SMART POLYMER MATERIALS

Thilini Dhakshina Kuruwita-Mudiyanselage

A Dissertation
Submitted to the Graduate College of Bowling Green State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

December 2008

Committee:

Douglas C. Neckers, Advisor
Robert I. Boughton
Graduate Faculty Representative
Michael A. J. Rodgers
John R. Cable
ABSTRACT

Douglas C. Neckers, Advisor.

Photochromic superabsorbent polymers with a hydrophilic core and a photochromic shell were prepared by inverse suspension polymerization using acrylic acid (AA) and acrylamide (AM) as monomers, potassium-persulfate as the initiator, \(N, N'\)-methylene bisacrylamide (BIS) as a crosslinker, sorbitan monostearate (Span60) as the dispersant, cyclohexane as the solvent and \(\text{bis(methacryloylamino)}\)-azobenzene (AC) as the photochromic surface cross-linker. The polymer was characterized by NMR, infrared spectroscopy, thermogravimetric analysis and differential scanning calorimetry.

The influence of the polymerization parameters on the properties of the SAPs, water absorption (Q), morphology of the SAPs, swelling kinetics, salt resistance, and the reversibility of water absorption were investigated. The prepared SAPs have excellent water absorption, rapid water uptake, and good resistance to NaCl solutions. Furthermore, they show better reversible water uptake than the previously reported SAPs. The average water absorbency is 2800 g/g and 181 g/g of liquid absorbance in 0.025 M NaCl solution. The initial water uptake rate is 1357 g/g/min and the reversibility of water absorption is 200 g/g in the repeated fourth cycle. The polymer is stable up to 210 °C. When the sample is irradiated at 350 nm water expulsion from the swollen PSAPs was observed.

Two new easily polymerizable dithienylethene compounds have been synthesized, analyzed and tested in polymerization. The new materials 1,2-Bis(5-ethyleneyl-2-methylthien-3-yl)cyclopentene (DT1) and 1,2-Bis(5-(2-methylprop-2-enoyl)-2-
methylthien-3-yl)cyclopentene (CT2) were obtained by incorporating polymerizable functional groups (ethyleneyl and methacryloyl) at the 5 and 5’ positions of the thiophene rings in a diarylethene structure. Both compounds act as photochromic materials. Color occurs reversibly by irradiating with UV and with visible light respectively. Thermal stability, fatigue resistance and polymerizability for both compounds were analysed. Both derivatives can be easily incorporated into polymer matrixes by either photo-curing or radical polymerization. Polymer materials incorporating DT derivatives undergo reversible color changes upon irradiation with UV and visible light respectively. The photochromic films were applied in an erasable recording photon mode.
ACKNOWLEDGMENTS

I would like to express my sincere gratitude and appreciation to my adviser, Dr. Douglas C. Neckers, for his guidance, support and help in conducting this scientific research throughout all these years.

I would also thank my dissertation committee members Dr. Michael A. J. Rodgers, Dr. John R. Cable and Dr. R. Boughton for their helpful suggestions, time and advice in the successful completion of my research.

I am grateful to Dr. Rex Lowe in Department of Biological Sciences, Bowling Green State University for recording the micrographs, Dr. Kelechi C. Anyaogu for recording the SEMs of the samples, the Wright Capital for the DSC instrumentation, Dr Andrey Ermoshkin for recording TGAs and Spectra Group Ltd for the TGA instrumentation. I’m sincerely appreciated for all the help from Dr. Thomas H. Kinstle.

My sincere appreciations go to the McMaster Endowment for providing a fellowship.

I’m thankful to all past and current members of Dr. Neckers’ group for their help, friendship and support. Specially, I am thankful to Dr. Dmitry Polyansky and Dr. Andrey Moiseev, my mentors for getting me started in the lab.

Sincere appreciation is extended to all my friends Priya, Sujeewa, Gayani, Erandi, Nishshanka, Rajib, Ravi, Hanna and specially Wasanthi, Amila, Aruni and Nileesha.

Friends are the most important reagent in the recipe of life, I treasure you all.

Finally, my deepest thanks go to my family, the greatest gift I ever received from God, for their encouragements and moral support to accomplish my Ph. D. degree.
# TABLE OF CONTENTS

**PART A: PHOTOCHROMIC SUPERABSORBENT POLYMERS**

**CHAPTER 1. INTRODUCTION** ................................................................. 1

1.1. HISTORY OF SUPERABSORBENT POLYMERS .......................... 1

1.2. CHEMISTRY ............................................................................. 2

1.3. APPLICATIONS AND RECENT DEVELOPMENTS ...................... 5

1.4. THE PROJECT ......................................................................... 8

1.5. REFERENCES .......................................................................... 10

**CHAPTER 2. SYNTHESIS AND CHARACTERIZATION** .................. 16

2.1. DESIGN OF THE NOVEL SUPERABSORBENT POLYMER .......... 16

2.2. EXPERIMENTAL .................................................................... 20

2.2.1. Materials .......................................................................... 20

2.2.2. Methods and Instrumentation ........................................ 20

2.2.3. Synthetic Procedure .......................................................... 21

2.2.4. Polymerization ................................................................. 23

2.3. CHARACTERIZATION ............................................................. 23

2.4. CONCLUSION ......................................................................... 29

2.5. REFERENCES .......................................................................... 30

**CHAPTER 3. ANALYSIS OF SUPERABSORBENT PROPERTIES** .... 32

3.1. BACKGROUND ....................................................................... 32

3.2. EXPERIMENTAL ................................................................. 33
PART B: SYNTHESIS AND PHOTOCHROMIC PROPERTIES OF NOVEL POLYMERIZABLE DITHIENYLETHENE DERIVATIVES AND THEIR POLYMER FILMS

CHAPTER 5. INTRODUCTION

5.1. PHOTOCHROMISM

5.2. PHOTOCHROMISM IN DITHIENYLETHENE COMPOUNDS

5.3. DITIENYLETHENE COMPOUNDS INCORPORATED IN POLYMER MATRICES

5.4. THE PROJECT

5.5. REFERENCES

CHAPTER 6. SYNTHESIS AND PROPERTIES OF NEW DITHIENYLETHENE CHROMOPHORES AND THEIR POLYMER FILMS

6.1. DESIGN OF NEW POLYMERIZABLE PHOTOCHROMIC SYSTEM

6.2. EXPERIMENTAL

6.2.1. Materials

6.2.2. General Methods and Instrumentations

6.2.3. Synthetic Procedures
6.2.4. Synthesis of dithienylethene, incorporated polymers ................. 86

6.3. RESULTS AND DISCUSSION .................................................... 87

6.3.1. Photochromism of Dithienylethene DT1 and DT2 Monomers......... 87

6.3.2. Thermal Stability ................................................................. 93

6.3.3. Fatigue Resistance ............................................................... 95

6.3.4. Polymerization ................................................................. 97

6.3.5. Dithienylethene Incorporated Polymer Films ......................... 100

6.4. CONCLUSION ................................................................. 103

6.5. REFERENCES ................................................................. 104

APPENDIX A ................................................................. 108

APPENDIX B ................................................................. 112
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1.</td>
<td>The structure of poly(acrylic acid)</td>
<td>3</td>
</tr>
<tr>
<td>1.2.</td>
<td>Schematic illustration of SAP particle</td>
<td>4</td>
</tr>
<tr>
<td>1.3.</td>
<td>SAP world market by product category in 2003</td>
<td>6</td>
</tr>
<tr>
<td>2.1.</td>
<td>The crosslinker $N,N'$-methylenebisacrylamide (BIS)</td>
<td>17</td>
</tr>
<tr>
<td>2.2.</td>
<td>Schematic representation of gel blocking (a) dry polymer particles (b) initial water diffusion (c) gel blocking hinder the water diffusion to the inner particles (c) more rigid particles diminish the gel blocking effect</td>
<td>18</td>
</tr>
<tr>
<td>2.3.</td>
<td>The surface crosslinker bis(methacryloylamino)azobenzene (AC)</td>
<td>19</td>
</tr>
<tr>
<td>2.4.</td>
<td>Schematic representation of the designed core-shell structured SAP particle</td>
<td>20</td>
</tr>
<tr>
<td>2.5.</td>
<td>Solid state $^{13}$C NMR spectrum of SAPs</td>
<td>25</td>
</tr>
<tr>
<td>2.6.</td>
<td>IR spectra of (a) surface crosslinker bis(methacryloylamino)azobenzene (b) dry SAPs and (c) swelled SAPs</td>
<td>27</td>
</tr>
<tr>
<td>2.7.</td>
<td>The DSC graph of SAPs</td>
<td>28</td>
</tr>
<tr>
<td>2.8.</td>
<td>TGA spectrum of (a) dry SAPs polymer (b) swelled SAPs and water</td>
<td>29</td>
</tr>
<tr>
<td>3.1.</td>
<td>Effect of the hydrophilic crosslinker (BIS) on water absorption (Q)</td>
<td>35</td>
</tr>
<tr>
<td>3.2.</td>
<td>Effect of cyclohexane to water (O/W) on water absorption (Q)</td>
<td>37</td>
</tr>
<tr>
<td>3.3.</td>
<td>Effect of acrylamide (AM) on water absorption (Q)</td>
<td>38</td>
</tr>
<tr>
<td>3.4.</td>
<td>Micrographs of superabsorbent polymer particles prepared with (a) 5 wt %, (b) 7 wt %, and (c) 10 wt % of Span 60</td>
<td>40</td>
</tr>
<tr>
<td>3.5.</td>
<td>Effect of dispersant (span 60) on water absorption (Q)</td>
<td>40</td>
</tr>
<tr>
<td>3.6.</td>
<td>Photograph of swollen super absorbent polymers</td>
<td>42</td>
</tr>
</tbody>
</table>
3.7. SEM micrograph of the super absorbent polymer ........................................... 43
3.8. Swelling kinetics of super absorbent polymers ........................................... 44
3.9. Reversibility of the super absorbent polymers ........................................... 45
3.10. Resistance to absorption of NaCl solutions .............................................. 46
3.11. (a) 0.08 g of dry super absorbent polymer (SAP); (b) when swollen
(210 g) ........................................................................................................... 47
4.1. *Trans* - *cis* photoisomerization of azobenzene ......................................... 51
4.2. Schematic illustration of water removal from swollen, photoresponsive
superabsorbent polymer (PSAP) following light absorption ........................... 52
4.3. (a) Surface cross-linker bis(methacryloylamino)azobenzene (AC) (b)
reference crosslinker 2-methyl-N-(4-{2-[4-(2-methyl-acryloylamino)phenyl]-ethyl}-phenyl)-acrylamide (RC) ............................................................... 54
4.4. Absorption spectra of the azo-crosslinker upon irradiation at 350 nm ............ 56
4.5. (a) The absorption spectra of PSAPs in THF/water (30/70) irradiated at 350
nm. (b) Cooling spectrum of the irradiated PSAPs ........................................... 57
4.6. Effects of AC on gel-to-liquid phase transition ............................................ 59
4.7. Weight loss of photochromic superabsorbent polymer on irradiation. Sample
PSAP1 is made with the photochromic surface cross-linker AC and ‘reff’
is made with the reference cross-linker RC. ‘irr’ indicates irradiated .............. 60
4.8. Volume contraction of the gel upon irradiation .......................................... 61
4.9. Photographs of (1) PSAPs swelled gel (2) SEM images (a) before and (b)
after irradiation .............................................................................................. 62
5.1. Examples of different organic photochromic processes ............................... 67
5.2. Photoisomerization of stilbene

5.3. Photochromism of a diarylethene type condensed ring system with thiophene rings

5.4. Open and closed dithienylethenes. The dashed lines show the $\pi$-electron conjugation paths

5.5. Polymerizable dithienylethene systems (1) 1, 2-Bis(5-ethylenyl-2-methylthien-3-yl)cyclopentene (2) 1, 2-bis (5-(2-methylprop-2-enoyle)-2-methylthien-3-yl)cyclopentene

6.1. Molecular structures of the dithienylethene derivatives studied in this work.

6.2. (A) Color change and (B) structural changes of dithienylethene derivative after photoisomerization (1) DT1 and (2) DT2

6.3.1. UV-Vis spectrum of DT1 photoisomerization from open to close state.

6.3.2. UV-Vis spectrum of the reverse photoisomerization of DT1 from closed to open isomer. DT1 in degassed dichloromethane, first irradiated at 300 nm for 30 s. then the UV sample irradiated with visible light from a Xe lamp (150 W) equiped with a 510 nm filter

6.4.1. UV-Vis spectrum of DT2 photoisomerization from open to close state.

DT2 in degassed dichloromethane, irradiation at 300 nm using a photoreactor
6.4.2. UV-Vis spectrum of the reverse photoisomerization of DT2 from closed to open state. DT2 in degassed dichloromethane, first irradiated at 300 nm for 40 s, then the UV irradiated sample irradiated at visible light with Xe lamp (150 W) equipped with 389 nm filter.

6.5. Thermal stability of DT1. Absorption spectra were recorded in degassed dichloromethane following irradiation at 300 nm at 27°C.

6.6. Thermal stability of DT2. Absorption spectra were recorded in degassed dichloromethane following irradiation at 300 nm at 27°C.

6.7. Multiple forward and reverse isomerizations of DT1 in dichloromethane solution.

6.8. Multiple forward and reverse isomerizations of DT2 in dichloromethane solution.

6.9. Schematic representation of the polymerization of DT1 via radical polymerization and photopolymerization.

6.10. IR spectra of (a) DT1 (b) DT1-co-styrene polymer (c) DT2 (d) DT2-co-1,6-hexanediol diacrylate polymer.

6.11. Color changes of dithienylethene polymer films (a) DT1 incorporated polymer films (DT1-co-1,6-hexanediol diacrylate) (b) DT2 homopolymer.

