STIMULI-RESPONSIVE POLYMERS

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ABSTRACT

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Stimuli-responsive polymers are of both fundamental and commercial interest. Such polymers respond dramatically to external stimuli such as changes in light, pH, temperature, mechanical force, electric field, or solvent composition. Hydrogels and organogels that can respond to external stimuli by changing their microstructures from collapsed to expanded as well as by reversibly returning to their initial state with or without the stimuli are important. Herein, three stimuli-responsive polymers have been explored. They are Photoresponsive oil sorbers, Photo- and thermo-responsive hydrogels, and photo- and electro-responsive hydrogels.

A photoresponsive oil sorber with a hydrophobic, photoresponsive core and shell has been synthesized via suspension polymerization. Lauryl acrylate (LA), isodecyl acrylate (IDA) and tert-butylstyrene (tBS) were used as monomers, 4-(methacrylamino)azobenzene (Azo-M) was used as a photoresponsive monomer, and bis(methacryloylamino)azobenzene (Azo-CL-M) was employed as a photoresponsive surface cross-linker. The oil sorber prefers non-polar solvents. It absorbed 15 times its dry weight in toluene, 19 times its dry weight in chloroform and 16 times its dry weight in dichloromethane. Rapid and photoresponsive desorption of solvent (86% of solvent expelled in 30 minutes) was characteristic. The new oil sorber is an excellent gasoline absorber rapidly increasing its body weight in its presence. And also, it is less dense than water, and can potentially be utilized for cleaning oil spills on water.
A dual-stimuli responsive hydrogel with a thermoresponsive backbone and photochromic pendant groups was synthesized via free radical polymerization using \(N\)-isopropylacrylamide (NIPAAm) as main monomer, 9’-Methacryloyloxy-1,3,3-trimethyl-spiro[indoline-2,3’-3H]naphth[2,1b][1,4]oxazine (MSp) (MSp) as photochromic monomer, the crosslinker \(N,N’\)-methylenebisacrylamide (BIS) and the initiator 2,2’-azobisisobutyronitrile (AIBN) in dimethylsulfoxide (DMSO). The polymers are dual responsive, in that poly(\(N\)-isopropylacrylamide) [PNIPAAm] responds to temperature changes while the pendant spironaphthoxazines respond to light. Irradiation enhanced the water absorption of the polymers while increases in temperature decreased it. The irradiated PNIPAAm-MSp showed best water absorption at 0 °C (\(Q = 3.25\)) while water desorbed at higher temperatures (35 °C; \(Q = 0.30\)); where \(Q\) is the amount of water absorbed by a gram of dry polymer.

Photoresponsive bending of rod shaped PNIPAAM-MSp hydrogels under a DC electric field have been investigated. The excited state formed by the absorption of light dissociated at the spiro C-O bond of the spironaphthoxazine moiety and generated charges in the polymer. These then aligned with the electric field to cause bending of the polymer. In the absence of light, the bent polymers reversibly straightened. The photoresponsive bending became faster in salt solutions and the direction of bending switched with the changing polarity of the electric field. No actuation was observed without photoirradiation.
This dissertation is dedicated to my family and my teachers
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# TABLE OF CONTENTS

## CHAPTER 1. INTRODUCTION  ..........................................................................................1

1.1 STIMULI- RESPONSIVE POLYMERS ..............................................................................1

1.2 RECENT DEVELOPMENT OF STIMULI-SENSITIVE POLYMERS.................................3

1.2.1 Photoresponsive Polymers ..........................................................................................3

1.2.1.1 Azobenzene Containing Polymers ..........................................................................6

1.2.1.2 Spironaphthoxazine/Spiropyran Containing Polymers ..............................................7

1.2.2 Thermoresponsive Polymers .....................................................................................8

1.2.2.1 PNIPAAm Containing Polymers ............................................................................11

1.2.3 Electro-responsive Polymers .......................................................................................12

1.2.4 pH Responsive Polymers ...............................................................................................13

1.2.5 Multi Stimuli-responsive Polymers ...............................................................................14

1.3 APPLICATIONS OF STIMULI-RESPONSIVE POLYMERS ..........................................14

1.4 REFERENCES ....................................................................................................................16

## CHAPTER 2. PHOTORESPONSIVE OIL SORBERS, A SUPER DUPER WAY TO CLEAN OIL SPILLS .........................................................................................................................21

2.1 WHAT ARE OIL SORBERS? .............................................................................................21

2.2 WHAT IS AN OIL SPILL? .................................................................................................21

2.3 CLEANING AN OIL SPILL ...........................................................................................23

2.4. RECENT DEVELOPMENTS OF OIL ABSORBENTS ....................................................26

2.5 THE PROJECT ................................................................................................................27
2.6 EXPERIMENTAL SECTION .................................................................29
  2.6.1. Materials ..................................................................................29
  2.6.2 Method and Instrumentation .......................................................29
  2.6.3 Synthesis ...................................................................................30
  2.6.4 Polymerization .........................................................................32

2.7 RESULTS AND DISCUSSION ..........................................................33
  2.7.1 Characterization .......................................................................33
  2.7.2 Toluene Absorption .................................................................34
  2.7.3 Photoresponse of the polymer ..................................................36
  2.7.4 Toluene desorption following irradiation .................................38
  2.7.5 Effect of Photochromic Monomer Content ...............................39
  2.7.6 Effect of Photochromic Cross-linker .......................................40
  2.7.7 Absorption of Solvents and Light-induced Desorption ..........41
  2.7.8 Absorption of Oils ...................................................................42
  2.7.9 Photoresponsive Oil Desorption ..............................................44
  2.7.10 Oil Absorption Over Water ....................................................45
  2.7.11 Morphology of the Polymer ..................................................45

2.8 CONCLUSION .................................................................................46

2.9 REFERENCES ..................................................................................47

CHAPTER 3. DUAL RESPONSIVE HYDROGELS, PHOTO- AND THERMO-
RESPONSIVE HYDROGELS .................................................................51

  3.1 POLYMERS THAT RESPOND TO MULTIPLE STIMULI ..............51
  3.2 WHAT ARE HYDROGELS AND SUPERABSORBANT POLYMERS? 51
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3 HISTORY OF HYDROGELS</td>
<td>51</td>
</tr>
<tr>
<td>3.4 CHEMISTRY OF HYDROGELS</td>
<td>53</td>
</tr>
<tr>
<td>3.5 APPLICATIONS AND RECENT DEVELOPMENTS</td>
<td>54</td>
</tr>
<tr>
<td>3.6 THE PROJECT</td>
<td>57</td>
</tr>
<tr>
<td>3.7 EXPERIMENTATION SECTION</td>
<td>58</td>
</tr>
<tr>
<td>3.7.1 Materials</td>
<td>58</td>
</tr>
<tr>
<td>3.7.2 General Methods and Instrumentation</td>
<td>59</td>
</tr>
<tr>
<td>3.7.3 Synthesis</td>
<td>60</td>
</tr>
<tr>
<td>3.7.4 Polymerization</td>
<td>63</td>
</tr>
<tr>
<td>3.8 RESULTS AND DISCUSSION</td>
<td>63</td>
</tr>
<tr>
<td>3.8.1 Photochromic Properties of the Monomer MSp</td>
<td>63</td>
</tr>
<tr>
<td>3.8.2 Dual Responsive PNIPAAm-MSp</td>
<td>66</td>
</tr>
<tr>
<td>3.8.3 Effect of Temperature on the Swelling of PNIPAAm-MSp</td>
<td>68</td>
</tr>
<tr>
<td>3.8.4 Effect of Light and Temperature on the Swelling of PNIPAAm-MSp</td>
<td>69</td>
</tr>
<tr>
<td>3.8.5 Effect of MSp content on the Swelling of PNIPAAm-MSp</td>
<td>71</td>
</tr>
<tr>
<td>3.8.6 Swelling of PNIPAAm-MSp in Tap Water</td>
<td>72</td>
</tr>
<tr>
<td>3.8.7 Morphology of PNIPAAm-MSp Hydrogel</td>
<td>73</td>
</tr>
<tr>
<td>3.9 CONCLUSIONS</td>
<td>74</td>
</tr>
<tr>
<td>3.10 REFERENCES</td>
<td>74</td>
</tr>
<tr>
<td>CHAPTER 4. ELECTRO AND LIGHT RESPONSIVE HYDROGELS,</td>
<td></td>
</tr>
<tr>
<td>PHOTOACTUATED BENDING OF POLYMERS</td>
<td>78</td>
</tr>
<tr>
<td>4.1 ELECTRORESPONSIVE POLYMERS</td>
<td>78</td>
</tr>
<tr>
<td>4.2 RECENT DEVELOPMENTS OF ELECTRORESPONSIVE HYDROGELS</td>
<td>81</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1. Schematic representation of responsive dimension changes. (Adapted from Reference 1)</td>
<td>2</td>
</tr>
<tr>
<td>1.2. Schematic representation of photoresponse</td>
<td>4</td>
</tr>
<tr>
<td>1.3. Examples of different organic photochromic compounds</td>
<td>6</td>
</tr>
<tr>
<td>1.4. Molecular structures of temperature responsive polymers</td>
<td>9</td>
</tr>
<tr>
<td>1.5. States of water in PNIPAAm hydrogels as a function of its equilibrium temperature (Adapted from ref. 22)</td>
<td>10</td>
</tr>
<tr>
<td>2.1. Physical impact of the great BP oil spill on a marine environment: (a) Burning Deep water Horizon oil rig after the explosion (b) Floating oil on the ocean surface (c) Heavily oil impacted marshlands of Mississippi delta in Louisiana (d) A struggling sea turtle to swim in oil slick (e) An oil-soaked bird at the site of the exploded oil rig (f) An oil-covered crab...</td>
<td>23</td>
</tr>
<tr>
<td>2.2. Cleaning of oil spills: (a) Oil soaked booms (b) Controlled burning of oil (c) A dispersant releasing aircraft (d) An oil removing skimmer. All the photographs are from the BP oil spill</td>
<td>26</td>
</tr>
<tr>
<td>2.3. Schematic representations of oil absorption and oil expulsion of photoresponsive oil absorbing polymers following light absorption</td>
<td>27</td>
</tr>
<tr>
<td>2.4. Photoisomerization of azobenzenes</td>
<td>28</td>
</tr>
<tr>
<td>2.5. Photos of (a) golden yellow color bis(methacryloylamino)azobenzene; (b) orange color 4-(methacrylamino)azobenzene</td>
<td>32</td>
</tr>
<tr>
<td>2.6. Schematic illustration of photoresponsive oil sorber</td>
<td>34</td>
</tr>
<tr>
<td>2.7. (a) Quantitative toluene absorption of photoresponsive oil sorber and blank oil sorber; (b) Dry polymer beads; and (c) Toluene absorbed polymer beads</td>
<td>35</td>
</tr>
</tbody>
</table>
2.8. Absorption spectra of Azo-M monomer in chloroform (a) upon irradiation at 350 nm; (b) upon irradiation at 450 nm. .................................................................................................................................36

