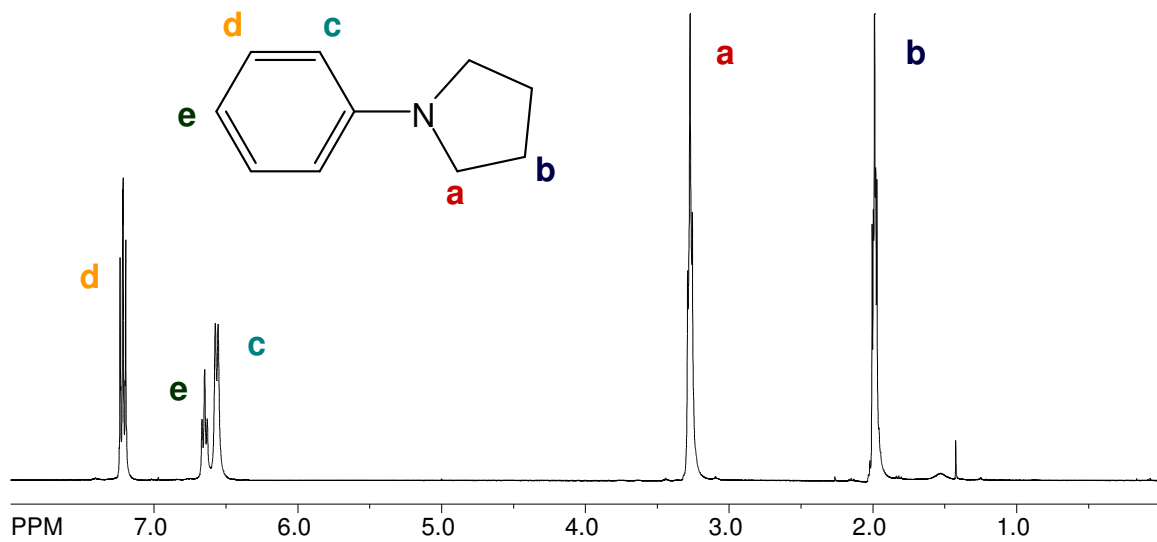


Figure A-3. ^1H NMR spectrum of N-phenyl pyrrolidine

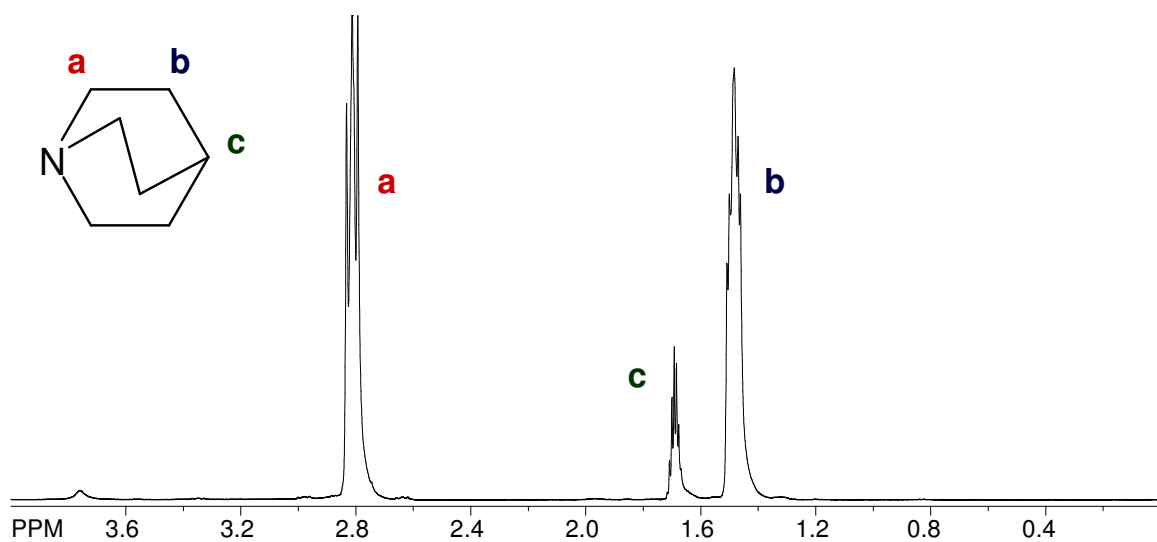


Figure A-4. ^1H NMR spectrum of quinuclidine

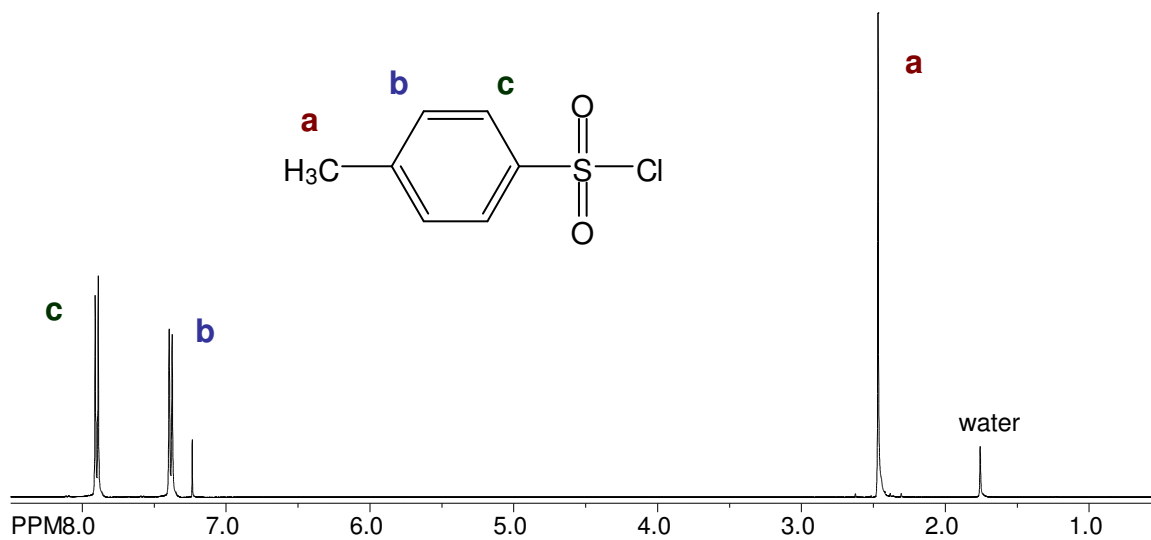


Figure A-5. ¹H NMR spectrum of tosyl chloride (TsCl)

VITA

Christopher Allen Hubbell was born on May 4, 1973 in Wilmington, Delaware. At the age of three his family relocated to North Branford, Connecticut where he lived until he was nine years old. In 1982, his father was transferred back to the family's original hometown of Atlanta, Georgia. Shortly after, Chris's brother Matt was born in June of 1984. Chris graduated from Norcross High School in the spring of 1991 and entered college at Georgia Tech that fall.

Chris received his Bachelor of Science in Polymer and Textile Chemistry from Georgia Tech in the spring of 1997 and his Master of Science degree under advisement from Dr. Wayne C. Tincher in the spring of 1999. His master's project involved garment dyeing with reactive dyes. During his studies at Georgia Tech, Chris met his future wife, Anna Jordan, and they were married in June of 1999 shortly after Chris' graduation.

Upon receipt of his master's degree, Chris took a job with Coats American in Toccoa, GA.. In January 2000, Chris was transferred to São Paulo, Brazil where he worked as a technical supervisor in the sample submission plant for Coats Corrente. Upon his return from Brazil in November of 2000, Chris was named Wet Processing Technical Manager at the Coats American plant in Toccoa, GA.

Chris returned to Georgia Tech in the fall of 2002 to pursue his Ph.D. from the School of Polymer, Textile and Fiber Engineering under advisement from Dr. Fred Cook and Dr. Haskell Beckham. In March 2007, Chris and Anna welcomed their first child, Carter Allen Hubbell, into the world. Chris successfully defended his dissertation and completed his degree in December 2008.