6.11. Photograph of photochromic recording on a DT1 polymer film with 300 nm light.

6.12. UV-Vis spectrum of thin polymer film of DT1-co-styrene (a) irradiation at 300 nm (b) Irradiation with visible light (Xe lamp, 510 nm filter).

B1. 1H NMR of 6 in CDCl₃ .............................................................. 112
B2. 1H NMR of 8 in CDCl₃ .............................................................. 112
<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1. Water Absorption (Q) of Super Absorbent Polymers</td>
<td>41</td>
</tr>
</tbody>
</table>
## LIST OF SCHEMES

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1. Synthetic procedure of the hydrophobic cross-linker bis(methacryloylamino)azobenzene (AC)</td>
<td>21</td>
</tr>
<tr>
<td>2.2. Synthesis of PSAPs</td>
<td>24</td>
</tr>
<tr>
<td>5.1. Parallel and antiparallel conformations of Dithienylethenes</td>
<td>71</td>
</tr>
<tr>
<td>6.1. Synthesis pathway for compound DT1 (6). Reagents: (i) NCS, HOAc, C₆H₆; (ii) glutaryl dichloride, AlCl₃, CS₂; (iii) TiCl₄, Zn dust, THF; (iv) nBuLi, DMF, THF; (v) NaN(TMS)₂, CH₃PPh₃⁺ Br⁻, THF</td>
<td>82</td>
</tr>
<tr>
<td>6.2. Synthesis pathway for compound DT2 (8). Reagents: (i) NaBH₄, I₂, THF; (ii) H₂C(H₃C)CCOCl, N(Et)₃, dioxane</td>
<td>82</td>
</tr>
</tbody>
</table>
PART A

PHOTOCHROMIC SUPERABSORBENT POLYMERS

CHAPTER 1. INTRODUCTION

1.1. HISTORY OF SUPERABSORBENT POLYMERS

Absorbing materials have been used ubiquitously throughout human history. Their applications vary from decorative gels to multi-functionalized oil-sorbers. In the early day’s cellulose or fiber based products were used as water absorbing materials. Though their water retention capacity is low being only 20 times their weight at most these included tissue paper, cotton, sponge, and fluff pulp.\(^1\text{-}^5\) In recent decades dramatic growth has taken place in the development of absorbing materials. Polymer materials that absorb substantial water are termed “hydrogels”.

In the early 1960s, the United States Department of Agriculture (USDA) first introduced a highly absorbing polymer material named “Super Slurper”\(^6\). This was proclaimed a material that could improve water conservation in soils for agricultural purposes. Super-slurper is a resin based on starch in which a resin produced by grafting acrylonitrile polymer onto the backbone of starch entities is used. The hydrolyzed product showed water absorption greater than 400 times its weight. The gel remains swelled without leaking solvent as do fiber based absorbers. The USDA gave permission to several USA companies to develop the Super-slurper concept further.\(^7\text{-}^{11}\)
Since that time wide range of grafting combinations with different co-monomers such as acrylic acid, acrylamide, polyvinyl alcohol and natural fibers like cellulose have been used to produce more water absorbing polymer materials. These have been termed “superabsorbent polymers” (SAPs).\textsuperscript{12-24}

The earliest SAPs were crosslinked starch-graft-polyacrylate polymers. In 1978, Japanese began the first commercial production of SAPs for feminine napkins.\textsuperscript{25} Wide developments improved SAPs and replaced earlier superabsorbent materials with partially neutralized poly(acrylic acids). Poly(acrylic acids) were first studied by Kern in 1938 and later Khun reported on their chemical and physical properties,\textsuperscript{26, 27} became the primary material used in SAP products. Generally SAPs are lightly crosslinked, partially neutralized, hydrophilic three dimensional polymer networks that expand during water absorption having the ability to absorb up to several hundred to thousand times their own dry weight.\textsuperscript{26-28}

SAP technology was first used in baby diapers by European countries in 1980. Initial commercial diapers consisted of small amounts of SAPs - approximately 1-2 grams. Later, in 1983 Japanese companies introduced thinner diapers using more SAPs (4-5 grams) and less fluff.\textsuperscript{29} Subsequently applications of SAPs have grown in many other fields. The global market for SAP was 1.53 million metric tons in 2007 of which USA consumes 30\% of the total.\textsuperscript{30}

1.2. CHEMISTRY

SAPs are hydrogels that have the ability to absorb and retain large amounts of water and aqueous solutions. Many theories and models have been developed to explain the mechanism of
the process. Generally SAPs are made from partially neutralized, lightly crosslinked poly(acrylic acids), which also prove to exhibit the best performance versus cost ratio. The structure of poly(acrylic acid) is shown in Figure 1.1. It contains ionizable carboxylic acid groups on each repeating unit.

![Figure 1.1. The structure of poly(acrylic acid)](image)

The polymer backbone of the SAPs are hydrophilic due to the carboxylic acid groups. The backbone is generally crosslinked with hydrophilic crosslinkers to avoid complete dissolution referred to trivially as “infinite swelling”. Therefore in the presence of water, polymer-solvent interactions are created from hydration and the formation of hydrogen bonds. When the SAP particles are partially neutralized ionic polymers, additional solvent-polymer interactions take place. Figure 1.2 illustrates schematically the inside of a SAP polymer network.
The overall electric neutrality in the SAP particle is created by the negative carboxylic groups balanced by positive counter ions.\textsuperscript{35} When water is introduced to the polymer, the counter ions hydrate rapidly and this reduces their interaction with carboxylate ions. Thus the hydrated counter ions move freely within the network increasing the osmotic pressure within the polymer. Although the counter ions are free to move about, they still are weakly attracted to the carboxylic groups along the polymer backbone. The polymer acts as a semi-permeable membrane that does not allow the counter ions to exit the polymer and move into the surrounding solution. Therefore due to the generated difference in osmotic pressure inside and outside the gel, more water molecules are driven to diffuse inside the polymer. Ionic solutions lower the osmotic pressure difference and, as a result, reduce the swelling capacity. And also the charged groups inside the
polymer tend to repel. The repulsion between these charges expands the polymer and contributes to the swelling capacity.

1.3. APPLICATIONS AND RECENT DEVELOPMENTS

SAPs can be used in a wide spectrum of applications. The largest application is in personal disposable hygiene products such as baby diapers, adult incontinence products, and feminine napkins. Figure 1.3 shows the SAPs world market by product category. The 75% of SAPs used are sold for dippers products by five major companies; Proctor & Gamble, Kimberly-Clark, Paragon Trade Brands, Molnycke and Unicharm. The SAPs used in Pampas diapers produced by Procter & Gamble hold approximately thirty times their own weight in body fluids. A cost analysis in 1996 on a diaper by AMCOL reported that 27.7% of the total materials in one diaper are superabsorbing materials. Consequently SAPs with higher absorption capacities and lower overall bulk will reduce the cost of the final product.

SAPs also play an important role in agriculture and forestry. SAPs used as soil amendments have reduced the water consumption for irrigation, lowered the death rate of plants, improved fertilizer retention, and increased plant growth rates. They have increased the water holding capacity and nutrient retention of sandy soils compared to silt, clay or loam. SAPs used in soils directly influence permeability, density, structure, texture, evaporation and infiltration rates of water. Though it has an outstanding ability to ameliorate the condition of soils, one still has to overcome the obstacles caused by saline containing water and soils.
Many other applications have been developed for the use of SAPs such as wire and cable water blocking, filtration applications, in spill control, as hot and cold therapy packs, composites and laminates, for medical waste solidifications, mortuary pads, motionless waterbeds, candles, waste stabilization, environmental remediation, as fragrance carriers, for wound design, in fire protection, as surgical pads, in controlled release, grow-in-water toys, and so on.\textsuperscript{58-67}

Due to the multiplications of usage, abundant attention has been paid to improve the properties of SAPs. Many new strategies and methods have resulted from this over last few decades. Different polymerization techniques have been developed for the synthesis of superabsorbent polymers such as inverse suspension polymerization, solution polymerization, suspension polymerization, bulk polymerization, foamed polymerization and graft polymerization.\textsuperscript{68-72}
Many different crosslinkers have been introduced to the SAP network such as tetraethylene glycol diacrylate, poly(ethylene glycol diglycidyl ether), ethylene glycol diglycidyl ether, and N,N’ methylene bis diacylamide, etc. 73-76

One way to achieve a desired fast response of a SAP particle is to introduce structural porosity. There are a few techniques used to build porous hydrogels:77-81 (1) phase separation, where porous hydrogels are synthesized above a lower critical solution temperature of a base polymer (2) pore generation into the polymerization mixture of which the latter can be extracted with a suitable solvent (3) use of a foaming agent to make a porous structure through inorganic carbonates such as (magnesium carbonate, calcium carbonate) (4) use of surfactants in the polymer preparation (5) introduction of porosity by freeze-dry and hydration processes.

Another approach for the preparation of fast responding SAPs is to synthesize a comb-like hydrogel by graft copolymerization.12-14, 22-24 The grafted comb-like SAP polymers exhibit improved molecular mobility because of their free mobile grafted chains. Therefore grafted SAPs display faster swelling rates. The drawbacks of this method are high production costs and lower gel strengths.

Reducing gel size is another strategy to achieve rapid kinetics. Tanakas’ theory of gel swelling states that the response rate for a gel is inversely proportional to the square of the smallest dimension of the gel.32 Smaller spherical shaped SAP particles can be prepared by suspension polymerization techniques.

Surface cross-linking has also been introduced in the preparation of SAPs to enhance the swelling rate and water absorption.82-84 However limited preparative detail is out there because it
is mostly held as proprietary information. Surface crosslinking allows SAP particles to have high capacity while preventing deformation under load.

To improve the salt resistance of SAPs, inorganic or ionic compounds have been inserted in the matrix. Many experiments have thus been carried out with nonionic, zwitterionic or cationic monomers along with poly(sodium acrylate) in order to prepare SAPs. Inorganic salt powders have also been mixed with SAP particles in order to gain salt resistance.

Though there is much interest in SAP products, today SAPs have also created an environmental hazard. Approximately 8,000 -10,000 disposable diapers are used in one infant’s lifetime. Each of these diapers takes approximately 500 years to degrade in a landfill. Therefore significant attention has been drawn to SAP preparation from natural polymers such as starch, chitosan, amino acids, and carrageenan which are biodegradable. Though a few products have been introduced to commerce from biodegradable SAPs, none have been commercially successful. Meanwhile synthetic polymers have been developed that show very large water absorptions so that fewer raw materials are needed in SAP applications.

1.4. THE PROJECT

We have attempted to introduce water absorbing SAPs such that a small quantity of SAPs are needed for a particular purpose. The SAPs designed consist of modified materials that potentially have a photochemically controlled water deswelling ability. We postulated that this could be achieved by combining a photochromic surface crosslinker and a hydrophilic polymer network. The thoroughly studied acrylic acid was chosen as the hydrophilic monomer.
Acrylamide co-monomer was introduced to overcome salt resistance. Partially neutralized acrylic acid (AA), acrylamide (AM) including the cross-linker \(N,N'-\text{methylene bisacrylamide (BIS)}\) was polymerized by inverse suspension polymerization to yield spherical shape SAP particles. Later the surface crosslinker (bis(methacryloylamino)azobenzene) (AC) was introduced producing a core-shell structure.

Thus SAP particles obtained exhibit stiffer shells that prevent the SAP polymers deforming under load in the swelling process. This reduces gel blocking, induces fast swelling and increases the overall water absorption. The influences of polymerization parameters on SAPs have been studied to find suitable polymerization conditions. Further, water absorption (Q), swelling kinetics, salt resistance, and the reversibility of water absorption properties have been investigated.

Our photochromic component of choice was the well known azobenzene chromophore. Azobenzene undergoes \(cis - trans\) photoisomerization upon irradiation and the isomerization is accompanied with a structural deformation of a longer isomer to a shorter isomer. Therefore photoirradiation will shrink the surface of the SAP hydrogel mimicking a sponge squeezing. This causes the water molecules to diffuse from the gel, and deswell the SAP particle. Photoirradiation induce deswelling kinetics of SAPs will be investigated.

If the proposed SAPs exhibit a higher water absorption capacity and rapid response as expected, various applications are possible. Due to the higher absorbency, the price of the overall final product will be lower. The proposed SAPs could attract interest in particular in sanitary products, where higher and faster absorbency is necessary. The photochromic deswelling property could open another area of applications such as soil amendments in dry environments.
like a desert where water deswelling can induced by the sun light after the water absorption process which takes place at night.

1.5. REFERENCES


35. www.functionalpolymers.basf.com
36. www.nexant.ecnext.com


58. www.wikipedia.org/wiki/Superabsorbent_polymer
63. Thomas, R. H.; Robinson, R. P.; Williams, D. J.; Logsdon, P. B. U.S. Pat. 6,589,444, 2003.


2.1. DESIGN OF THE NOVEL SUPERABSORBENT POLYMER

The two main components of efficient SAPs are higher absorption capacity and fast swelling rate. In order to achieve this, we designed core-shell structured SAP particles. The excellent hydrophilicity of acrylic acid was the ideal choice for the main polymer backbone. In addition acrylic acid is cheap and easily polymerizable.\textsuperscript{1,2} Acrylic acid was partially neutralized with NaCl. Partially neutralized acrylic acids polymers swell faster with better water absorbing capacity due to the increment of total ionic chargers inside the polymer network.\textsuperscript{3-5} This ionic charge difference between inside and outside the polymer network creates higher osmotic pressure difference.\textsuperscript{6} Therefore more water molecules tend to diffuse inside the polymer network.