2.9. Absorption spectra of Azo-CL-M cross-linker in DMSO (a) upon irradiation at 350 nm; (b) upon irradiation at 450 nm. .................................................................................................................................37

2.10. The absorption spectra of photoresponsive oil sorber in chloroform; (a) irradiated at 350 nm; (b) irradiated at 450 nm. .................................................................................................................................38

2.11. Toluene desorption with and without irradiation of light at 350 nm. ........................................38

2.12. (a) Toluene absorption of oil sorbers containing different percentages Azo-M; (b) Toluene desorption of oil sorbers with different Azo-M concentrations. .........................................................39

2.13. (a) Toluene absorption of oil sorbers differing in Azo-CL-M content. (b) Photo-induced toluene desorption of oil sorbers differing in Azo-CL-M content. .........................................................40

2.14. (a) Dry polymer beads before solvent absorption; (b) Absorption of different solvents by the oil sorber. .................................................................................................................................41

2.15. (a) Dry polymer beads; (b) Floating toluene colored with blue dye on water; (c) Polymer beads that had absorbed toluene solvent floating on water. .................................................................45

2.16. SEM images of; (a) Oil sorber beads and (b) A cross-section of a polymer bead. ..................46

3.1. Schematic representation of a part of a polymer network of sodium polyacrylate. ..............53

3.2. Photoisomerization of 1,3,3-trimethylspiro[indoline-2,3’-[3H]naphtha[2,1b][1,4]oxazines.58

3.3. The reversible color change of MSp. .......................................................................................64

3.4. (a) Forward reaction of MSp with time; Irradiation at \( \lambda \sim 350 \) nm (b) Reverse reaction of MSp with time under room light. Both reactions were carried at 0 °C in ethanol. .................65

3.5. IR spectra of (a) Dry PNIPAAm-Msp and (b) Swollen PNIPAAm-Msp....................................68

3.6. Thermoresponsive swelling of the PNIPAAm-MSp hydrogels..............................................69
3.7. Swelling of the irradiated polymers at different temperatures 23, 0, and 35 °C during one hour. ......................................................................................................................................70

3.8. Water absorption of PNIPAAm-MSp in distilled water and tap water at (a) 23 °C and (b) 0 °C ...........................................................................................................................................72

3.9. The swollen hydrogel samples; (a) Non-irradiated (red color), (b) Irradiated, (blue color), and their corresponding SEM images. ........................................................................................................73

4.1. Electroresponsive contractile behavior of water swollen poly(2-acrylamido-2-methyl-1-propanesulfonic acid): (a) before and (b) after applying the electric field. (Adapted from reference 4) ........................................................................................................................................79

4.2. Schematic representation of; (a) the water pool used for measurement; (b) position of the polymer gel in the water pool. ...........................................................................................................84

4.3. Reversible bending of the rod-shaped PNIPAAm-MSp gel (25 mm length and 1 mm cross-section diameter) in an electric field. .........................................................................................................85

4.4. Reversible isomerization of spironaphthoxazine moiety in the gel network. .........................86

4.5. Schematic representation of the alignment of charges on spironaphthoxazine pendant groups upon UV irradiation in the electric field. .........................................................................................86

4.6. (a) Schematic representation of the distance travelled by the ends of the gel; (b) Bending of the gel with time. .................................................................................................................................87

4.7. Straightening of the gel after removal of the UV light. (a) Distance travelled by the gel ends with time; (b) Photographs of gel straightening with time........................................................................88

4.8. Effect of MSp content on gel bending. (a) Gel bending as a function of time; (b) Photographs of gel bending with time.................................................................................................................................90
4.9. Gel bending with Cross-linking density. (a) Distance travelled by gel ends as a function of time; (b) Photographs of gel bending with time..........................91

4.10. Bending of PNIPAAm-MSp rod-shaped gels in 0.01 M NaCl solution.................................92
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1. Methods for treating oil spills.</td>
<td>23</td>
</tr>
<tr>
<td>2.2. Monomer composition for polymerization</td>
<td>33</td>
</tr>
<tr>
<td>2.3. Maximum solvent absorptions of the new photoresponsive oil sorber</td>
<td>42</td>
</tr>
<tr>
<td>2.4. Maximum absorptions of new oil sorber in different oils</td>
<td>43</td>
</tr>
<tr>
<td>2.5. Oil desorption percentages induced by light with respect to time</td>
<td>44</td>
</tr>
<tr>
<td>3. 1. Swelling of PNIPAAm-MSp at different temperatures with and without irradiation for one hour. PNIPAAm-MSp with 1.9% MSp was used to study the swelling</td>
<td>71</td>
</tr>
<tr>
<td>3. 2. Swelling of PNIPAAm-MSp with different MSp percentages at 0 °C</td>
<td>72</td>
</tr>
</tbody>
</table>
LIST OF SCHEMES

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1. Synthesis of (a) 4-(methacrylamino)azobenzene (Azo-M); (b) bis(methacryloxylamino)azobenzene (Azo-CL-M).</td>
<td>31</td>
</tr>
<tr>
<td>3.1. Schematic synthetic pathway of photochromic monomer (MSp). (i) 0.6 M NaOH, 0 °C, NaNO₂, and conc. H₂SO₄; (ii) 1,3,3-Trimethyl-2-methyleneindoline, 1 h reflux; (iii) Methacryloyl chloride.</td>
<td>61</td>
</tr>
<tr>
<td>3.2. Cartoon of the dual responsiveness of the PNIPAAm-MSp hydrogel. The white oval shapes represent the closed spironaphthoxazine pendant groups before irradiation and the black lines show the PNIPAAm backbone. The ash oval shapes show the open merocyanine form of the spironaphthoxazine pendant groups after irradiation.</td>
<td>66</td>
</tr>
</tbody>
</table>
1.1 STIMULI-RESPONSIVE POLYMERS

The design and development of novel materials or systems capable of responding to external stimuli is inspired by nature. Mimicking biological systems in a controllable and predictable fashion is challenging and many stimuli-responsive polymeric systems have been developed. A majority of previous studies deal with altering the physical states of polymers, including polymeric solutions, gels, surfaces or interfaces, and polymeric solids.  