 Partially neutralized acrylic acid will show better absorption properties only in distilled or deionized water. In salt solutions, osmotic pressure reducers drastically and thus will show poor water absorbance. SAP particles behavior in salt solutions is important because of the common applications of SAPs involve salt solutions.\textsuperscript{7-11} Therefore it is necessary to introduce a non ionic co-monomer into the network to reduce the salt resistance. Acrylamide monomer is the best choice due to its low cost, ease of use and most of all, its non ionic yet hydrophilic character. Acrylamide thus can suppress the salt resistance.\textsuperscript{12-14}

 Poly acrylic-co-polyamide can dissolve or swell infinitely in water due to their higher water affinity. To avoid this, need to introduce a suitable crosslinker. Crosslinker itself has to be hydrophilic to enhance the swelling capacity yet should have the ability to hold the polymer
backbone preventing of dissolving. The suitable candidate for this purpose was \( N,N' \)-methylenebisacrylamide (BIS)\(^{15,16} \) (Figure 2.1).

![Figure 2.1. The crosslinker \( N,N' \)-methylenebisacrylamide (BIS)](image)

The choice of method of polymerization was inverse suspension polymerization technique. Inverse suspension polymerization results granular particles and the particle size can easily control by the reaction conditions.\(^{17} \) The idea of preparing the granular SAP particles was supported by many facts. According to the Tanakas’ theory of gel swelling, response rate of the gel is inversely proportional to the square of the smallest dimension of the gel.\(^{18-20} \) Therefore reducing gel size increase the swelling kinetics. Additionally smaller particles have higher surface to volume ratio and thus have higher area to contact with the surrounding water molecules. Sorbitan monostearate (Span 60) has chosen as the surfactant in the polymerization process.

When SAP particles swell, they could display structural deformations (Figure 2.2). This deformation of SAP particles blocks the water molecules diffuse into the inner particles, behaving as a sealer.\(^{21,22} \) This is called “gel blocking”.
Figure 2.2. Schematic representation of gel blocking (a) dry polymer particles (b) initial water diffusion (c) gel blocking hinder the water diffusion to the inner particles (c) more rigid particles diminish the gel blocking effect

Deformation can reduce by increasing the crosslinking concentration in the polymer network. But this will sacrifice the water absorbing capacity. Therefore to achieve both these properties, higher absorption and lower deformation, we modify the SAP particles by introducing a hydrophobic surface crosslinker to gain a shell structure. According to the gel swelling kinetic theory advanced by Tanaka,\textsuperscript{18} surface cross-linking increases the swelling rate of SAPs.\textsuperscript{15} The rate of swelling can be represented by the cooperative diffusion coefficient of the network. The cooperative diffusion coefficient is inversely proportional to the friction coefficient which describes the viscous interaction between polymer chains and solvent and is directly proportional
to the osmotic longitudinal modulus.\textsuperscript{18} Surface crosslinking increases the modulus of swelling while the friction coefficient remains almost unchanged, thus increasing the swelling rate of the SAPs.\textsuperscript{15} There are various reports that consider SAPs to have a highly surface crosslinked shell with a less crosslinked core or a core-shell structure.\textsuperscript{23-28} And also when surface cross-linked SAP particles are fully swollen, adjacent SAP domains are independent of one another (Figure 2.2. (c)). This impedes the capillary blocking (gel-blocking) that exist between the swollen SAP particles.\textsuperscript{18}

We have chosen bis(methacryloylamino)azobenzene (Figure 2.3) as the surface crosslinker. Azobenzene derivatives were the best choice as the surface crosslinker due to their environment stability, easy processability and photosensitive behavior.\textsuperscript{29}

\begin{figure}
\centering
\includegraphics[width=0.4\textwidth]{AC.png}
\caption{The surface crosslinker bis(methacryloylamino)azobenzene (AC)}
\end{figure}

Thus we have design and developed a simple method to prepare highly efficient SAP particles. Hydrophobic surface cross-linked SAPs were prepared via an inverse suspension polymerization. An acrylic acid (AA), acrylamide (AM) copolymer was cross-linked with \textit{N,N\textquotesingle}-methylene bisacrylamide (BIS). After initial polymerization, a hydrophobic surface cross-linker (bis(methacryloylamino)-azobenzene) was introduced to the polymer.\textsuperscript{30} The design core -shell structured SAP particles (Figure 2.4) are expected to exhibit higher water absorption capacity and faster swelling rates.
2.2. EXPERIMENTAL

2.2.1. Materials

All commonly available materials were used without further purification. 4,4’-Azodianiline was purchased from either Acros Organics or Aldrich. Reagents were purified using conventional literature methods.

2.2.2. Methods and Instrumentation

NMR spectra were recorded on a Bruker Advance 300 instrument at 300 MHz. Chemical shifts are expressed in ppm relative to TMS. GC/MS were taken on a Hewlett Packard 5988 mass spectrometer coupled to a HP 5880A GC with a 30 m × 0.25 mm ID 0.25 film thickness DB-5 ms column (J & B Scientific) interfaced to a HP 2623A data processor. High resolution
mass spectra were measured in the Mass Spectrometry laboratory at the University of Illinois at Urbana Champaign. IR spectra were obtained with Thermo Nicolet IR200 spectrometer. Column chromatography was carried out using silica gel (60 Å, 32-63 μm, standard grade) purchased from Sorbent Technologies. Solid state $^{13}$C NMR experiments were carried out on Varian Unity +400 system and IR spectra were obtained with Thermo Nicolet IR200 spectrometer. Differential scanning calorimetry (DSC) was carried out using Shimadzu DSC-60 with a Shimadzu TA-60WS thermal analysis data station. Calibrations were performed at scanning ratio of 10 °C/min from 25-300 °C in nitrogen. Thermal stability studies of the SAPs were performed on a Perkin Elmer Thermogravimetric Analyser TGA-6 with a scan rate of 20 °C min⁻¹ under nitrogen flow (20 ml min⁻¹).

### 2.2.3. Synthetic Procedure

Synthesis pathway for the hydrophobic cross-linker bis(methacryloylamino)-azobenzene (AC) is shown in Scheme 2.1.³¹

**Scheme 2.1.** Synthetic procedure of the hydrophobic cross-linker bis(methacryloylamino)azobenzene (AC)
**Synthesis of 4, 4’diaminoazobenzene**

Ammonium persulphate (17.34 g, 0.076 mol) was added to a solution mixture of p-nitroaniline (5 g, 0.036 mol) in sulfuric acid (12 ml of conc. H₂SO₄ in 75 ml of water). Solution mixture was stirred for 4h at 45 °C. The brown product was separated by filtration, washed with water and air dried. To a suspension of 2 g of dried brown product in a mixture of ethanol/ water (20/ 10 ml), slowly added sodium sulfide (11.80 g, 0.15 mol) and let the mixture reflux for 30 min at 80 °C. 4, 4’Diaminoazobenzene was collected by filtration and air dried. The product was reprecipitate by dissolving in conc. HCl solution and subsequently adding NaOH solution. Precipitate recrystalized from ethanol to obtained pure 4, 4’diaminoazobenzene as brown solid (5.34 g, 90%). Melting point: 249-251 °C, ¹H NMR: δ = 3.94 (broad peak, 4H), 6.75 (d, 4H), 7.74 (d, 4H) ppm. ¹³C NMR: δ = 114.79, 124.37, 145.83, 140.51 ppm. GCMS: m/z = 212 [M⁺].

**Synthesis of bis(methacryloylamino)azobenzene (AC)**

4, 4’diaminoazobenzene (2.0 g, 9.43 mmol) was dissolve in dry pyridine (20 ml). Methacryloyl chloride (2.10 ml, 19.8 mmol) was added dropwise using a dropping funnel under an argon atmosphere. The reaction mixture was heated for 1h at 60 °C. Cold mixture poured into ice, acidifies with HCl, filtered, and washed with saturated Na₂HCO₃ and water. The crude product was recrystalized from ethanol to yield orange colored pure bis(methacryloylamino)azobenzene (1.64 g, 50%). Melting point: 259-260 °C, ¹H NMR: δ = 1.56 (broad, 2H), 2.09 (s, 6H), 2.27 (s, 2H), 5.89 (s, 2H), 7.75 (d, 4H), 7.92 (d, 4H) ppm. ¹³C NMR: δ = 18.78, 37.31, 119.60, 120.04, 129.04, 135.5, 137.80, 141.0, 166.50 ppm. DIP: m/z = 348 [M⁺].
2.2.4. Polymerization

A predetermined amount of AA was partially neutralized (50%) by drop-by-drop addition of NaOH solution cooling under ice water to prevent an exothermic reaction and AA precipitation. Then the mixture of monomers (AA: AM = 2:1), BIS (2 wt %), and initiator (potassium-persulfate) (1 wt %) in distilled water was degassed for 15 min. Sorbitan monostearate (Span 60) (5 wt %) was dissolved in cyclohexane and the solution degassed for 15 min. Weight percentages were calculated with respect to the total monomer (AA and AM) content. The aqueous phase was introduced into the organic phase through a dropping funnel and the mixture allowed to polymerize at 55-60 °C under argon. After 1 h, the azo cross-linker (AC) (25 wt %) in tetrahydrofuran was introduced to the polymerization mixture and the polymerization continued for another 2 h at 65 °C. The resulting orange colored SAPs were poured into cold methanol, filtered, and later dried in vacuo at 60-70 °C until a constant weight was achieved. The dried yellow polymer was ground when necessary. The dried sample was immersed in methanol, while changing the methanol periodically, to eliminate any residual unbound materials. Finally, the resulting yellow powdery polymer was dried in vacuo at 60 °C.

2.3. CHARACTERIZATION

Scheme 2.2 shows the schematic illustration of the synthesized polymer. AA, AM copolymer superabsorbents were prepared via inverse suspension polymerization. The hydrophilic cross-linker BIS was added before the start of polymerization generating a hydrophilic core, and the photochromic crosslinker (AC) was introduced after the initial polymerization. As a result, a polymer with a hydrophilic core and photoresponsive shell is obtained.
Scheme 2.2. Synthesis of PSAPs

Solid state $^{13}$C NMR spectra (Figure 2.5) reflect all the expected signals; carbonyl carbons around 170 ppm, aromatic carbons at 85 ppm, and aliphatic $\text{–CH}_2$- carbons at 30 ppm.$^{32}$
Figure 2.5. Solid state $^{13}$C NMR spectrum of SAPs

Figure 2.6(a) represent the IR spectrum of the surface crosslinker bis(methacryloylamino)azobenzene. The corresponding ethylene stretching vibrational frequency at 1624 cm$^{-1}$ diminished in the IR spectrum of the polymer (Figure 2.6(b)) implying the complete polymerization of the crosslinker. As shown in Figure 2.6 (b), IR transmission peaks are characteristic of the expected functional groups of the SAP polymer with the following vibrational frequencies: NH stretching of amide groups at 3710 and 3680 cm$^{-1}$, carbonyl stretching at 1635 cm$^{-1}$, aromatic –C-H stretching at 2972- 2722 cm$^{-1}$, and alkane stretching at 2865, 2825, 1056 cm$^{-1}$. The swollen gel was also characterized by IR spectroscopy (Figure 2.6(c)). Intramolecular bonded –O-H stretching is clearly seen at 3330 cm$^{-1}$. This broad -O-H stretching peak has submerged the nearby amide –N-H peaks around 3700 cm$^{-1}$. The carbonyl stretching peak appears at 1635 cm$^{-1}$, while alkane peaks appear at 1033, 1055 cm$^{-1}$.
Figure 2.6. IR spectra of (a) surface crosslinker bis(methacryloylamino)azobenzene (b) dry SAPs and (c) swelled SAPs

DSC analysis (Figure 2.7) shows three endothermic peaks around 100 °C, 210 °C and 270 °C. Melting point measures carried out parallel to the DSC analysis showed that no significant change of the polymer was observed around 100 °C. Therefore, the endothermic peak at 100 °C on DSC analysis is probably due to absorbed moisture. Around 210 °C a volume change was observed. This could be due to the destruction of the polymer network. The melting point of the AC crosslinker at 260 °C is reflected in DSC curve with a endothermic peak around 270 °C. Thus the DSC analysis concludes that the SAP network is stable up to 210 °C.
Figure 2.7. The DSC graph of SAPs
Thermo gravimetric analysis (TGA) of dry SAPs, water and swollen SAPs is shown in Fig. 2.8. Dry SAPs showed a small weight loss (8 %) below 100 °C, implying a loss of moisture and shows a broad decomposition pattern with a major weight loss around 350 °C. Swollen SAPs and distilled water show very similar TGA plots. This means that the gel behaves like water.

### 2.4. CONCLUSION

In conclusion we have designed, synthesized and characterized a novel surface crosslinked SAPs which expected to show higher water absorbance and rapid swelling kinetics. Inverse suspension polymerization was carried out in the presence of AA, AM, BIS, and azo surface crosslinker to synthesize the SAP particles. Solid state $^{13}$C NMR and IR spectroscopy confirms
the complete polymerization process and the existence of the surface crosslinker in the polymer network. DSC analysis determines that the SAP particles are stable to 210°C temperature which was also confirmed by the melting point analysis of the dry polymer. TGA analysis of the swelled polymer and water displayed a similar behavior implies that the polymer particles absorbs large amount of water.