The response of a polymer can be defined in different ways depending on the restrictions on the mobility of the polymeric segments. For instance, the dimensional change of a polymeric solution can be higher than the dimensional change in a gel, because of relative restricted mobility within the network in the latter. Therefore, there can be limitations to a “response.” A response can be a size change, a change in secondary structure, a color change, a solubility change, or changes in the degree of intermolecular association. A schematic representation of such responses is outlined in Figure 1.1.
The scientific interest in stimuli-responsive polymers has persisted over several decades, and great work dedicated to devising examples of environmentally sensitive macromolecules that can be crafted into new smart materials. External stimuli can be either chemical or physical signals. Chemical signals, such as pH, ionic species, or metabolites interfere with the molecular interactions between polymeric chains and solutes. Physical signals such as light, temperature, electric potential, and pressure modify the energies of chain dynamics and molecular interactions. Ionic interactions and hydrogen bonding or hydrophobic interactions of
polymeric systems can be modified by the external stimuli, causing changes in the physical state of the system. The removal of the stimulus should result in a reversion to the original physical state.

1.2 RECENT DEVELOPMENT OF STIMULI-SENSITIVE POLYMERS

Physical properties of polymeric materials can be modified by controlling various parameters. Chain conformation, configuration, color and solubility can be induced by external stimuli. Swelling/deswelling of hydrogels, shape memory of thin films, and self assembly of polymers in solution to produce aggregates with respect to the external stimuli are a few examples. In the following sections, the properties of stimuli responsive polymers are discussed.

1.2.1 Photoresponsive Polymers

Photoresponsive polymeric systems have been widely studied in many areas, such as photo-optical media, photo-switches, photo-mechanical systems, micropatterning, and non-linear optical media. These systems are important because light is non destructive, can be localized as well as remotely activated. Thus delivering energy to systems results in photo-triggered sensing, actuating, and transporting.

A photoresponsive polymer exhibits conformational changes in response to light. Such polymers can be constructed by incorporating chromophores that can translate light energy into a change in conformation. Through the introduction of photochromic functionalities, physical and chemical property changes following irradiation have been exploited. Photo-stimulated conformational changes at the microscopic level are amplified to shape changes (contraction or
expansion) at the macroscopic level, effectively converting energy from a light beam into mechanical energy.\textsuperscript{19}

Photochromism is defined as a reversible transformation of chemical species between two states having observable light absorptions in different regions induced in one or both directions by electromagnetic radiation, (Figure 1.2).\textsuperscript{3} During photoisomerization, changes are not restricted to absorption spectra, but various physicochemical properties are altered, such as the refractive index, dielectric constant\textsuperscript{4-6}, oxidation/reduction potential\textsuperscript{7}, geometrical structure\textsuperscript{8} and luminescence\textsuperscript{9-10}.

\begin{center}
\begin{align*}
A(\lambda_1) & \xleftrightarrow{h\nu_1} B(\lambda_2) \\
& \xleftrightarrow{h\nu_2 \text{ or } \Delta}
\end{align*}
\end{center}

\textbf{Figure 1.2.} Schematic representation of photoresponse.

In photoresponsive functionalities, the response may be associated with chemical processes involving either isomerization or cleavage of chemical bonds. The main chemical processes involved in photochromism are \textit{cis-trans} isomerization (azo compounds, stilbenes)\textsuperscript{11}, pericyclic reactions (spiropyrans, diarylethenes, and anthracenes)\textsuperscript{3}, dissociation reactions (triphenylmethane leuco derivatives), electron transfer (viologens), intramolecular hydrogen transfer (salicylates, triazoles and oxazoles), and intramolecular group transfer (polycyclic quinones). Figure 1.3 shows some photoresponsive functionalities.
(a) Isomerization: Azo compounds

(b) Pericyclic reactions: Spiropyans

(c) Ionization: Triphenylmethane leuco derivatives

(d) Electron transfer: viologens
(e) Intramolecular hydrogen transfer: polycyclic quinones

![Image of chemical structures]

**Figure 1.3.** Examples of different organic photochromic compounds

In each process, the original molecule changes chemical structure and the light absorption, as well as chemical and physical properties, change as a result.

**1.2.1.1 Azobenzene Containing Polymers**

Photoresponsive polymers containing azobenzenes as the chromophore have been widely studied.\textsuperscript{15,20,21} The isomerization of azobenzene following UV irradiation results in changes in geometry, absorption spectra, and dipole moments.\textsuperscript{22} The distance between the 4- and 4’- carbon atoms of the aromatic rings in azobenzene is less in the *cis* isomer (5.5 Å) than the *trans* isomer (9 Å). Therefore incorporation of an azobenzene group, substituted at 4- and 4’- positions into a polymer network, either to the backbone or as pendant groups, causes a macroscopic change in volume upon photoisomerization.\textsuperscript{20,21} A *trans*- to *cis*- isomerization causes a decrease absorption at 330-380 nm due to $\pi-\pi^*$ transition and an increase in absorption at 420 nm due to n-$\pi^*$ transition.\textsuperscript{22,23} Thus incorporation of azobenzene into a polymer network causes a change in the
absorption spectra following UV irradiation. Likewise, trans-azobenzene has no dipole moment while the dipole moment of the non-planar cis compound is 3.0 D.\textsuperscript{22,23}

Agolini and Gay\textsuperscript{22} were the first to describe a photo-mechanical effect in the case of a semicrystalline poliimide with azo chromophores in the backbone. Contraction of polymers under heat and UV irradiation was observed due to the isomerization from the trans- to the cis-form in the amorphous regions of the film. Similar contractions of azobenzene containing polymers were discussed by Irie, Eisenbach,\textsuperscript{22,23} Van der Veen and Prins,\textsuperscript{22} and Matejka.\textsuperscript{22} Reversible contraction to expel absorbed liquids in hydrogels/ organogels with the isomerization of incorporated azobenzene derivatives has also been studied.\textsuperscript{20,21} Photocontrollable bending of a single film of a liquid crystal network containing an azobenzene was reported.\textsuperscript{25} The bending direction was changed with respect to the wavelength of the irradiated light.

1.2.1.2 Spironaphthoxazine/Spiropyran Containing Polymers

Polymers containing spiropyrans/spironaphthoxazines have been studied widely because of their resistance to photofatigue and high coloring power. Upon UV irradiation, spiro compounds undergo ring opening, forming an intensely colored merocyanine isomer which exists as a zwitter ion. The merocyanine reverts thermally or photochemically to the colorless closed isomer. Shining light on either the spiropyran or the merocyanine changes the physical properties of the compound, including changes in the absorption spectra, dipole moments, and geometries.\textsuperscript{22}

In 1979, Irie and coworkers studied photoregulated viscosity changes in poly(methyl methacrylate) containing spirobenzopyran side groups.\textsuperscript{26} During UV irradiation, the solution viscosity of the polymer was reduced, but this reverted to the original value in time after
removing the UV light. Formation of the merocyanine isomer leads to an increase in the dipole moment of the side groups, thus causing a reduction in viscosity. Similarly, photoresponsive reversible solubility changes in polystyrenes containing spirobenzopyran pendant groups in cyclohexane was discussed by Irie in 1985. Isomerization of the non-polar spirobenzopyran to the polar merocyanine decreased the polymer-solvent interactions, therefore fractional precipitation of the polymer was observed. Hydrogels containing spironaphthoxazine/spiropyran pendant groups were also subsequently reported. Spiropyran containing poly(N-isopropylacrylamide) hydrogels were investigated for potential applications in photo-optical data storage. Photoresponsive polyether dendrimers bearing spironaphthoxazine in their peripheries were studied by Zhang et al. The dendrimers complexed with different metal ions following UV illumination and released the metal ion with visible light irradiation. The photoresponsive properties can be tuned by changing the size of the dendrimer.

1.2.2 Thermoresponsive Polymers

Thermoresponsive polymers have widely studied because of their projected uses in many fields such as biomedicine (drug delivery and release), functional materials, surface modifiers, and chromatography. Polymer gels first appeared in the 1970s that were capable of varying shape or volumes in response to changes in temperature. The thermoresponse can also be a color change (thermochromic).