2.5. REFERENCES

6. www.functionalpolymers.basf.com


CHAPTER 3. ANALYSIS OF SUPERABSORBENT PROPERTIES

3.1. BACKGROUND

Superabsorbent polymers (SAPs) are hydrogels having the ability to absorb up to several hundred to a thousand times their own dry weight of water.\textsuperscript{1-3} Generally, SAPs are partially neutralized, lightly cross-linked, three-dimensional polymer networks that expand during the water absorption process.\textsuperscript{4-9} The absorbing capacity, liquid uptake rate, mechanical strength and liquid retention are indispensable properties of SAP particles to be considered. Extraordinarily absorbing SAPs with good liquid uptake rates would be a major advance in the field.

We have designed a new core-shell SAP particles to achieve higher water absorbance and fast liquid uptake rate.\textsuperscript{10} A lightly cross-linked core is covered by flakes of a hydrophobic shell. The proposed new surface cross-linked SAPs were prepared via an inverse suspension polymerization. An acrylic acid (AA) acrylamide (AM) copolymer was cross-linked with $N,N'$-methylene bisacrylamide (BIS). After initial polymerization, a hydrophobic surface cross-linker (bis(methacryloylamino)azobenzene) (AC) was introduced to achieve the shell structure. The hydrophobic core makes the swelled SAP particles stiffer and reduce gel blocking. Therefore a higher overall water absorption and faster rate of absorbance could be expected.

Polymerization parameters such as the concentration of the crosslinker, the phase ratio, the co-monomer and the dispersant can affect dramatically the final polymer product. Thus the influences of each of these polymerization parameters on the SAPs need to be investigated to reveal the most suitable conditions for the polymerization process. Water absorption ($Q$),
swelling kinetics, salt resistance, and the reversibility of water absorption are other important characteristics that clarify the benefits of the SAPs and these are thus analyzed and discussed.

3.2. EXPERIMENTAL

3.2.1. Characterization

To measure Q, the water absorption coefficient of the gel, 0.02 g of dry sample was immersed in 250 ml of distilled water for at least 24 h in order to allow it to reach swelling equilibrium at room temperature. The completely swollen gel was filtered through a 100 mesh Sigma-Aldrich, # 100 U.S. standard testing sieve. After 0.5 h the remaining gel was collected and weighed. Water absorption was calculated using the following equation:

\[ Q = \frac{(w_g - w_d)}{w_d} \]  \hspace{1cm} (3.1.)

where \( w_d \) and \( w_g \) are the weights of the dry sample and the gel, respectively. The procedure was repeated three times to get an accurate average Q value.

The reversibility of water absorption was determined by repeated swelling and drying of the polymer sample. The swollen sample was completely dried in an oven at 100 °C, and then immersed in excess distilled water until the gel reverted to its equilibrium swelling. This procedure was repeated several times, while the \( Q_n \) values were tested in sequence and calculated using the equation 3.1. The \( Q_n \) value is the \( n^{\text{th}} \) water absorption.

Salt resistance of SAPs was determined by absorbencies from NaCl solutions of various concentrations. The liquid absorption in NaCl solutions was calculated using the equation 3.1.

A freeze-dry instrument (Labconco, freeze dry system/freezone 4.5) was used to prepare samples for morphological studies. A scanning electron microscope (SEM) (Hitachi S-2700 SEM) was used to study the morphology of the SAPs. The specimens were prepared by freeze-
drying the swollen gels as reported previously.\textsuperscript{11} Shapes and particle sizes were determined with a microscope (Olymps EX51).

3.3. INFLUENCE OF THE POLYMERIZATION PARAMETERS

The properties of the SAPs and the degree of polymerization depend on the polymerization parameters such as the crosslinker concentrations (hydrophilic/hydrophobic), organic-to-aqueous phase ratio (O/W), monomer concentration ratios and the concentration of the dispersant. The effect of these parameters on $Q$ is discussed below.

3.3.1. Effect of crosslinker

The crosslinking agent is a major factor in modifying the properties of the superabsorbents. The function of the crosslinking is in joining two or more molecules from a smaller molecule. Concentrated solutions of acrylic acid exhibit self-crosslinking via hydrogen bonding to the polymer backbone.\textsuperscript{12} Self-crosslinking creates many problems such as the reduction of the water absorption and lower absorption rates. Furthermore self-crosslinked SAPs do not have a particle-like structure and separation from the solvent is also difficult. In general crosslinking agents are introduced in the preparation of most SAP’s.

Crosslinker concentration is directly proportional to the crosslink density and this, in turn, has an immense effect on water absorption. In general, the crosslink density determines the swelling capacity and the dissolution of the SAPs in aqueous solutions.\textsuperscript{13} The effect of the hydrophilic, interior crosslinker concentration on $Q$ is shown in Figure 3.1.
Figure 3.1. Effect of the hydrophilic crosslinker (BIS) on water absorption (Q)

Water absorption increases with increasing crosslinking concentration until an optimum point, and then decreases. Maximum water absorption occurs when BIS crosslinker is 0.5 wt % of the weight of the monomer. A low crosslinker density increases the soluble polymer (sol-fraction) percentage of the SAPs. This results in a decrease in Q. Nonetheless, higher crosslinker concentrations increase crosslink density in the polymer network and reduce the swelling capacity of the polymer. Hence, a higher concentration of crosslinking reagent decreases the value of Q.
3.3.2. Effect of phase ratio (O/W)

In inverse suspension polymerization there are two separate phases throughout the whole process, the water phase and the organic phase.\textsuperscript{14,15} The phase ratio is the volume ratio of organic solvent to water (i.e. cyclohexane to water) comprising the suspension. In inverse suspension polymerization, partially neutralized acrylic acid polymer particles dissolved in the organic phase convert to droplets. These expand when they move into the aqueous phase.\textsuperscript{12} Hydrophilic BIS crosslinker diffuses into the droplets and participates in the crosslinking reaction inside the particles. Surface crosslinking of the hydrophobic crosslinker occurs in the vicinity of the organic to aqueous interface.\textsuperscript{16} Therefore, the O/W has an enormous influence on the surface crosslinking reaction, inner crosslinking polymerization, degree of crosslinking, expansion of polymer particles, and the amount of water absorption. The effect of O/W on Q is shows a maximum (Figure 3.2).

An O/W ratio of 2/1 seems critical. At a low O/W ratio highly expanded polymer particles make it easy for the crosslinker to diffuse into the particle and participate in the crosslinking process.\textsuperscript{18} This ultimately results in a higher crosslink density, a thicker gel, and hence a lower Q. When the O/W ratio increases, the reacting particles swell slightly making it difficult for surface crosslinking to occur. Therefore, higher O/W ratios reduce Q.
Figure 3.2. Effect of cyclohexane to water (O/W) on water absorption (Q)

3.3.3. Effect of acrylamide (AM)

A major obstacle in application of polyacrylic acid SAPs is their poor resistance to salts. Because it is unavoidable in most circumstances in which SAPs are used in practice in liquid solutions containing salts. As a consequence, anti-electrolyte character, as in the ability to absorb salt solutions, is an important property of SAPs. This is why the nonionic monomer (AM) is co-polymerized with partially neutralized acrylic acid. Figure 3.3 shows that Q increases to an optimum and decreases with an increasing AM concentration.
Figure 3.3. Effect of acrylamide (AM) on water absorption (Q)

SAPs prepared using a low concentration of AM show a decrease in Q due to the weakening of the hydrogen bonding between the carboxylic groups and water and also due to the synergistic effect of the different hydrophilic groups.\textsuperscript{18} However, water absorption decreases due to the low dissociation degree of the AM even at higher AM concentrations.

3.3.4. Effect of dispersant

In inverse suspension/suspension polymerization, the effect of the dispersant is to reduce the surface tension of the droplets and hence protect them from aggregation.\textsuperscript{16} Therefore the higher the dispersant concentrations, the smaller the size of granular particles. The photographs of SAPs prepared with different percentages of dispersant clearly show the well-established spherical shape of the polymer particles (Figure 3.4). Figure 3.5 shows the effect of dispersant (Span 60)
on the Q values. The absorbance increases with an increase in dispersant concentration (Figure 3.5) and a decrease in particle sizes.
Figure 3.4. Micrographs of superabsorbent polymer particles prepared with (a) 5 wt %, (b) 7 wt %, and (c) 10 wt % of Span 60.

Figure 3.5. Effect of dispersant (span 60) on water absorption (Q).
There are many theories and models to explain the mechanism of hydration of polymers and the interactions between the polymer molecules and water.\textsuperscript{19-23} In general, the water involved with hydrogels can be categorized into three states: (a) bound water, which forms hydrogen bonds with the hydrophilic sites of the network, (b) freezing bound water, which bounds weakly with polymer network, and (c) free water, which has no direct interaction with the polymer molecules and is hydrogen bonded to itself.

Small particles have a higher surface-to-volume ratio. Therefore, they have higher bound water content. A more hydrated surface may enable more rapid diffusion of water from the outside to the inside of the particle. This explains the higher absorbance of water by SAPs of smaller sizes.

### 3.2. WATER ABSORPTION AND MORPHOLOGY OF AZO SURFACE

#### CROSSLINKED SAP

Table 3.1. Water Absorption (Q) of Super Absorbent Polymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Q1 (g/g)</th>
<th>Q2 (g/g)</th>
<th>Q3 (g/g)</th>
<th>Average value for water absorption (g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAP1</td>
<td>2700</td>
<td>2750</td>
<td>3000</td>
<td>2816</td>
</tr>
<tr>
<td>SAP2</td>
<td>2700</td>
<td>2750</td>
<td>2750</td>
<td>2733</td>
</tr>
</tbody>
</table>
The water absorption of two similarly prepared SAPs are shown in Table 3.1. When SAP particles swell they deform their structure and block the internal capillaries within adjacent SAP particles from further diffusion of water into the inner particles\textsuperscript{24, 25}.

As clearly seen in Figure 3.6, swollen SAPs retain their original spherical shape having a colored boundary, indicating that azobenzene surface cross-linking has taken place. Due to the surface crosslinking the SAP has gained a huge gel elastic modulus thus reducing “gel blocking” and this contributes to higher absorption of water.

**Figure 3.6.** Photograph of swollen superabsorbent polymers

Figure 3.7 is an SEM micrograph that shows the surface morphology of the SAPs. The surface consists of many hollows along with a shell-like polymer wrapping, a core-shell structure. This thick surface crosslinked shell allows the SAPs to have high absorbency capacity because it prevents the diffusion of the inner soluble polymer particles. This reduces the overall sol-fraction
of the SAPs, while preventing the deformation of the swollen particles under load. This explains the remarkable absorption behavior of the prepared SAPs.

![SEM micrograph of the superabsorbent polymer](image)

**Figure 3.7.** SEM micrograph of the superabsorbent polymer

### 3.3. SWELLING KINETICS AND REVERSIBILITY OF THE SAP

As shown in Figure 3.8, the SAPs show a rapid water uptake. Within 1 min $Q$ increases to one thousand and after 3 h it begins to reaches its equilibrium state. The reason for this efficient water uptake is the surface cross-linking effect and could be explained by the Tanaka theory. According to the theory, the rate of swelling is proportional to the cooperative diffusion coefficient. The cooperative diffusion coefficient ($D$) can be represented as in Equation 3.2.

$$D = E/f$$  \hspace{1cm} (3.2)
Where $E$ is the longitudinal bulk modulus and $f$ is the friction coefficient between the gel network and the fluid. The friction coefficient describes the viscous interaction between polymer chains and the solvent. The swelling rate of the SAPs increases because the surface crosslinking increases the modulus of swelling, while the friction coefficient remains almost unchanged.

Figure 3.8. Swelling kinetics of superabsorbent polymers

The reversibility of the water absorption by the SAPs is shown in Figure 3.9. Water retention decreases with repetitive absorptions and depends on the percentage of soluble polymers and the stability of the chemical bonds in the polymer matrix. The amide bond is susceptible to hydrolysis with repetitive absorption/desorption, and this eventually reduces the Q value.
Nevertheless, the synthesized SAPs show better absorbances even in the fourth repetitive cycle. This could be due to strong surface cross-linking. The thick surface crosslinking holds the inner core and prevents it from dissolving into the surrounding liquid.

![Graph showing water absorption vs. number of times of absorption](image)

**Figure 3.9.** Reversibility of the superabsorbent polymers

### 3.4. RESISTANCE TO ABSORPTION OF NaCl SOLUTIONS OF THE SAP

Salt resistance of SAPs, the ability to absorb liquids in salt solutions, is an important aspect in many regards. In the main applications of SAPs, as in hygienic products or as in agricultural applications, the liquid that interacts with the SAPs contains a variety of electrolytes or salts. Therefore, we studied the resistance of the SAPs to absorb different concentrations of water from NaCl solutions. As shown in Figure 3.10, Q decreases with increasing salt concentration.
Electrostatic repulsion in an ionic gel is one of the major forces that determine the swelling ratio of a hydrogel.\textsuperscript{3} Polymer gels have low electric potential difference between its interior and surrounding ionic solution. This results in a low swelling ratio and hence low Q. In polar solutions, SAP particles show aggregation due to the hydrophobic surface of the cross-linking agent. The intermolecular hydrophobic associations due to the increase in the polarity of the salt solution may be responsible for the aggregation of the particles. This causes the hydrodynamic size of the chains to increase.\textsuperscript{17} Therefore, our SAPs show better absorptions from salt solutions and good salt resistance in NaCl solutions.