If polymers are placed in a solvent, the polymers could either be soluble/swellable or precipitated. Neutral polymers form hydrogen bonds with water at room temperature, thus becoming soluble or evidencing water absorption at room temperature. As the temperature was increased, the solubility of such polymers decreased. Above this temperature, termed the lower
critical solution temperature (LCST), the polymers become insoluble.\textsuperscript{12} There have been reports of such thermal behavior of different polymers due to their LCST. Poly\((N\text{-isopropylacrylamide})\) (PNIPAAm), poly\((N\text{-vinylcaprolactone})\) (PVCL), poly\((N\text{-}(DL)-(1\text{-hydroxymethyl}) propylmethacrylamide)\) (P(DL)-HMPMA), poly\((N,N'^{'}\text{-diethacrylamide})\) (PDEAAM), and polyethylene glycol (PEG)\textsuperscript{1,12} are a few examples of polymers that exhibit this behavior (Figure 1.4). The LCST’s of the polymers above are 32, 32, 37, 33 and >90 °C respectively.

![Molecular structures of temperature responsive polymers.](image)

**Figure 1.4.** Molecular structures of temperature responsive polymers.

PNIPAAm is one of the more extensively studied thermoresponsive polymers. It undergoes sharp phase transitions close to physiological temperature. Figure 1.5 shows the state of water in the thermoresponsive gel as a function of temperature.\textsuperscript{22} As the temperature
increases, the polymer network collapses. Therefore swelling or shrinking is discontinuous and a small change in temperature can cause a larger volume/mass/shape change.

**Figure 1.5.** States of water in PNIPAAm hydrogels as a function of its equilibrium temperature (Adapted from ref. 22)

Reversible color change as a result of temperature changes are also known, and numerous photoresponsive functional groups are also thermoresponsive. For example, spiropyrans, fulgides, [2H]-pyrans and Schiff bases display thermochromic behavior. For many photochromic compounds such as spiropyrans, triphenylmethane leuco derivatives, and azo compounds, for which the color change photochemically induced, bleaching is partially controlled thermally.36
1.2.2.1 PNIPAAm Containing Polymers

Volume phase transition of PNIPAAM was first reported by Hirokawa and Tanaka in 1984.\textsuperscript{37} PNIPAAm undergoes a liquid–solid phase transition near 32 °C, and this alters the distribution of hydrophilic (hydorgen bonding) and hydrophobic interactions. Thus beyond the LCST, stable chain coils transform into a globule form.\textsuperscript{12} This thermal responsive behavior was focused on many applications in targeted drug delivery,\textsuperscript{12,38} artificial muscles,\textsuperscript{37} and nanotechnology.\textsuperscript{12,39} Incorporation or modification with hydrophilic moieties increases the phase transition temperature, while modification of the hydrophobic moieties decreases it.\textsuperscript{12,40,41,42} This behavior is most effective for low molecular weight systems, and as the molecular weight decreases, the phase transition temperature decreases.\textsuperscript{12,43}

A thermoresponsive polymer, poly(\(N\)-isopropylacrylamide-co-\(N\)-hydroxymethylacrylamide) containing cholesteryl side groups, was developed for the controlled release of hydrophobic drugs.\textsuperscript{44} The cholesteryl grafted polymer showed a slow phase transition at 40 °C. Increasing the percentage of cholesteryl groups in the polymer decreased the response to temperature changes. Since such polymers have a LCST above body temperature, they should be suitable for controlled release of anti-cancer drugs.\textsuperscript{45} A thermoresponsive ABA block copolymer of PNIPAAm and PPO (polypropylene glycol) was prepared by Hasan et. al.\textsuperscript{46} As different LCST’s of PNIPAAm and PPO were made, thermoassociative properties were attained, i.e. domains of the polymer have PNIPAAm segments with higher transition temperature and PPO segments of lower transition temperature.
1.2.3 Electro-responsive Polymers

Polymers capable of executing mechanical work under the influence of an electric field, such as expansion, contraction, elongation, and bending, are called electro-responsive polymers. Electric fields have advantages as external stimuli. One can conveniently and precisely control the magnitude of the current, as well as the duration of and the intervals between pulses.\textsuperscript{54} Ease of actuation and miniaturization, low noise, and mechanical properties similar to those of biological systems are some properties of these polymers.\textsuperscript{52} Polyelectrolyte gels, conductive polymers, ionic-polymer metal composites, and dielectric elastomers are also included in this category.\textsuperscript{52,53} These materials have attracted a great deal of attention in medicine and mechanical engineering and have projected uses in the delivery of precise doses of drugs, as contact lenses, as artificial muscles, in mechanical grippers, and as sensors.\textsuperscript{52,53}

Among many electro-responsive polymers, electro-responsive hydrogels have become tempting because of their use in controlled drug delivery as well as their biocompatibility. In 1982, Tanaka observed an electro-responsive contraction and a phase separation of a partially hydrolyzed polyacrylamide gel in contact with platinum electrodes. Tanaka and his colleagues recognized deswelling that is due to an electrophoretic pressure gradient.\textsuperscript{55} A similar effect for water swollen poly(2-acrylamido-2-methyl-1-propanesulfonic acid) gel was found by Osada and Hasebe in 1985. These workers observed up to 30% loss of absorbed water from a gel in the presence of an electric field.\textsuperscript{56}

Response depends on the shape of the gel and its position relative to the electric field. When a hydrogel lies perpendicular to the electrodes, or the gels are touching the electrodes, deswelling/contraction is noticeable.\textsuperscript{52} Bending can be observed when the gel lies parallel and
are not touching the electrodes.\textsuperscript{57,58} The bending of hydrogels has been studied mostly for production of mechanical devices such as artificial muscles, valves, switches, “soft actuators”, and “molecular machines”.\textsuperscript{54,56,59} Deswelling or contractile behavior of hydrogels has been mainly studied in controlled drug delivery.

Moschou and coworkers\textsuperscript{57,58} synthesized a voltage switchable artificial muscle consisting of an acrylic acid/acrylamide backbone and a polypyrrole composite with 20\% (w/w) carbon black additive. A cylindrical shaped gel was placed in a 0.15 M sodium chloride solution, parallel to the platinum electrodes. The gel bent towards the cathode and changed reversibly bending direction with the changing polarity of the electric field. When an applied potential was turned off, the gel relaxed to its original straight position. Shrinkage of partially hydrolyzed stacked six gel layers in an electric field was studied by Liu and Calvert.\textsuperscript{60} Platinum electrodes were embedded inbetween layers 1 and 2 (polyacrylic acid) and layers 5 and 6 (layers 3 to 6 are polyacrylamide). The gel stack was electroactuated on a dry plate with acrylic acid side positive and acrylamide side negative. Under the electric field, the stack contracted 50\% along x and y axes and exudes 20 – 30\% water.\textsuperscript{60}

1.2.4 pH Responsive Polymers

Polymers which contain ionic groups in main or side chains are suitable for monitoring changes in the environment. Ionic interactions in polymers can be altered by pH changes, and they can be pH responsive. Polymers such as ionic polymers, polyelectrolytes, conjugated polymers doped with ions, and uncharged polymers that have been swollen in ionic liquids are potentially pH responsive polymers.\textsuperscript{53} These polymers exhibit ionization changes with respect to a pH change, and a reversible change in volume/shape may be observed.\textsuperscript{61,62} This particular
behavior has been used to induce controlled release of model compounds (caffeine), drugs (indomethacin), and proteins (lysozome).\textsuperscript{62} The pH responsive polymers have been used to develop microfluidic systems.\textsuperscript{53} As pH is varied, the gel network changes from neutral to negatively charged causing the gel to expand due to osmotic pressure. A flow control valve using this system was made of poly(acrylic acid) and polyhydroxyethylmethacrylate. This can respond to changes in the pH allowing an opening or closing of the valve.

### 1.2.5 Multi Stimuli-responsive Polymers

Polymers can also exhibit responsive behavior to multiple stimuli, and numerous dual stimuli responsive systems have been studied. Combinations of light and temperature,\textsuperscript{30,63,66,67} pH and temperature,\textsuperscript{64,65} and light and electric field\textsuperscript{19} have been reported. There are reports on triple stimuli responsive polymers that respond to light, heat and pH.\textsuperscript{29} Multi stimuli responsive polymeric materials can be obtained from the incorporation of different functional groups responding to different stimuli. For example, free radical copolymerization of $N$-isopropylacrylamide and a polymerizable spiropyran derivative with a $N,N'$-methylenebisacrylamide cross-linker produces a thermo- and light- responsive polymer. The PNIPAAm backbone will respond to the temperature whereas the spiropyran will respond to light.\textsuperscript{67}

### 1.3 APPLICATIONS OF STIMULI-RESPONSIVE POLYMERS

One may fashion tailorable “smart” functional materials from stimuli responsive polymers. These find applications in controlled drug delivery, industrial paints and coatings,
sensors and actuators, viscosity modifiers, microfluidic devices, colloid stabilization, surface modification, and water remediation.\textsuperscript{12}

Stimuli-responsive polymers following the normal physiological process of the disease state as used for slow drug release in which the amount of drug released is affected by physiological need.\textsuperscript{68} Thermoresponsive “on-off” drug releasing systems for indomethacin (a non-steroidal anti-inflammatory drug) are previously reported.\textsuperscript{68,69} Poly(N-isopropylacrylamide) cross-linked butyl methacrylate [P(NIAAm-co-BMA)] hydrogels loaded with indomethacin was “on” and released drug at lower temperature but “off” at higher temperature. With an increase of the temperature, the gel surface collapsed and denser, and thus less permeable. Reports on electrosensitive hydrogels used to control drug delivery are also known.\textsuperscript{69} Poly(2-acrylamido-2-methylpropane sulfonic acid-co-n-butylmethacrylate) hydrogels exhibit electric current responsive release of edrophonium chloride and hydrocortisone in a pulsatile manner. Controlled “on-off” drug release was accomplished by varying the intensity of the electric current.\textsuperscript{70}

Stimuli-responsive super hydrophobic surfaces may be self cleaning. This idea was inspired by natural lotus leaves and water strider legs.\textsuperscript{71} Reports on photoresponsive surface wettability changes of a spiropyran coated silicon nano wire surfaces, show that UV light irradiation induces a more hydrophilic surface. With visible light irradiation, this reverted to a surface of superhydrophobic nature. Self healing polymer composites and coatings are also important in industrial applications. Thermoresponsive, photoresponsive,\textsuperscript{73} and solvent responsive\textsuperscript{74} self healing was also reported. Finally, new polymer gels that produce nanoscale fractal patterns for renewable energy applications were designed.\textsuperscript{53}
1.4 REFERENCES


CHAPTER 2
PHOTORESPONSIVE OIL SORBERS
A SUPER DUPER WAY TO CLEAN OIL SPILLS….

2.1 WHAT ARE OIL SORBERS?

Oil sorbers are oil/hydrophobic liquid absorbing materials, used to remove spilled oily substances.

2.2 WHAT IS AN OIL SPILL?

An oil spill is defined as the release of oily substances into the environment. It can be either small or large, and man-made or natural. Small oil spills, such as a spill of cooking oil on a counter top, or some grease/oil on a garage floor can be easily cleaned with a paper towel or by washing the area with soapy water. Of greater concern are larger oil spills, which involve the release of larger volumes of oil, this being especially harmful to aquatic environments. Every year, more than 3 million metric tons of oil contaminants flow into the seas and oceans. These oil spills take place because of ship collisions, oil well blow outs, oil contaminated water run off from industries, parking lots and garages, dumping of oil bilge water, and leaking of underground storage tanks.

The ongoing oil spill, also referred to as Deep Water Horizon oil spill, the BP oil spill, the Gulf of Mexico oil spill, is the worst oil spill in the history of United States. It is thought to be more devastating than the Exxon-Valdes oil spill in 1989. The spill began when the deep
water horizon oil exploration platform sank after the oil rig exploded 5000 feet below the ocean surface, situated about 40 miles southeast, coast of Louisiana on April 20th, 2010. According to estimates, between 12,000-25,000 barrels (504,000 -1,050,000 US gallons) of crude oil is discharging per day. This oil spill tends to spread faster than a normal ship wreck oil spill, because it starts at deep of the ocean and discharges under pressure. The spreading of the spill is accelerated as a result of the wind, currents, and tides. Consequent emulsification, evaporation, sedimentation, and photooxidation of floating oil contributes to polluting both the water column and the sea bed.

It is found that the leaking oil contains high levels of Asphaltenes, high molecular weight compounds contained in crude oil. These compounds promote emulsification (mixing of oil and water). Since the oil spill occurred on the sea floor, the oil could emulsify as it proceeds the 5000 ft. to the surface. Emulsified oil floating just below the ocean surface slows down the evaporation, hence concentrating more toxic chemicals in the oil. When these oil layers hit the sea shore, they are expected to be much more toxic than the floating oil slick.

Spilled oil poses serious threats to fresh water and marine environments. This directly affects wildlife (coating birds, fish and mammals with a layer of oil), animal habitats, and poisons exposed organisms. Figure 2.1 shows oil impacted seashores and affected wildlife in BP oil spill.
**Figure 2.1.** Physical impact of the great BP oil spill on a marine environment: (a) Burning Deep water Horizon oil rig after the explosion,\(^6\) (b) Floating oil on the ocean surface,\(^7\) (c) Heavily oil impacted marshlands of Mississippi delta in Louisiana,\(^8\) (d) A struggling sea turtle trying to swim in oil slick,\(^9\) (e) An oil-soaked bird at the site of the exploded oil rig,\(^10\) (f) An oil-covered crab.\(^11\)

The size of the on-going BP oil spill is yet to be determined. The Gulf War oil spill in 1991 (1,360,000-1,500,000 tons of crude oil) and the Ixotoc I oil well explosion in 1979 (454,000-480,000 tons of crude oil) are two examples of the world’s largest oil spills. The damages from such spills are tremendous, their effects persisting over prolonged periods of time.

**2.3 CLEANING AN OIL SPILL**

Many methods have been employed to clean and control oil spills. Most are only partially effective. Table 2.1 summerizes common methods used to clean oil spills.

**Table 2.1.** Methods for treating oil spills.
<table>
<thead>
<tr>
<th>Method</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural cleansing /Bioremediation</td>
<td>Natural digestion of oils by microbes</td>
</tr>
<tr>
<td>Oil dispersents</td>
<td>Emulsifying the spilt oil</td>
</tr>
<tr>
<td>Oil sinking agents</td>
<td>Sinking the spilt oil to the sea bed</td>
</tr>
<tr>
<td>Oil gelling agents</td>
<td>Coagulating and solidifying the spilt oil</td>
</tr>
<tr>
<td>Oil absorbents</td>
<td>Absorbing the oil</td>
</tr>
<tr>
<td>Booms</td>
<td>Floating and acting as a barrier to avoid spreading and also absorbs oil</td>
</tr>
<tr>
<td>Skimmers</td>
<td>Boats that pump or vacuum to remove oil from water</td>
</tr>
<tr>
<td>Controlled burning</td>
<td>Burning the oil before further spreading</td>
</tr>
</tbody>
</table>

Cleaning or controlling oil spills on land is often conducted manually. Scooping, scraping and cleansing rocks and sand, as well as vacuuming until all the oil has been removed are all common practices. Natural cleansing takes a long time to degrade and remove oils. Introducing microbes to the oil spill can accelerate the degradation; however, it is still an overall slow process.

Introduction of oil dispersants or oil sinking agents enhance the cleansing processes by breaking down the oil into small oil droplets and inhibiting emulsion formation. During the first
month of the BP oil spill, 60,000 gallons of dispersant have been deployed to the ocean surface, that is four times greater than the dispersent deployed for the Exxon Valdes spill. Consequently, small oil droplets degrade by the action of marine microbes. Oil gelling agents coagulate the spilt oil by modifying the surface tension and the solidified oil can then be recovered by using nets. In such cases, the recovered oil cannot be reused, and is therefore disposed as toxic waste. Skimmers have also been employed to collect spilled oil. A skimmer is a piece of equipment which absorbs/adsorbs floating oil from a water/oil mixture. The skimmer selectively collects the oil, but not the aqueous layer. In the BP oil spill, 3.6 million gallons of oil has been recovered using skimmers. Moreover, controlled in-situ burning is occasionally performed to control oil spreading. However, this must be done taking into account wind and weather conditions. This method is considered as a last resort because of resulting air pollution.

Oil absorbents have been recently studied as agents to treat oil. Polypropylene fiber or non-woven fabrics, polyurethane foam sheets, and melt brown polyesters are employed in this regard. However, because of their bulkiness; the use of such absorbents remains disadvantageous. Moreover, the disposal of such materials has either environmental and economic disadvantages, as the “products” need to be incinerated or buried.
2.4. RECENT DEVELOPMENTS OF OIL ABSORBENTS

Various polymers have been used as oil absorbents (or oil sorbers). Alkyl acrylates and aromatic polymers with non-polar side chains are of interest. There have been a few reports of oil sorbers consisting of vulcunized styrene-butadiene rubber and ethylene-propylene-diene (EPDM) polymers that have high elasticity and are resistant to degradation by light, heat or by oxygen. Gel type structures consisting of hydrophobic elastic networks render such polymers most effective. However, conventional oil sorbers have many limitations, as they are slow and inefficient. There have been other reports on oil recovery using oil stripping and inoculation process, where 99% of the oil was recovered from the absorbing material and reused in a short time period of about 6 hours. Fast oil recovery of oil absorbers by incorporating photoresponsive groups is outlined in the following sections.