**Figure 3.10.** Resistance to absorption of NaCl solutions
Figure 3.11. (a) 0.08 g of dry superabsorbent polymer (SAP); (b) when swollen (210 g)
3.5. CONCLUSION

Highly efficient surface cross-linked SAPs have been prepared via inverse suspension polymerization. A hydrophobic azo cross-linker (AC) was used as a surface crosslinking agent. The influence of polymerization parameters upon water absorption was analyzed to obtain the most suitable conditions for the preparation of the SAP. Yellow granular superabsorbents obtained with 50% partially neutralized acrylic acid, AM, BIS, and AC demonstrate excellent water absorption approaching nearly 2500 g/g swelling capacity (Figure 3.11). Liquid absorbance in a 0.025 M NaCl solution is 181 g/g; initial water uptake rate is 1357 g/g/min; and the reversibility of the SAPs is 200 g/g for the repeated fourth cycle. The new SAP exhibit ameliorated absorbing properties and the potential to be use in highly water absorbing materials.

3.6. REFERENCES


CHAPTER 4. PHOTOCHROMIC PROPERTIES

4.1. BACKGROUND

Significant advances have been made in stimuli-sensitive materials in recent years. Such substances can respond in a specific way to external stimuli such as light, heat, pH, ionic strength, electric field and solvent composition.\(^1\)\(^2\) Photoresponsive materials have been of wide interest. The major advantage of using light as a trigger is that light can be applied without disturbing the surroundings. As a consequence, numerous experimental and theoretical studies suggest a high potential for photoresponsive applications such as in smart materials, devices, actuators for micro-scale or nano-scale applications, optical sensors, for controlled release, and as separators.\(^3\)\(^7\)

By incorporating a photoresponsive chromophore into a polymer system, microscopic deformations of the chromophore efficiently transfer into macroscopic deformations of the polymer. Incorporating such a photoresponsive chromophore into a polymer network, which can thereby undergo photo-contractions, is a well-established strategy to convert light energy to mechanical energy.\(^8\) Numerous photosensitive compounds have been used in this regard. Functionalized azobenzene compounds, leucodye derivatives, cinnamic acids, and spirobenzopyran derivatives are of particular interest.\(^9\)\(^11\)

The isomerization of azobenzenes is well known, extensively studied and widely used. Many strategies and approaches use azobenzenes as part of a polymer network. Specific monomers have been co-polymerized with other monomers, introducing the azobenzene as a side chain or pendant group, functionalized cross-linker, as liquid crystal networks, in interpenetrating polymer networks (IPN), or in semi-IPN systems.\(^12\)\(^23\) Azobenzenes undergo reversible
photoisomerization. The more stable trans isomer converts photochemically to the less stable cis isomer, and the latter may subsequently revert to the trans either thermally or photochemically. Isomers, by definition, have different molecular and structural properties. Trans–to-cis photoisomerization changes the molecular dimensions in that the distance between the 4- and 4’-carbons of the aromatic rings is reduced from 9.0 to 5.5 Å (Figure 4.1). Therefore, introducing azobenzene groups substituted at the 4- and 4’-positions, and connecting them to a polymer network can be used to cause a macroscopic volume change in the polymer upon photoisomerization.

Figure 4.1. Trans - cis photoisomerization of azobenzene

In this work, we highlight a spherically shaped water-absorbing superabsorbent polymer (SAP) that is thoroughly surface cross-linked with functionalized azobenzenes. Upon light absorption, trans isomerization to the cis form induces contractions of the polymer network. Our work focused on the effect of such a macroscopic contraction on swelled superabsorbent polymers. Contractions of the polymer force water molecules to move out from the polymer network mimicking the squeezing of a swollen sponge. The mechanical energy needed to
squeeze the hydrogel is gained from light energy through the photoresponsive azobenzenes (Figure 4.2).

![Figure 4.2. Schematic illustration of water removal from swollen, photoresponsive superabsorbent polymer (SAP) following light absorption](image)

The hydrogel in the current work was synthesized via inverse suspension polymerization using acrylic acid (AA) and acrylamide (AM) as the monomers, potassium persulfate as the initiator, N,N’-methylene bisacrylamide (BIS) as a cross-linker, sorbitan monostearate (Span60) as the dispersant, cyclohexane as the solvent and bis(methacryloylamino)azobenzene (AC) as the photoresponsive surface cross-linker.
4.2. EXPERIMENTAL

4.2.1. Materials

All commonly available materials were used without further purification. All chemicals were purchased from either Aldrich or Acros Organics. Reagents were purified using conventional literature methods. Freshly distilled spectroscopic grade solvents were used for all spectroscopic analyses.

4.2.2. Methods and Instrumentation

Water absorption (Q) was calculated using equation 3.1 as demonstrated in chapter 3. NMR spectra were recorded on a Bruker Advance 300 instrument at 300 MHz. Chemical shifts are expressed in ppm relative to TMS. A freeze-drying instrument (Labconco, freeze dry system/freezone 4.5) was used to prepare the samples for scanning electron microscopy (SEM) analysis. A Hitachi S-2700 SEM was used. Irradiation was carried out with Southern New England Ultraviolet Co. Rayonet reactor using RPR-3500 A° lamps in a 16 bulb array. UV-Vis absorption spectra of the SAPs in water–THF ¼ 30: 70 were recorded from Shimadzu Multispec-1501 spectrometer. Density modulations were measured with a dual scale specific gravity/Baume heavy hydrometer (Spectrum Chemicals and Laboratory Products).

Volume contraction was measured using a volumetric cylinder. A known volume of gel was placed on a 100 mesh sieve and irradiated at 350 nm. After a given time to allow the expelled water to drain from the polymer gel, the remaining gel was carefully transferred to a volumetric flask. Care was taken not to trap any air bubbles.

Weight loss of the gel upon irradiation was measured as follows: a weighed amount of a prepared gel was placed on a 100 mesh sieve. The sieve was kept in a photochemical reactor and
irradiated at 350 nm. The water expelled from the polymer was allowed to drain. The remaining
gel samples were weighed and their weight loss calculated.

4.2.3. Synthetic Procedure

The synthesis and characterization of the surface cross-linker
bis(methacryloylamino)azobenzene (AC) (Figure 4.3(a)) was reported in chapter 2. The
reference cross-linker (Figure 4.3(b)) 2-methyl-N-(4-{2-[4-(2-methyl-acryloylamino)-phenyl]-
ethyl}-phenyl)-acrylamide (RC) was synthesized in a similar way using 4,4’-ethylenediamine as
the reactant.29

Figure 4.3. (a) Surface cross-linker bis(methacryloylamino)azobenzene (AC) (b) reference
crosslinker 2-methyl-N-(4-{2-[4-(2-methyl-acryloylamino)-phenyl]-ethyl}-phenyl)-acrylamide
(RC)
Synthesis of 2-methyl-N-(4-{2-[4-(2-methyl-acryloylamino)-phenyl]-ethyl}-phenyl)-acrylamide (RC)

4, 4’-Ethynlenedianiline (2.0 g, 9.43 mmol) was dissolved in dry pyridine (20 ml). Methacryloyl chloride (2.10 ml, 19.8 mmol) was added dropwise using a dropping funnel under an argon atmosphere. The reaction mixture was heated for 1h at 60 °C. The cold mixture was poured into ice/water, acidified with HCl, filtered, and washed with saturated Na₂HCO₃ and then water. The crude product was recrystallized from ethanol to yield orange colored pure N, N’-(1,2-ethanediylidene-4,1-phenylene) bis [2-methyl-2-propenamide]. (2.29 g, 50%). ¹H NMR: δ = 1.54 (broad, 2H), 2.06 (s, 6H), 2.87 (s, 4H), 5.45 (s, 2H), 5.78 (s, 2H), 7.12 (d, 4H), 7.46 (d, 4H). DIP: m/z = 348 [M⁺].

4.4. RESULTS AND DISCUSSION

4.4.1. Photoresponse

The photoinduced isomerization was investigated by UV-Vis spectroscopy and measured as a function of time. The absorption spectra of the azo cross-linkers (AC) were recorded following absorption at 350 nm for time intervals of 0, 5, 10, 20, and 30 min, and the irradiated sample was subsequently kept in the dark overnight (Figure 4.4).
Figure 4.4. Absorption spectra of the azo-crosslinker upon irradiation at 350 nm

The absorption peak around 375 nm is due to the intense $\pi-\pi^*$ transition of the trans-azobenzene unit. Upon irradiation, the peak at 375 nm diminishes while a peak around 460 nm corresponding to cis-azobenzene appears. Reappearance of the 375 nm peak following dark storage indicates that cis isomer has reverted to its trans isomeric form.
Figure 4.5. (a) The absorption spectra of SAPs in THF/water (30/70) irradiated at 350 nm. (b) Cooling spectrum of the irradiated SAPs.
UV-Vis spectra of the irradiated SAP polymer (350 nm for time intervals of 0, 1, 5, and 10 min) and the cooling spectrum of the irradiated sample (for 30 min at 350 nm) for time intervals of 10 min, 1 h, 2 h, 3 h, and 4 h are shown in Figure 4.5. The modulations of the absorption peak around 380 nm are due to the isomerization of the azo cross-linker in the polymer network. Following storage in the dark, the reappearance of the peak at 380 nm indicates that reverse isomerization (cis to trans) of the azo cross-linker has taken place.

4.4.2. Volume Phase Transition of the SAPs on Irradiation

When the swollen, thick gel is irradiated at 350 nm, the gel liquefies. The surface of the swollen polymer sphere is squeezed by the azo chromophore inducing water to move from the polymer network. Therefore, the volume of water in the container containing the gel increases while the mass of the system remains constant. Hence the density of the solution decreases and a gel-to liquid phase transition is observed.

It can be clearly seen in Figure 4.6 that density modulations of the polymer with higher AC content show a sharper trend than do the polymers with a lower AC content. The mechanical energy generated by irradiation is higher when the polymer consists of a higher incorporated concentration of AC.

Weight loss of the SAPs on irradiation at 350 nm was determined at 30 min time intervals (Figure 4.7). A small degree of weight loss could be observed even with no irradiation of the sample. This could probably be due to some draining of free water trapped among the SAPs particles. Irradiation of the samples made with photochromic surface cross-linker AC showed better water removal, though weight loss is not that prominent. Volume contraction of the sample
upon irradiation at 350 nm is shown in Figure 4.8. Volume of the gel decreases gradually with irradiation time.

**Figure 4.6.** Effects of AC on gel-to-liquid phase transition
Figure 4.7. Weight loss of photochromic superabsorbent polymer on irradiation. Sample SAP1 is made with the photochromic surface cross-linker AC and ‘reff’ is made with the reference cross-linker RC. ‘irr’ indicates irradiated.
Figure 4.8. Volume contraction of the gel upon irradiation

Figure 4.9 shows a photograph taken of the swelled SAPs and SEM images of SAPs particles before and after irradiation. In this instance, 0.02 g of dry SAP swelled to 55 g indicating a water absorption value of 2700 g g⁻¹. Irradiation shrank the surface and induced water to diffuse from the network. Therefore the thick gel converts to a more liquefied form by UV irradiation. The trans–cis isomerization of the photoresponsive surface cross-linker destroys the smooth shell-like structure of the surface as well as the spherical shape of the polymer. As a result, the inner core of more soluble polymer particles can diffuse out increasing the overall sol-fraction of polymer. This is probably the reason for the increase in density upon irradiation.
4.5. CONCLUSION

SAPs with a hydrophilic core and a photoresponsive shell have been synthesized via inverse suspension polymerization. Yellow granular superabsorbents obtained with 50% partially neutralized acrylic acid, AM, BIS, and AC demonstrate excellent water absorption of nearly 2500 g/g swelling capacity. *Cis-trans* photoisomerization of the surface crosslinker included in the polymer was observed. The photoresponse of the polymer is consistent with the content of
the azo crosslinker AC. The effects of irradiation on water removal of PSAPs were observed, though it is modest.

4.6. REFERENCES


PART B

SYNTHESIS AND PHOTOCHROMIC PROPERTIES OF NOVEL POLYMERIZABLE
DITHIENYLETHENE DERIVATIVES AND THEIR POLYMER FILMS

CHAPTER 5. INTRODUCTION

5.1. PHOTOCHROMISM

“Photochromism” is a reversible change of color caused by light which even dates back to the era of the Alexander the Great.\(^1\) Earliest literature reports of photochromism in 1867 by Fritzsche reported the color bleaching of a tetracene solution in daylight and regeneration of the color in the dark.\(^2\) Later, in 1899, Markwald proposed this phenomenon be called “phototropy” based on studies of the reversible color change of 2, 3, 4, 4-tetrachloronaphthalen-1(4H)-one (\(\beta\)-TCDHN). In 1950, with many mechanistic and synthetic studies, Hirshberg in Israel suggested the term “photochromism” from the Greek words: photo (light) and chrom (color). Since then the field of photochromism has developed and grown widely into many novel potential applications.

Photochromism is a reversible transformation between two different chemical species in which reaction in one or both directions can be induced by the absorption of light.\(^3\) Two isomers possess different absorption bands located in the UV-Vis spectrum. The isomers have different chemical and physical properties. Not only do isomers have different absorption spectra,\(^4\) they are different in their dielectric constants,\(^5\) refractive indexes,\(^6-9\) optical rotations,\(^10-11\) oxidation potentials,\(^12\) luminescence,\(^13-17\) and geometrical structures.\(^18\) A photochemical interconversion of isomers is, by necessity, a photochromic change.
In organic photochromism, the photochromic response may be associated with chemical processes involving either isomerization or cleavage of chemical bonds. The main chemical processes involved in organic photochromism include pericyclic reactions (e. g.: spiropyrans, diarylethenes, anthracenes, and phenanthrenes), intramolecular hydrogen transfer (e. g.: salicylates, triazoles, and oxazoles), intramolecular group transfer (e. g.: polycyclic quinones), cis-trans isomerization (e. g.: azo compounds, stilbenes), electron transfer (e. g.: viologens) and dissociation reactions (e. g.: triarylmethanes, hydrazines) (Figure 5.1).