Figure 2.2. Cleaning of oil spills: (a) Oil soaked booms, (b) Controlled burning of oil, (c) A dispersant releasing aircraft, (d) An oil removing skimmer. All the photographs are from the BP oil spill.
2.5 THE PROJECT

The incorporation of photoresponsive functionalities into an oil absorbing polymer that can control oil-absorption and desorption has, to our knowledge, not been explored. In this work we highlight a spherical shaped oil sorber consisting of functionalized azobenzene monomers and functionalized azobenzene cross-linkers. Oil sorbers consisting of hydrophobic three-dimensionally cross-linked polymers are able to absorb oil and swell. Following light absorption, isomerization of the azobenzene moiety induces contractions in the polymer network. Our work focuses on the effect of such contraction on the properties of a swollen oil sorber. We expected this action to force the oil to move out of the polymer network, mimicking mechanical “squeezing” of a swollen sponge, (Figure 2.3).

![Figure 2.3](image)

**Figure 2.3.** Schematic representations of oil absorption and oil expulsion of photoresponsive oil absorbing polymers following light absorption.

Azobenzenes undergo reversible photoisomerization.\(^\text{32}\) The more stable *trans* isomer converts, as a result of light absorption, to its less stable *cis* isomer. If left to its own devices,
such polymers containing an azobenzene function undergo reverse isomerization to the equilibrium composition favoring the trans compound. The reverse reaction, however, can also be induced photochemically. The isomerization of azobenzene results in significant size changes caused by the change in geometry. The distance between 4- and 4’- carbon atoms of aromatic rings in azobenzene is less in the cis isomer (5.5 Å) than the trans isomer (9 Å) (Figure 2.4). Therefore incorporation of an azobenzene group, substituted at the 4- and 4’- positions, into a polymer network causes macroscopic changes in volume upon photoisomerization.

**Figure 2.4.** Photoisomerization of azobenzenes.

Our new photoresponsive oil absorbing polymer, synthesized via suspension polymerization, is a basic polymer complex consisting of isodecyl acrylate (IDA), lauryl acrylate (LA), and tert-butylstyrene (tBS) with divinylbenzene (DVB) as the internal cross-linker and poly(vinyl alcohol) (PVA) as a surfactant. Benzoyl peroxide (BPO) was used to initiate the polymerization event and photoresponsive functionalities, 4-(methacrylamino)azobenzene (Azo-M) as well as bis(methacryloylamino)azobenzene (Azo-CL-M), were also included. Subsequently, oil absorbency and the effect of photoresponse of the new polymers were investigated.
2.6 EXPERIMENTAL SECTION

2.6.1. Materials

4,4’-Azodianiline was purchased from Acros Organics and all other chemicals were purchased from Aldrich. tert-Butylstyrene and divinylbenzene were purified by standard procedures. Benzoyl peroxide was recrystallized from methanol. Other reagents were purified using conventional literature methods. Freshly distilled spectroscopic grade solvents were used for all spectroscopic analyses.

2.6.2. Method 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 recorded on a Hewlett Packard 5988 mass spectrometer coupled to a HP 5880A GC with a 30 m×0.35 mm ID 0.25 film thickness DB-5 ms column (J & B scientific) interfaced to a HP 2623A data processor. IR spectra were obtained with Thermo Nicolet IR 200 spectrometer. UV-Vis absorption spectra were recorded using a Shimadzu Multispec–1501 spectrometer. Irradiation was carried out using a Southern New England Ultraviolet Co. Rayonet reactor fitted RPR-3500 Å lamps in an 8 bulb array. Column chromatography was carried out using silica gel (60 Å, 32-63 µm, standard grade) purchased from Sorbent technologies.

Oil absorbency was determined by the American Society for Testing and Materials method, ASTM F726-81 test: 0.1g of polymer was placed in a stainless steel mesh and immersed in toluene. The sample and the mesh were removed together from the toluene, drained for 2
minutes and weighed. The weight of the sample and the mesh was measured every 15 minutes.

The oil/toluene absorbency (Q) was calculated using equation (1):

\[ Q \text{ (g/g)} = \frac{(W_t - W_0)}{W_0} \quad (1) \]

where \( W_t \) is the weight of the polymer at time \( t \) and \( W_0 \) is the weight of the initial dry weight of the polymer. The procedure was repeated three times to get an accurate \( Q \) value.

The swollen oil sorbers were continuously illuminated at 350 nm on a stainless steel mesh and weights were recorded at 10 minute intervals. The oil desorption was measured as a result of the irradiation. The procedures were repeated three times and the mean value for \( Q \) calculated. Oil desorption of the polymer without its having been exposed to 350 nm light was also measured.

2.6.3 Synthesis

The synthetic procedures for modified azobenzene monomer and cross-linker are shown in scheme 2.1.
Scheme 2.1. Synthesis of (a) 4-(methacrylamino)azobenzene (Azo-M); (b) bis(methacryloylamino)azobenzene (Azo-CL-M).

Synthesis of Bis(methacryloylamino)azobenzene (Azo-CL-M). 33

4,4’-Diaminoazobenzene (2.0 g, 9.43 mmol) was dissolved in anhydrous pyridine (20 ml). Methacryloyl chloride (2.10 ml, 19.8 mmol) was added dropwise using a dropping funnel under argon atmosphere. The reaction mixture was heated at 60 °C for one hour. The mixture was cooled to room temperature and poured into ice. Acidified with HCl (pH 4), filtered, and washed the precipitate with saturated sodium bicarbonate solution and then with water. The crude product was recrystallized from ethanol to yield a golden yellow color pure bis(methacryloylamino)azobenzene (Figure 2.5) (1.64 g, 50%). Melting Point: 259-260 °C. DIP: $m/z = 348$ [M$^+$]. $^1$H NMR (DMSO, δ, ppm): 1.97 (s, 6H), 5.55 (s, 2H), 5.9 (s, 2H), 7.90 (d, 8H), 10.1 (s, 2H).
Figure 2.5. Photos of (a) golden yellow color bis(methacryloylamino)azobenzene; (b) orange color 4-(methacrylamino)azobenzene

Synthesis of 4-(Methacrylamino)azobenzene (Azo-M).\textsuperscript{33}

4-(Methacrylamino)azobenzene (Azo-M) (Figure 2.5) was synthesized similarly from 4-aminoazobenzene. Melting point: 154-155 °C. GCMS: \( m/z = 265 \). \(^1\text{H} \text{NMR (CDCl}_3, \delta, \text{ppm)}: 2.1 (s, 3H), 5.5 (s, 1H), 5.85 (s, 1H), 7.5 (m, 3H), 7.8 (dd, 2H), 7.95 (m, 4H).

2.6.4 Polymerization

Polymerization was carried out in suspension. Poly(vinylalcohol) (PVA) (0.175 g, 20%) was suspended in distilled water (200 mL) in a 250 mL three-neck flask, equipped with a stir bar at the bottom, degassed for 30 minutes and heated to 76 °C. The monomers (IDA: LA: tBS=5:5:1), DVB (1%), Azo-M (9%), as well as BPO (20%) and chloroform (3 mL) were added to another round bottom flask and degassed for 15 minutes. All weight percentages were calculated with respect to the tBS monomer content and the monomer compositions are shown in table 2.2. This organic solution was then introduced into the aqueous phase through a dropping
funnel at a stirring speed of 1200 rpm. The solution was allowed to polymerize for 2 hours at 90 °C. The photochromic surface cross-linker, Azo-CL-M (20%) in DMSO/toluene (2:3) mixture (25 mL), was then introduced into the mixture, and polymerization continued for another 2h. Finally, the polymer was collected as orange-brown beads, washed with acetone and distilled water, and dried in a vacuum until a constant weight was achieved. The beads that formed were between 0.7 and 2 mm in diameter.

Table 2.2. Monomer composition for polymerization

<table>
<thead>
<tr>
<th></th>
<th>IDA (mL)</th>
<th>LA (mL)</th>
<th>tBS (mL)</th>
<th>DVB (mL)</th>
<th>Azo-M (g)</th>
<th>Azo-CL-M (g)</th>
<th>PVA (g)</th>
<th>BPO (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.8</td>
<td>2.8</td>
<td>0.56</td>
<td>10</td>
<td>0.044</td>
<td>0.097</td>
<td>0.175</td>
<td>0.175</td>
</tr>
</tbody>
</table>

2.7 RESULTS AND DISCUSSION

2.7.1 Characterization

It is well known that oil sorbers must be hydrophobic to swell in an oil/non-polar medium. DVB was added before the start of polymerization to generate a hydrophobic core. Photoresponsive Azo-M provided higher hydrophobicity as well as more light-sensitivity to the polymer. Photoresponsive surface cross-linker, Azo-CL-M, was introduced after beginning the polymerization. Thus a polymer with a hydrophobic and photosensitive core and a photosensitive shell is formed (Figure 2.6).
Figure 2.6. Schematic illustration of photoresponsive oil sorber.

The driving force for oil absorption by hydrophobic networks is mainly due to van der Waals interactions between the material and the oil. Bulkiness and longer alkyl substituents in constituent monomers seems to improve polymer oil absorption. For this reason, lauryl acrylate with a twelve carbon alkyl chain and isodecyl acrylate with a ten carbon alkyl chain were used as the main monomers. The butyl function of 4-tert-butylstyrene (tBS) may have some steric effect on the fabrication of the cross-linked polymer providing larger cavities into which the oil molecules can fit. Thus polymers with good porosity, such as the polymers containing tBS, can effectively absorb more oil.

2.7.2 Toluene Absorption

Toluene is widely used in industry as a solvent, a coolant for nuclear reactors, and an octane booster in gasoline fuels. Due to its low viscosity and density, it can easily become part of oil based organic pollutants. Thus runoffs of toluene into water bodies cause pollution similar to
other oil wastes. We used toluene as a base solvent on which to test our newly synthesized polymeric oil absorbers.

Photoresponsive oil sorber beads absorbed more toluene than blank polymer beads (polymers without photoresponsive functionalities) because of the higher hydrophobicity induced by the incorporated Azo-M monomers and Azo-CL-M surface cross-linkers. The polymer beads absorbed 15 times their dry weight in toluene and became swollen (Figure 2.7). The oil sorber attained maximum absorption in approximately 50 minutes, thus being quite satisfactory for oil absorbing applications.

**Figure 2.7.** (a) Quantitative toluene absorption of photoresponsive oil sorber and blank oil sorber; (b) Dry polymer beads; and (c) Toluene absorbed polymer beads.
2.7.3 Photoresponse of the polymer

Absorption spectra of the azo monomer (Azo-M) (Figure 2.8 (a)) and azo cross-linker (Azo-CL-M) (Figure 2.9 (a)) were measured following irradiation at 350 nm light for various time intervals. The absorptions around 350 nm for Azo-M and 375 nm for Azo-CL-M, both of which diminish upon irradiation, are due to intense trans-azobenzene $\pi-\pi^*$ transitions. Concomitantly other peaks around 450 nm, corresponding to the cis-isomers, appear. Reversion to trans Azo-M and Azo-CL-M following irradiation at 450 nm is confirmed by the concomitant changes in absorption spectra (Figure 2.8 (b) and 2.9 (b)).

Figure 2.8. Absorption spectra of Azo-M monomer in chloroform (a) upon irradiation at 350 nm; (b) upon irradiation at 450 nm.
Figure 2.9. Absorption spectra of Azo-CL-M cross-linker in DMSO (a) upon irradiation at 350 nm; (b) upon irradiation at 450 nm.

UV-Vis absorption spectra of the photoresponsive oil sorber following irradiation at 350 nm and 450 nm are shown in Figure 2.10.
Figure 2.10. The absorption spectra of photoresponsive oil sorber in chloroform; (a) irradiated at 350 nm; (b) irradiated at 450 nm.

2.7.4 Toluene desorption following irradiation

While the non-irradiated gels took more than one day to desorb toluene when irradiated at 350 nm, a swollen gel containing a photoresponsive cross-linker shrinks rapidly as absorbed toluene is expelled (Figure 2.11). The azo chromophores inside and around the surface induce expulsion of solvent by the polymer network and about 86% of the absorbed toluene is expelled in 30 minutes. Slower desorption is observed polymers that are not irradiated because of lower diffusion rates of solvent from the polymer network. Thus the photoresponsive oil sorber can be used in applications where efficient oil recovery is needed.

Figure 2.11. Toluene desorption with and without irradiation of light at 350 nm.
2.7.5 Effect of Photochromic Monomer Content

The percent photochromic monomer affects toluene absorption and desorption, Figure 2.12 (a). A polymer with 5% Azo-M content absorbs less toluene (Q = 13.7) relative to the 9% Azo-M (Q = 15). Both polymers absorb more toluene than the blank polymer.

Figure 2.12. (a) Toluene absorption of oil sorbers containing different percentages Azo-M; (b) Toluene desorption of oil sorbers with different Azo-M concentrations.

The content of photochromic monomer also affects toluene desorption. As Azo-M content in the polymers was increased, the photo-induced desorption rate of toluene is increased because a higher contraction of the polymer is induced by the azobenzene functionality. An oil sorber containing 5% Azo-M showed 73% of the absorbed toluene removal after 30 minutes of irradiation, while an oil sorber with 9% Azo-M content caused 86% of absorbed toluene to be expelled following irradiation with 350 nm light (Figure 2.12 (b)).
2.7.6 Effect of Photochromic Cross-linker

Changing the photochromic cross-linker content caused little change in toluene absorption, Figure 2.13 (a).

Figure 2.13. (a) Toluene absorption of oil sorbers differing in Azo-CL-M content. (b) Photo-induced toluene desorption of oil sorbers differing in Azo-CL-M content.

With 10% Azo-CL-M, 71% absorbed toluene was desorbed in 30 minutes, Figure 2.13 (b); with 20% Azo-CL-M content, 86% was desorbed in 30 minutes. The more thoroughly cross-linked surface allows the polymer to contract more than the lightly cross-linked polymer. With an increase of the Azo-CL-M to more than 20%, there is no change in desorption time from 20% cross-linked.
2.7.7 Absorption of Solvents and Light-induced Desorption

The new photoresponsive oil sorber beads absorbed 15 times their own dry weight in toluene. Solvents of various polarities, water, ethanol, acetone, dichloromethane, chloroform, and heptane, are absorbed differently (Figure 2.14 (a)).

Figure 2.14. (a) Dry polymer beads before solvent absorption; (b) Absorption of different solvents by the oil sorber.

The new oil sorbers absorbed non-polar solvents better than polar solvents (Figure 2.14) and seem to prefer chlorinated solvents by showing higher absorptions toward chloroform (Q = 19.5) and dichloromethane (Q = 16.2) (Table 2.3).
Table 2.3. Maximum solvent absorptions of the new photoresponsive oil sorber.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$Q_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1.08</td>
</tr>
<tr>
<td>Ethanol</td>
<td>2.51</td>
</tr>
<tr>
<td>Acetone</td>
<td>2.24</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>16.2</td>
</tr>
<tr>
<td>Chloroform</td>
<td>19.5</td>
</tr>
<tr>
<td>Heptane</td>
<td>9.2</td>
</tr>
<tr>
<td>Toluene</td>
<td>15</td>
</tr>
</tbody>
</table>

2.7.8 Absorption of Oils

Absorptions of differing samples of gasoline, kerosene, citronella, and olive oils were also explored. Diffusion of such highly viscous oils is slow because swelling is primarily due to penetration of oils into the polymeric network through capillary action and diffusion.\(^{19}\) But oil diluted with toluene easily diffuses into the core of a polymeric network via the external surface of the polymer. Table 2.4 data reports maximum absorptions ($Q_{\text{max}}$) and maximum absorption times ($T_{\text{max}}$) of the polymers in oils of differing compositions.
Table 2.4. Maximum absorptions of new oil sorber in different oils.