Pericyclic reactions: Spiropyrans

\[
\begin{align*}
\text{Closed form} & \quad \longleftrightarrow \quad \text{Open form (Merocyanine)} \\
\text{(Quinonic form)} & \quad \text{hv}_1 \\
\text{hv}_2 \text{ or } \Delta
\end{align*}
\]

Intramolecular group transfer: Polycyclic quinines

\[
\begin{align*}
\text{hv}_1 \\
\text{hv}_2 \text{ or } \Delta
\end{align*}
\]

Electron transfer: Viologens
Isomerization: Azo compounds

Dissociation reactions: Triarylmethanes

Figure 5.1. Examples of different organic photochromic processes

In most organic photochromic compounds, absorption in the UV region induces coloration or darkening and this may fade or discolor on exposure to visible light or upon heating. Thus photochromic compounds divide into two groups; T-type or thermally reversible and P-type or thermally irreversible and photochemically reversible. Both groups have many interesting
applications. T-type photochromic compounds have been used in self developing photography, actinometry, displays and plastic lenses.\textsuperscript{30, 31}

P-type photochromic compounds such as diarylethenes and fulgide derivatives have gained much attention in recent decades because they have been used in photon-mode erasable optical switches, various optical storages, displays, nonlinear optics, and as recording media.\textsuperscript{32-38} Thermally irreversible photochromic compounds are of great interest because the reverse reaction can be initiated by only one external stimuli; the absorption of a suitable wavelength of light. Therefore both isomers must be thermally stable and are only photoresponsive compounds. That is, reaction in each direction can be triggered only by the absorption of a quantum of light. The major advantage of using light as the external stimulus is that it can be applied to a specific point without disturbing the nearby environment.

5.2. PHOTOCHROMISM IN DITHIENYLETHENE COMPOUNDS

Photochromism in diarylethenes is well known. Diarylethenes have aromatic groups at each end of the carbon-carbon double bond of which stilbene is the best known. Stilbene shows two reversible isomerizations upon irradiation. It undergoes $E$-$Z$ isomerization followed by photocyclization to dihydrophenanthrene and returns to starting material in the dark in deaerated solutions (Figure 5.2.).\textsuperscript{39}
In the presence of air dihydrophenanthrene converts irreversibly to phenanthrene. The elimination reaction can hinder by replacing the hydrogen ortho to the carbon-carbon double bond with groups that cannot be removed during oxidation. Therefore substituted stilbene undergoes a reversible photocyclization process even in the presence of oxygen because these compounds cannot be further oxidized. However the closed isomer is of less importance because of its short life time. For example, 2, 3-dimesityl-2-butene is reported to have a low thermodynamic stability such that it has a half-life of 90 seconds at 20 °C. \(^{40}\)

Heterocyclic diarylenes were first introduced by Kellogg in 1967 who discovered that the life time of the closed dihydro isomers or their thermal stability can increased by replacing phenyl rings by thiophene rings (Figure 5.3.). \(^{41}\) Thus the resulting diarylenes with thiophene rings have the properties of thermally irreversible photochromic systems. Some dithienylethene derivatives have been reported to be thermal stable for three months even after heating at 80 °C. \(^{42}\)

**Figure 5.2.** Photoisomerization of stilbene
Since this first discovery, intense studies of these compounds have resulted in highly durable dithienylethene derivatives with better chemical and physical properties. Five to six membered rings were introduced on each of the two free $\alpha$-positions on the double bonds to prohibit $E$ to $Z$ isomerization (Figure 5.4.).

**Figure 5.3.** Photochromism of a diarylethene type condensed ring system with thiophene rings

**Figure 5.4.** Open and closed dithienylethenes. The dashed lines show the $\pi$-electron conjugation paths
The closed isomer is thermally stable, but readily can revert to its original form following irradiation with visible light. Another important difference is the $\pi$ system of the two isomers. In the open ring isomer, the $\pi$ system is separated, while in closed ring isomer $\pi$ conjugation is delocalized throughout the molecule. Typically these molecules have show excellent fatigue resistance. Diarylethenes with benzo thiophene groups have been reported to be resistant to fatigue over 10,000 coloration and discoloration cycles.\textsuperscript{44,45} Moreover rapid responses and high reactivity in the solid state are further positive properties.\textsuperscript{46,47}

As a result dithienylethenes become the most interesting potential candidates in optoelectric applications. Diarylethenes exists in almost equal amounts of two conformations in solution, parallel and antiparallel, (Scheme 5.1) and they interconvert each other.\textsuperscript{44} Only the antiparallel conformer undergoes conrotatory photocyclization reaction. Since the lifetime of the excited state is shorter than a few nanoseconds,\textsuperscript{20} there is no chance for the excited photoinactive parallel conformer to convert to the photoreactive antiparallel one in the excited state.\textsuperscript{21}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Scheme5.1.png}
\caption{Parallel and antiparallel conformations of Dithienylethenes}
\end{figure}

The photochromic reaction of dithienylethene derivatives belongs to a 1,3,5-hexatriene to cyclohexadiene type reaction. According to the Woodward-Hoffmann rule the photocyclization
reaction proceeds in a conrotatory mode. From the two dithienylethene conformations, with the two rings in mirror and $\text{C}_2$ symmetries, only the conrotatory cyclization is allowed from the conformation with the rings in $\text{C}_2$ symmetry. This means that the parallel conformer where the heterocyclic rings are fixed to the mirror symmetry cannot undergo photocyclization, while the reaction can proceed when the conformation converts to the $\text{C}_2$ symmetry, or antiparallel orientation.

5.3. DITIENYLETHENE COMPOUNDS INCORPORATED IN POLYMER MATRICES

Dithienylethenes are the most promising candidates among various photoresponsive compounds for optoelectronic devices because of their outstanding chemical and physical properties. These properties exist in solution as well as in solid phase. Moreover, photochromes in polymer matrices or films are a demanding media for device applications in optoelectric technology. Photochromic changes at the molecular level can lead to the global changes in bulk materials. Thus many studies have been reported regarding the fabrication of photochromic dyes dispersed, impregnated or bound in to polymer networks. Photochromic dyes usually have been dispersed in polymer matrices such as PMMA, polystyrene and polyethylenes. Photochromes consisting of long alkyl chains in LB films, crystals of photochromes, and amorphous films containing photochromes with bulky substitutions are also reported.

Photochromic compounds being dispersed into polymer matrices is the most convenient way to produce photochromic polymer films. However this process has numerous drawbacks. The polymer matrix may phase separate polymer from chromophore. To improve the photochromic
efficiency of the films it may be necessary to increase the photochrome dye concentration in the matrix. But dispersing high concentration of dyes into a polymer matrix can lead to segregation after long term storage.\textsuperscript{54} Aggregation of the dye results in low photochromic conversion of the polymer material. To overcome such barriers the photochromic compounds can be directly bound to a polymer matrix. Thus polymer films with high chromophore concentration can be prepared without crystallization, phase separation or formation of concentration gradients.\textsuperscript{55} Another advantage is that the motion of the chromophore may be hindered by chemical bonding in bound systems. Therefore these may be more stable over time than the dispersed systems.

**5.4. THE PROJECT**

Photochromic compounds in polymer matrices are of much interest from fundamental as well as practical points of view because of their possible applications in optoelectronics. Directly bound photochromes in a polymer matrix have substantial advantage in durability and potential applications over other methods. Therefore we have introduced two unique photochromic molecules and found that they can easily incorporated into polymer network.

The photochromic moiety of the chromophore chosen is the well studied dithienylethene chromophore. We find it is the most suitable candidate for the preparation of optoelectronic devices. We proposed two new polymerizable dithiaenylethene molecules (Figure 5.5.). We have introduced polymerizable ethyleneyl functionality and methacryloyl moiety into the 5 and 5’ positions in thiophene rings.
A simple but efficient synthesis was proposed. Further, the photochromic properties of the monomers, their polymerization and the photochromic properties of the polymers will be reported.

Our objective was to synthesize an easily polymerizable dithienylethene which shows color change in solution as well as in polymer matrices where it has better photochromic properties. The compounds thus synthesized are expected to exhibit reversible open to close isomerization upon UV and visible light irradiation. The system we chose to develop will introduce a most simple preparation of photochromic films with photochromophores directly attached to the polymer network. Thus photochromic films prepared are expected to exhibit erasable photon mode recording. This is possible using UV light in photocured colorless films or with visible light in UV irradiated colored films. Erasing could result using one irradiation mode or the other.
5.5. REFERENCES

1. www.tci.asiapacific.com


43. www.wikipedia.org/wiki/Photochromic


CHAPTER 6. SYNTHESIS AND PROPERTIES OF NEW DITHIENYLETHENE CHROMOPHORES AND THEIR POLYMER FILMS

6.1. DESIGN OF NEW POLYMERIZABLE PHOTOCHROMIC SYSTEM

We selected the dithienylethene moiety as the photochrome because of its remarkable chemical and physical properties. It is a p-type chromophore; that is the conversion between the two isomers can induced only by an absorption of a suitable wavelength of light.\textsuperscript{1-5} The two isomers are thermally stable, some derivatives of dithienylethene are reported to be stable for months in dark.\textsuperscript{6, 7} Furthermore, dithienylethenes are famous for their fatigue resistance properties.\textsuperscript{8-10} Generally they can undergo isomerization cycles for more than 10,000 times.\textsuperscript{11-12} They have high sensitivity and show fast responses.\textsuperscript{13} Because of these excellent chemical and physical properties dithienylethenes have become the most suitable candidates for optoelectronic devices.\textsuperscript{14-17}

Optoelectronic devices can be prepared by incorporating the photoreactive chromophore into a polymer network.\textsuperscript{18-23} Many attempts have been reported to introduce dithienylethenes into a polymer matrix that might produce better photochromic films.\textsuperscript{24-26} The most convenient method is to disperse the chromophore into the polymer.\textsuperscript{27, 28} This method has many drawbacks such as aggregation of the dye, segregation of dye molecules, concentration gradients, etc.\textsuperscript{29, 30} The best way to overcome these barriers is to introduce chromophores that can directly bond to a polymer network. To the best of our knowledge dithienylethene derivatives directly bound polymer systems are rare. Thus we proposed to prepare two new easily polymerizable dithienylethene chromophores (Figure 6.1).
Two polymerizable functional groups, ethenyl and methacryloyl, are introduced to 5 and 5’ positions of the dithienylethene chromophore to produce the novel dithienylethene derivatives 1,2-bis(5-ethylenyl-2-methylthien-3-yl)cyclopentene (DT1) and 1,2-bis(5-(2-methylprop-2-enoyl)-2-methylthien-3-yl)cyclopentene (DT2). The chromophore with ethylenyl functionality DT1 shows a longer $\pi$– conjugation in the closed isomer than the other chromophore DT2 and therefore one expects it to show better photochromic properties. The chromophore with acryloyl functionality is easier to polymerize. Two methyl groups were introducing to 2 and 2’ positions in the thiophene rings to prohibit further oxidation of the phenanthrene structure with the latter preventing reversibility.$^{31}$ A five membered ring was introduced at the two free $\alpha$-positions on the C-C double bonds to hinder $E$ to $Z$ isomerization.$^{32}$
6.2. EXPERIMENTAL

6.2.1. Materials

All commonly available materials were used without further purification. Compounds were purchased from either Acros Organics or Aldrich. Irgacure 819 was purchased from Ciba Specialty Chemicals. Reagents were purified using conventional literature methods when necessary. \(^{33}\) Freshly distilled spectroscopic grade solvents were used for all spectroscopic analysis.

6.2.2. General Methods and Instrumentations

NMR spectra were recorded on a Bruker Advance 300 instrument at 300 MHz. Chemical shifts are expressed in ppm relative to TMS. GC/MS were taken on a Hewlett Packard 5988 mass spectrometer coupled to a HP 5880A GC with a 30 m × 0.25 mm ID 0.25 film thickness DB-5 ms column (J & B Scientific) interfaced to a HP 2623A data processor. High resolution mass spectra were measured in the Mass Spectrometry laboratory at the University of Illinois at Urbana Champaign. IR spectra were obtained with Thermo Nicolet IR200 spectrometer. Column chromatography was carried out using silica gel (60 Å, 32-63 μm, standard grade) purchased from Sorbent Technologies. UV irradiations employed a Southern New England Ultraviolet Co. Rayonet reactor using RPR-3500 Å or 3000 Å lamps in a 16 bulb array. A Xe lamp (Oriel, 68805 Universal power supply, 180 W) was used as the visible light source with suitable filters. UV-vis absorption spectra were recorded from Shimadzu Multispec-1501 spectrometer. For the UV curing process we used a CF 1000 Clearstone Tech UV-Vis LED source (395 nm).
6.2.3. Synthetic Procedures

The synthesis of compounds DT1 and DT2 is shown in Scheme 6.1 and Scheme 6.2.

Scheme 6.1. Synthesis pathway for compound DT1 (6). Reagents: (i) NCS, HOAc, C$_6$H$_6$; (ii) glutaryl dichloride, AlCl$_3$, CS$_2$; (iii) TiCl$_4$, Zn dust, THF; (iv) nBuLi, DMF, THF; (v) NaN(TMS)$_2$, CH$_3$PPh$_3^+$ Br$^-$, THF

Scheme 6.2. Synthesis pathway for compound DT2 (8). Reagents: (i) NaBH$_4$, I$_2$, THF; (ii) H$_2$C(H$_3$C)CCOCl, N(Et)$_3$, dioxane
Synthesis of 2-chloro-5-methylthiophene (2) \(^{34}\)

A solution of 2-methylthiophene (100.0 ml, 1.03 mol), N- chlorosuccinimide (150.0 g, 1.13 mol), benzene (400 ml) and acetic acid (400 ml) was stirred for 30 min at room temperature. The mixture was reflux for 1 h. 3 M NaOH solution was powered into the cooled mixture and the organic phase was extracted and washed further with NaOH (3 × 100 ml) solution, dried (anhydrous Na\(_2\)SO\(_4\)), filtered and the solvent evaporated in vacuum to yield a yellowish liquid. The crude product was purified by vacuum distillation to yield a colorless liquid (107.0 g, 80%).

\(^1\)H NMR: \(\delta = 2.33 \text{ (s, 3H)}, 6.44 \text{ (m, 1H)}, 6.62 \text{ (d, 1H)} \text{ ppm.} \)

\(^{13}\)C NMR: \(\delta = 14.28 \text{ (s)}, 123.38 \text{ (s), 124.75 (s), 125.49 (s), 137.43 (s) ppm.} \)

GC-MS: \(m/z = 131 \text{ [M\(^+\)].} \)

Synthesis of 1, 5-bis(5-chloro-2-methylthien-3-yl) pentane-1, 5-dione (3) \(^{34}\)

Compound 2 (100.0 ml, 0.76 mol) and glutaryl dichloride (64.5 ml, 0.38 mol) was added to CS\(_2\) (500 ml) and the mixture cooled in an ice bath. AlCl\(_3\) (121.00 g, 0.91 mol) was added to the cold vigorously stirring previously prepared solution and the mixture stirred for additional 2 h at room temperature. Cold water (200 ml) was carefully added to the mixture to quench the reaction. The water layer was extracted by diethyl ether (3×100 ml). The combined organic phase was washed with water (100 ml), dried with anhydrous Na\(_2\)SO\(_4\), filtered and the solvent evaporated in vacuum. The crude brown tar was purified by chromatography (silica gel; hexane/ethyl acetate: 6/1) to yield a light yellow solid (59.4 g, 55%).

\(^1\)H NMR: \(\delta = 2\text{-}2.1 \text{ (m, 2H), 2.66 (s, 6H), 2.86 (t, 2H), 7.19 (s, 2H) ppm.} \)

GC-MS: \(m/z = 360 \text{ [M\(^+\)].} \)
Synthesis of 1, 2-bis(5-chloro-2-methylthien-3-yl) cyclopentene (4) \(^{34}\)

TiCl\(_4\) (43.6 ml, 0.21 mol) was added very cautiously to a stirring suspension of Zn dust (18.16 g, 0.28 mol) in dry THF (200 ml) under argon. The solution was refluxed for 45 min, the mixture cooled in an ice-bath and compound 3 (50.0 g, 0.14 mol) in THF (200 ml) was added using a double ended needle under an argon flow. The mixture was refluxed further for 2 h and the cold mixture quenched with 10 % aq. K\(_2\)CO\(_3\) (150 ml). The aqueous layer was extracted with diethyl ether. The combined organic phase was washed with water (100 ml), dried (anhydrous Na\(_2\)SO\(_4\)) and the solvent evaporated in vacuum. The crude product was purified by flash chromatography (silica gel; hexane/ethyl acetate: 6/1) yielding yellow colored product (18.1 g, 40%) used in next step without further purification. \(^1\)H NMR: \(\delta = 1.9\ (s, \ 6H), 2-2.1\ (m, \ 2H), 2.7\ (t, \ 2H), 6.6\ (s, \ 2H)\) ppm. GC-MS: \(m/z = 328\ [M^+]\).

Synthesis of 1, 2-bis(5-formyl-2-methylthien-3-yl)cyclopentene (5) \(^{34}\)

n-BuLi (25.0 ml of 2.5 M solution in hexane, 0.06 mol) was added to a solution of compound 4 (10.0 g, 0.03 mol) in anhydrous THF (100 ml) under argon. The mixture was stirred for 1 h and anhydrous dimethyl formamide (4.38 g, 0.06 M) subsequently added. The resulting solution was stirred further for 1 h at room temperature and poured into aqueous HCl (2 M, 100 ml). The organic layer was extracted with diethyl ether and the combined organic phases washed with saturated NaHCO\(_3\) (100 ml), water (100 ml), dried (anhydrous Na\(_2\)SO\(_4\)), filtered and the solvent evaporated in vacuum. The crude brown-yellow oil so obtained was purified by column chromatography on silica-gel (hexane/ethyl acetate: 3/1) afford a product of brown-yellow solid (5.68 g, 60%). \(^1\)H NMR: \(\delta = 2.05\ (s, \ 6H), 2-2.1\ (m, \ 2H), 2.84\ (t, \ 2H), 7.45\ (s, \ 2H), 9.75\ (s, \ 2H)\) ppm. GC-MS: \(m/z = 316\ [M^+]\).
Synthesis of 1, 2-bis(5-ethyleneyl-2-methylthien-3-yl)cyclopentene (DT1) (6)\textsuperscript{35}

Sodium bis(trimethylsilyl)amide (2.31 g, 6.32 mmol) was added to a slurry of the Wittig reagent, methyltriphenylphosphonium bromide (4.45 g, 0.02 mol), in THF (60 ml) under an argon atmosphere. After 30 min stirring at room temperature, a solution of compound 5 (2.0 g, 6.32 mmol) in THF (60 ml) was added using a dropping funnel over the period of 10 min. The mixture was stirred further for 30 min after which water (20 ml) was carefully added to quench the reaction mixture. The aqueous layer was extracted with diethyl ether (30 ml). The combined organic phases were washed with saturated brine (20 ml), dried (anhydrous Na$_2$SO$_4$), filtered and the solvent evaporated in vacuum. A brick brown oily compound was obtained (1.77 g, 90%).

The crude product was purified by column chromatography (silica gel; hexane/ethyl acetate: 9/1) to yield a red colored viscose liquid (0.98 g, 50%). $^1$H NMR: $\delta = 1.85$ (s, 6H), 1.93-1.99 (m, 2H), 2.69 (t, 2H), 4.94 (d, 2H), 5.29 (d, 2H), 6.51 (m, 2H), 6.59 (s, 2H) ppm. $^{13}$C NMR: $\delta = 12.3$ (q), 21.1 (d), 36.6 (s), 110 (s), 125.3 (d), 128.2 (s), 132.1 (s), 132.5 (s), 134 (s), 136 (s) ppm. IR: $\nu = 1618$ cm$^{-1}$ (C=C). GC-MS: $m/z = 316$ [M$^+$] HRMS: calculated for C$_{19}$H$_{20}$S$_2$ 312.1007, found 312.1003.

Synthesis of 1, 2-bis(5-methanoyl-2-methylthien-3-yl)cyclopentene (7)\textsuperscript{36}

To a stirred suspension of NaBH$_4$ (4.55 g, 0.12 mol) in dry THF (10 ml) was added compound 5 (18.0 g, 0.05 mol) using a dropping funnel under argon atmosphere. The mixture was then cooled in an ice-bath and I$_2$ (14.51 g, 0.05 mol) slowly added in dry THF (10 ml). The mixture was stirred further for 15 minutes, subsequently quenched with 3 M HCl and extracted with diethyl ether. The combined organic layers were washed with 3 M NaOH, brine, dried (anhydrous Na$_2$SO$_4$), filtered and solvents evaporated in vacuum to yield a dark brown solid.
Yellow colored pure 7 was obtained after purification by column chromatography on silica gel (hexane/ethyl acetate, 3/1) (14.6 g, 80%). $^1$H NMR: δ = 1.45 (broad OH peak), 1.94 (s, 6H), 2.0-2.1 (m, 2H), 2.75 (t, 2H), 4.65 (s, 4H), 5.29 (d, 2H), 6.65 (s, 2H) ppm. $^{13}$C NMR: δ = 14.3 (d), 22.9 (s), 38.3 (d), 60.0 (s), 126.8 (s), 134.5 (s), 134.9 (s), 135.3 (s), 134 (s), 136 (s) ppm. GC-MS: $m/z$ = 320 [M$^+$]. HRMS: calculated for C$_{17}$H$_{20}$O$_2$S$_2$ 320.09048, found 320.09030.

**Synthesis of 1, 2-bis(5-(2-methylprop-2-enoyl)-2-methylthien-3-yl)cyclopentene (DT2) (8)**

Methacryloyl chloride (0.65 ml, 6.2 mmol) was added drop wise to a stirred ice cold solution of 7 (1.0 g, 3.1 mmol) and triethylamine (1.26 g, 1.2 mmol) in 50 ml dioxane. The mixture was stirred overnight at room temperature under argon. Solvents were removed in vacuum to yield a yellow-brown viscous liquid. Chromatography on silica gel (hexane/ethyl acetate, 6/1) affords the product as the yellowish brown viscose liquid (0.85 g, 60 %). $^1$H NMR: δ = 1.81 (m, 6H), 1.82 (s, 6H), 1.86 (m, 2H), 2.66 (t, 2H), 5.05 (s, 4H), 5.55 (s, 2H), 5.95 (s, 2H), 6.70 (s, 2H) ppm. $^{13}$C NMR: δ = 13.0, 17.1, 22.3, 37.6, 60.3, 124.9, 128.9, 133.9, 134.4, 135.1, 135.6, 136.1, 166.3 ppm. DIP: $m/z$ = 456 [M$^+$]. IR: $\tilde{\nu}$ = 1634 cm$^{-1}$ (C=C). HRMS: calculated for C$_{28}$H$_{25}$O$_4$S$_2$ 456.14248, found 456.14291.

**6.2.4. Synthesis of dithienylethene, incorporated polymers**

**Photopolymerization**

A mixture containing Irgacure 819 as the photoinitiator (2 wt % with respect to the total monomer), dithienylethene (DT1 or DT2) and/or comonomer was mixed in a sonicator for 10 minutes to yield a homogeneous solution. The mixture was cast on a slide glass and polymerized
by exposure to 395 nm UV light in 5-10 min. The coated films were dried at 60 °C overnight in a vacuum oven.

**Radical polymerization**

A mixture containing AIBN (2 wt % with respect to the total monomer), DT and/or comonomer in 10 ml THF was refluxed under argon for 12 h. The cooled mixture was evaporated *in vacuo* to remove solvents and volatile reactants. The polymer obtained was dissolved in toluene at 60 °C. The solution was filtered using membrane of 0.45 μm pore size attached to a syringe on to a slide glass and dried at 60 °C for 12 h in a vacuum oven to yield a homogeneous polymer film.

### 6.3. RESULTS AND DISCUSSION

#### 6.3.1. Photochromism of Dithienylethene DT1 and DT2 Monomers

Figure 6.2 shows the color and structural changes upon photoisomerization of dithienylethene derivatives DT1 and DT2 in degassed dichloromethane at room temperature (27 °C). The open ring isomer of DT1 is colorless in solution. Upon irradiation with UV light (300 nm) the open isomer converts to its red colored closed isomer. The closed isomer returns to its open form under irradiation with visible light (< 510 nm filter) or under room light. Similarly colorless DT2 turns brown upon UV irradiation (300 nm) and reverse isomerizes to its open form under visible light (< 450 nm filter).
Figure 6.2. (A) Color change and (B) structural changes of dithienylethene derivative after photoisomerization (1) DT1 and (2) DT2
The changes in the absorption spectrum of the open isomer and closed isomer of DT1 and DT2 upon irradiation with either UV or visible light are shown in Figure 6.3 and Figure 6.4. The colorless open isomer of DT1 in degassed dichloromethane shows a maximum absorption at 269 nm. Upon irradiation at 300 nm the peak at shorter wavelength gradually decreases while a new peak appears at 517 nm. The spectral shift of the photoisomerization is about 248 nm. An isosbestic point could be observed at 314 nm. The closed isomer was irradiated with visible light (Xe lamp equipped with 510 nm filter) to study the reverse isomerization (Figure 6.3.2). The peak generated due to UV irradiation at 517 nm starts decreasing upon irradiation with visible light.

![UV-Vis spectrum of DT1 photoisomerization from open to close state. DT1 in degassed dichloromethane, irradiation at 300 nm using a photoreactor](image)

**Figure 6.3.1.** UV-Vis spectrum of DT1 photoisomerization from open to close state. DT1 in degassed dichloromethane, irradiation at 300 nm using a photoreactor
Figure 6.3.2. UV-Vis spectrum of the reverse photoisomerization of DT1 from closed to open isomer. DT1 in degassed dichloromethane, first irradiated at 300 nm for 30 s. then the UV sample irradiated with visible light from a Xe lamp (150 W) equipped with a 510 nm filter.

The open ring isomer of colorless DT2 shows maximum absorbance at 273 nm. When irradiated at 300 nm UV light a new peak appears at 373 nm (Figure 6.4.1). An isosbestic point of open-to-closed isomer conversion of DT2 is at 264 nm. A small spectral shift of 100 nm was observed due to the photoisomerization of DT2. The reverse isomerization was carried out with visible light irradiation using Xe lamp with 389 nm filter. The peak responsible for the closed isomer which is at longer wavelength (373 nm) disappears with irradiation.
Figure 6.4.1. UV-Vis spectrum of DT2 photoisomerization from open to close state. DT2 in degassed dichloromethane, irradiation at 300 nm using a photoreactor

The absorption maxima of the open ring isomers of the new dithienylethene derivatives appear at shorter wavelengths. In the open isomeric structures π-conjugation is localized in the thiophene moieties. Upon UV irradiation a new C-C bond forms between 2 and 2’ carbon atoms on the thiophene rings to form a system with four conjugated double bonds. Therefore π-conjugation is delocalized throughout the two condensed thiophene rings in the isomerized closed ring state. This long π-conjugation causes the closed isomers to absorb at longer wavelengths. The conjugation further extends to the substituent at 5 and 5’ positions in the closed isomer and therefore DT1 has six conjugated double bonds while DT2 has only four π-
electrons in conjugation. Due to this $\pi$-delocalization DT1 closed isomer absorbs at relatively higher wavelength (517 nm) than does DT2 (373 nm). The open isomer of DT1 is red while that of DT2 is brown.

Figure 6.4.2. UV-Vis spectrum of the reverse photoisomerization of DT2 from closed to open state. DT2 in degassed dichloromethane, first irradiated at 300 nm for 40 s, then the UV irradiated sample irradiated at visible light with Xe lamp (150 W) equipped with 389 nm filter.

The molar absorption coefficients of DT1 are $(1.4 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ at 269 nm and $3 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ at 517 nm) in dichloromethane while the $\varepsilon$ value for DT2 is low $(200 \text{ M}^{-1}\text{cm}^{-1}$ at 456 nm in dichloromethane). The absorption maximum is affected by both electron rich substituent as well as by long conjugated systems. Thus by introducing an electron rich substituent at 5, 5’ positions
such as an ethyleneyl moiety, which extends the π-conjugation in the closed isomer, enhance the value of the molar absorption coefficients. Therefore DT1 showed higher absorption than DT2.

6.3.2. Thermal Stability

In general, diarylethenes are not thermochromic. Both isomers, open and closed, are thermally stable. The thermal stability of the closed isomer depends on the type of the aryl groups attached to the ethylene moiety. Aryl groups with the low aromatic stabilization energies such as thiophene, furane or thioazole rings thermally stabilize the closed isomer.\textsuperscript{1,40} Therefore dithienylethenes are thermochromic. Some dithienylethene derivatives are reported to be stable for months even at high temperatures while few reported to be stable only for hours. Thermal stability of DT1 and DT2 were studied and shown in Figure 6.5 and Figure 6.6 respectively.

DT1 in degassed dichloromethane was irradiated at 300 nm and the irradiated sample kept in the dark at 27 °C. The absorption spectra recorded after 24 h indicates the sample has not bleached. Even after 1 month in the dark no bleaching was observed. A similar procedure followed to study the thermal stability of compound DT2 which was less thermally stable than DT1. DT2 degassed in dichloromethane was irradiated at 300 nm and kept in dark at 27 °C. After 24 h diminutive decrease in the absorption was observed.
Figure 6.5. Thermal stability of DT1. Absorption spectra were recorded in degassed dichloromethane following irradiation at 300 nm at 27 °C.

Figure 6.6. Thermal stability of DT2. Absorption spectra were recorded in degassed dichloromethane following irradiation at 300 nm at 27 °C.
The closed ring isomer of DT1 has extended $\pi$-conjugation. Therefore the thermal stability of the closed ring DT1 isomer is ascribed to the enhanced strength of the photogenerated central carbon – carbon bond. DT2 consists of two bulky substituents at 5 and 5' positions of the thiophene rings. These bulky substituents weaken the central carbon – carbon bond in the closed ring isomer. Therefore DT2 has lesser thermal stability.

6.3.3. Fatigue Resistance

Fatigue resistance plays a major role in the applications of photochromic compounds. It is difficult to obtain more fatigue resistant compounds from photoisomerization processes. Equation 6.1 shows the possibilities in photoirradiation of compound A.

\[
\begin{align*}
\Phi_s &\quad \lambda_1, \Phi_A \rightarrow B \\
A &\quad \lambda_2, \Phi_B \rightarrow A
\end{align*}
\]

(6.1)

Compound A could undergo photoisomerization to B and reverse isomerization to A along with side product formation of B’. Even if the side reaction quantum yield, $\Phi_s$ is small (such as 0.001) and B converts perfectly to A ($\Phi_B \rightarrow A$ = 1), after 1,000 coloration/decoloration cycles 63 % of the initial concentration of A will have produced B’. Thus good fatigue resistance is rare.

Dithienylethenes are reported to exhibit good fatigue resistance properties. Irie reported a dithienylethene derivative that remains stable over 10,000 cycles. The fatigue resistance of DT1 and DT2 are reported in Figure 6.7 and Figure 6.8. Dithienylethene in degassed dichloromethane solution was irradiated with UV and visible light in a consecutive fashion. A Rayonet reactor equipped with 300 nm bulbs and a Xe lamp equipped with suitable 510 nm or
389 nm filters were used as the light sources. Absorbance measurements were taken at the
beginning and at the end of each cycle. Absorbance measurements showed little deviation due to
experimental errors. The absorption was quite consistent for both compounds after each cycle.

Figure 6.7. Multiple forward and reverse isomerizations of DT1 in dichloromethane solution

Figure 6.8. Multiple forward and reverse isomerizations of DT2 in dichloromethane solution
6.3.4. Polymerization

For an efficient and durable fabrication of an optoelectronic device, it is necessary to incorporate the organic photochromes into a polymer matrix. Since DT1 and DT2 are functionalized with polymerizable functional groups the polymerization process would easy and efficient. Polymerization was carried out by two different processes; photopolymerization and radical polymerization. Figure 6.9 shows the polymerization pathways for the dithienylethene derivative DT1.

![Figure 6.9. Schematic representation of the polymerization of DT1 via radical polymerization and photopolymerization](image)

Photopolymerization yields a polymer film with a closed dithienylethene moiety which can convert to its open form following irradiation with visible light. However radical polymerization results a polymer with an open dithienylethene isomer, which converts to its closed isomer upon
irradiation with UV light. Both ways produce photochromic polymer films in which a reversible photosensitive material was incorporated. A colored polymer film was generated from photopolymerization while radical polymerization led to a colorless polymer film.

Photopolymerization was carried out using a mixture of dithienylethene derivative, photoinitiator (Irgacure 819) and with/without a co-monomer. The mixture was poured onto a glass slides and irradiated with a UV light (UV-Vis LED source at 395 nm). The homopolymer of DT2 is a flexible pale yellow colored rubbery polymer while that of DT1 is a brittle red colored hard polymer. DT2 was compatible with many co-monomers and polymerized easily while DT1 exhibit lack of polymerization. DT2 efficiently copolymerized with many acrylic monomers such as dipropylene glycol diacrylate, n-hexyl acrylate, 2-hydroxyethyl acrylate, trimethylolpropane triacrylate (TMPTA), methacrylic acid, styrene and 1,6-hexanediol diacrylate while DT1 polymerizes with 1,6-hexanediol diacrylate, TMPTA, and n-hexyl acrylate. Both derivatives generate UV cured colored polymers, the color of which bleached upon irradiation with visible light. Red colored polymers were obtained upon UV curing of a DT1 polymer solution while DT2 yield a brown polymer. Radical polymerization was carried out on a mixture containing the DT derivative, and the radical initiator (AIBN) with/without a co-monomer in THF at reflux under argon. Polymerization was followed by IR spectroscopy. Figure 6.10 shows the IR spectra of the DT derivatives and one example for the corresponding polymers.

The IR transmission peak for the ethylene moiety in DT1 monomer is at 1618 cm\(^{-1}\) (Figure 6.10. (a))\(^{41}\). The corresponding peak disappears in the IR spectrum of the polymer which implies the complete polymerization of DT1 (Figure 6.10. (b)). Similarly the corresponding peak for the
ethylene moiety in DT2 (1634 cm$^{-1}$) disappears from the IR spectrum of its polymer (Figure 6.10. (d)).
Figure 6.10. IR spectra of (a) DT1 (b) DT1-co-styrene polymer (c) DT2 (d) DT2-co-1,6-hexanediol diacrylate polymer

6.3.5. Dithienylethene Incorporated Polymer Films

Dithienylethene containing polymer films prepared either from UV curing or radical polymerization show excellent and reversible photochromism. DT1 incorporated polymers turned to red with irradiation in the UV and bleached under room light or visible light (Figure 6.11). DT2 polymers are pale yellow and turn brown following UV irradiation. They are converted to the initial color under visible light.
Figure 6.11. Color changes of dithienylethene polymer films (a) DT1 incorporated polymer films (DT1-co-1,6-hexanediol diacrylate) (b) DT2 homopolymer

The potential applications of dithienylethene incorporated photochromic films are in erasable photon-mode recording. The recording is possible with UV light on colorless films or with visible light on previously exposed to UV colored films. Writing can be done through a mask on the films. Figure 6.12 shows mask images transferred on a film by writing with a 300 nm UV light. The images can completely erased by irradiating with visible light and a second image can record again in the erased films. The process can be repeated for many cycles of recording and erasing.
Figure 6.12. Photograph of photochromic recording on a DT1 polymer film with 300 nm light

Figure 6.13. UV-Vis spectrum of thin polymer film of DT1-co-styrene (a) irradiation at 300 nm (b) Irradiation with visible light (Xe lamp, 510 nm filter)
The absorption spectrum of a thin polymer film of DT1 was recorded (Figure 6.14). Upon UV irradiation a new peak appears at 510 nm and the film turns red. In the presence of visible light the red color disappears with the peak at 510 nm. The process was carried out repeatedly without any loss of intensity at 510 nm (Figure 6.15).

**Figure 6.14.** Multiple coloration and decoloration of DT1-co-styrene polymer films

### 6.4. CONCLUSION

Novel polymerizable dithiaenylethenes DT1 and DT2 have been synthesized by incorporating polymerizable functional groups (ethynyl and methacryloyl) at the 5 and 5’ positions of the thiophene rings. Both compounds act as photochromic materials. Color occurs reversibly by irradiating with UV and with visible light respectively. The closed isomer of DT1 is red while DT2 is brown in dichloromethane solution. DT1 evidences good thermal stability and fatigue resistance being much better than DT2. DT1 has good sensitivity in the longer wavelength region.
with higher absorption coefficient values. These are indispensable for applications as optical memory media. Both derivatives can be easily incorporated into polymer matrixes by either photo-curing or radical polymerization. DT2 is easier to polymerize than DT1. Polymer materials incorporating DT derivatives undergo reversible color changes upon irradiation with UV and visible light respectively. The photochromic films were applied in an erasable recording photon mode.

6.5. REFERENCES


APPENDIX A

LIST OF ABBREVIATIONS:

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>USDA</td>
<td>United States Department of Agriculture</td>
</tr>
<tr>
<td>SAP</td>
<td>Superabsorbent polymer</td>
</tr>
<tr>
<td>AA</td>
<td>Acrylic acid</td>
</tr>
<tr>
<td>AM</td>
<td>Acrylic amide</td>
</tr>
<tr>
<td>BIS</td>
<td>$N,N'$-methylenebisacrylamide</td>
</tr>
<tr>
<td>AC</td>
<td>Azo crosslinker</td>
</tr>
<tr>
<td>RC</td>
<td>Reference crosslinker</td>
</tr>
<tr>
<td>NaCl</td>
<td>Sodium Chloride</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>MHz</td>
<td>Mega hertz</td>
</tr>
<tr>
<td>TMS</td>
<td>Tetramethylsilane</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatography</td>
</tr>
<tr>
<td>MS</td>
<td>Mass spectrometry</td>
</tr>
<tr>
<td>m</td>
<td>Meter</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>mm</td>
<td>Millimeter</td>
</tr>
<tr>
<td>IR</td>
<td>Infra red</td>
</tr>
<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>°C</td>
<td>Degree Celsius</td>
</tr>
<tr>
<td>min</td>
<td>Minuit</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>h</td>
<td>Hour</td>
</tr>
<tr>
<td>g</td>
<td>Gram</td>
</tr>
<tr>
<td>mol</td>
<td>Mole</td>
</tr>
<tr>
<td>mmol</td>
<td>Millimole</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>Sulfuric acid</td>
</tr>
<tr>
<td>ml</td>
<td>Milliliter</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric acid</td>
</tr>
<tr>
<td>NaOH</td>
<td>Sodium hydroxide</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>s (for NMR)</td>
<td>Singlet</td>
</tr>
<tr>
<td>d (for NMR)</td>
<td>Doublet</td>
</tr>
<tr>
<td>t (for NMR)</td>
<td>Triplet</td>
</tr>
<tr>
<td>m (for NMR)</td>
<td>Multiplet</td>
</tr>
<tr>
<td>δ</td>
<td>Chemical shift</td>
</tr>
<tr>
<td>wt%</td>
<td>Weight percentage</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>hv</td>
<td>Photon</td>
</tr>
<tr>
<td>H₂O</td>
<td>Water</td>
</tr>
<tr>
<td>DIP</td>
<td>Direct Ionization Probe</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>Δ</td>
<td>Heat</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
</tr>
<tr>
<td>CS₂</td>
<td>Carbon disulfide</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>Sodium sulphate</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>----------------------------</td>
</tr>
<tr>
<td>M</td>
<td>Moles per liter</td>
</tr>
<tr>
<td>AlCl₃</td>
<td>Aluminum Chloride</td>
</tr>
<tr>
<td>Zn</td>
<td>Zinc</td>
</tr>
<tr>
<td>HRMS</td>
<td>High-resolution mass spectrometry</td>
</tr>
<tr>
<td>AIBN</td>
<td>Azobisisobutyronitrile</td>
</tr>
<tr>
<td>ε</td>
<td>Molar absorption coefficient</td>
</tr>
<tr>
<td>Φ</td>
<td>Quantum yield</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra Violet</td>
</tr>
<tr>
<td>Vis</td>
<td>Visible</td>
</tr>
</tbody>
</table>
APPENDIX B

Figure B1. 1H NMR of 6 in CDCl₃

Figure B2. 1H NMR of 8 in CDCl₃