<table>
<thead>
<tr>
<th>Oil</th>
<th>$Q_{\text{max}}$</th>
<th>$T_{\text{max}}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline (100%)</td>
<td>12</td>
<td>47</td>
</tr>
<tr>
<td>Gasoline (50%)</td>
<td>12.4</td>
<td>26</td>
</tr>
<tr>
<td>Gasoline (10%)</td>
<td>13.8</td>
<td>21</td>
</tr>
<tr>
<td>Olive oil (100%)</td>
<td>4.2</td>
<td>204</td>
</tr>
<tr>
<td>Olive oil (50%)</td>
<td>8.14</td>
<td>214</td>
</tr>
<tr>
<td>Olive oil (10%)</td>
<td>12.9</td>
<td>47</td>
</tr>
<tr>
<td>Kerosene (100%)</td>
<td>12.5</td>
<td>110</td>
</tr>
<tr>
<td>Kerosene (50%)</td>
<td>13.6</td>
<td>77</td>
</tr>
<tr>
<td>Kerosene (10%)</td>
<td>14.3</td>
<td>69</td>
</tr>
<tr>
<td>Citronella oil (100%)</td>
<td>10.2</td>
<td>85</td>
</tr>
<tr>
<td>Citronella oil (50%)</td>
<td>13.3</td>
<td>73</td>
</tr>
<tr>
<td>Citronella oil (10%)</td>
<td>15.2</td>
<td>40</td>
</tr>
</tbody>
</table>

Olive oil has the highest viscosity; thus its maximum oil absorption without dilution is least among the oils tested ($Q_{\text{max}} = 4.2$). When olive oil is diluted with toluene, $Q_{\text{max}}$ increased and saturation time decreased.
2.7.9 Photoresponsive Oil Desorption

Desorption without UV irradiation, i.e., recovery of the oil from an oil sorber, often took more than one day. Desorption of especially viscous liquids is incomplete even after one week (Table 2.5).

Table 2.5. Oil desorption percentages induced by light with respect to time

<table>
<thead>
<tr>
<th>Oil</th>
<th>Desorbed oil%</th>
<th>Desorbed oil%</th>
<th>Desorbed oil%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T = 30 min</td>
<td>t = 60 min</td>
<td>t = 90 min</td>
</tr>
<tr>
<td>Gasoline</td>
<td>50</td>
<td>66</td>
<td>74</td>
</tr>
<tr>
<td>50% gasoline</td>
<td>74</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>10% gasoline</td>
<td>76</td>
<td>94</td>
<td></td>
</tr>
<tr>
<td>Kerosene</td>
<td>8</td>
<td>26</td>
<td>30</td>
</tr>
<tr>
<td>50% Kerosene</td>
<td>36</td>
<td>49</td>
<td>56</td>
</tr>
<tr>
<td>10% Kerosene</td>
<td>65</td>
<td>88</td>
<td>95</td>
</tr>
<tr>
<td>Citronella candle oil</td>
<td>7</td>
<td>17</td>
<td>24</td>
</tr>
<tr>
<td>50% citronella</td>
<td>29</td>
<td>41</td>
<td>46</td>
</tr>
<tr>
<td>10% citronella</td>
<td>66</td>
<td>87</td>
<td>92</td>
</tr>
<tr>
<td>10% Olive oil</td>
<td>53</td>
<td>77</td>
<td>84</td>
</tr>
<tr>
<td>50% Olive oil</td>
<td>21</td>
<td>33</td>
<td>41</td>
</tr>
</tbody>
</table>
As dilution is increased, both oil absorption and desorption become faster. Polymers that absorbed diluted gasoline desorbed 94-95% of the gasoline/toluene mixture within one hour.

2.7.10 Oil Absorption Over Water

The figure shows vividly that a polymer floating on water absorbed oil (Figure 2.15).

![Figure 2.15](image1)

**Figure 2.15.** (a) Dry polymer beads; (b) Floating toluene colored with blue dye on water; (c) Polymer beads that had absorbed toluene solvent floating on water.

2.7.11 Morphology of the Polymer

Figure 2.16 shows scanning electron microscopy (SEM) images of polymer beads and their cross-sections. SEM images indicated the polymer beads have smooth surfaces because of the thoroughly cross-linked surface cross-linking. The SEM images also clearly indicate there are interstitial spaces inside the polymer bead.
2.8 CONCLUSION

A new photoresponsive oil sorber containing functionalized azobenzene monomers (Azo-M) and azobenzene surface cross-linkers (Azo-CL-M) have been synthesized. The polymer, obtained as orange-brown beads, absorbs 15 times more toluene than its dry weight. Following irradiation at 350 nm, 84% of the absorbed toluene is desorbed in 30 minutes.

A higher photoresponsive monomer content (Azo-M) leads to increased toluene absorption. With 350 nm radiation, 86% absorbed toluene is excluded from the polymer in 30 minutes.

Increasing surface cross-linking encourages faster photo-induced oil desorption. This leads more repelling of oil from the polymeric network. The higher the surface cross-linking, the more the contraction resulting from trans-cis isomerization of the azobenzene functionality.
The photoresponsive oil sorber absorbs non-polar solvents more than polar solvents. The hydrophobic bead core and shell repel polar solvents. The polymer beads absorb more chloroform, dichloromethane and toluene.

The polymer is both selective for gasoline absorption and gasoline is dislodged by light-induced desorption more rapidly than any of the other hydrophobic solvents tested. The polymer attained maximum gasoline absorption \((Q = 12)\) within 47 minutes with 74% of the absorbed gasoline was removed after 90 minutes irradiation. 94-95% of the absorbed diluted gasoline can be photochemically desorbed within one hour.

Viscous oils attain maximum absorption slowly and photo-induced desorption is also slower. Diluting the oils with toluene increases the absorption rate as well as the light induced desorption rate.

2.9 REFERENCES


CHAPTER 3
DUAL RESPONSIVE HYDROGELS
PHOTO- AND THERMO- RESPONSIVE HYDROGELS

3.1 POLYMERS THAT RESPOND TO MULTIPLE STIMULI

Polymers that can respond to multiple stimuli are important in many potential applications, such as controlled drug delivery, bio-seperations, viscosity modulations, surface modifications, memory elements, and water remediations. Among many stimuli-responsive polymeric materials, hydrogels are promising materials with a wide range of applications. They show reversible volume phase transitions depending on the choice of external stimuli. Thus these materials find applications in biotechnology, pharmaceutics, agriculture and industry.

3.2 WHAT ARE HYDROGELS AND SUPERABSORBANT POLYMERS?

Hydrogels are polymer networks that absorb and retain large amounts of water. In some cases, the amount of water retained can be several thousand times their own dry weight. These are termed superabsorbent polymers.

3.3 HISTORY OF HYDROGELS

The first cross-linked, swellable poly(acrylic acid) polymer was studied in 1938 by W. Kern. Kuhn, Katchalsky, and coworkers studied poly(methacrylic acid) in the early 1950’s. Bashaw and Harper (Dow Chemical Co.) demonstrated the first practical use of cross-linked
potassium polyacrylates as water immobilizing agents in fire fighting. In 1968, Harper and coworkers claimed the use of cross-linked polyacrylates as absorbents in diapers. Several patents exist that claim the use of similar materials as absorbents for medical use and as personal care products. In the early 1980’s Japanese companies commercialized diapers containing superabsorbent materials. Superabsorbant polymers in diapers was brought to the USA in 1984 and products were marketed in Europe in the late 1980’s. Today the superabsorbant polymer industry is a multi billion dollar industry with a broad spectrum of applications including children/adult diapers, agriculture and erosion control, medical dressings, floor protection pads, waste water treatment, wire and cable water blocking, etc.

In 1936, the first contact lenses, referred to as “hard” contact lenses, based on polymethylmethacrylate (PMMA) were produced. These lenses were made commercially available to American’s in the 1930’s, and in the late 1950s, Czechoslovakian chemist Otto Wichterle and his assistant Dr. Drahoslav Lim began to experiment with methods to produce contact lenses using a soft, water-absorbing plastic called hydroxyethyl methacrylate (HEMA) created by Dr. Lim in 1945. In 1971, Bausch and Lomb introduced the first commercially available soft contact lenses resulting from Wichterle’s research. Today approximately 125 million people use contact lenses worldwide (2%), including 28 to 38 million people in the United States, and 13 million people in Japan.
3.4 CHEMISTRY OF HYDROGELS

Hydrogels are cross-linked polymer networks with polymer backbones that are hydrophilic due to presence of alcohol, carboxylic acid, and amide groups. Figure 3.1 shows a schematic illustration of a hydrogel/superabsorbant polymer particle.

Figure 3.1. Schematic representation of a part of a polymer network of sodium polyacrylate.

Cross-linking typically connects polymer chains by joining two macromolecules through a smaller molecule. In manufacturing hydrogels/superabsorbant polymers, the most common cross-linker is a hydrophilic molecule with two or more polymerizable double bonds. Cross-links between the polymer chains form a three dimensional network, preventing the polymer from swelling to infinity (prevent dissolution). The degree of cross-linking affects the level of swelling. That is, the higher the cross-linking density, the lower the swelling capacity and the stronger the polymer.
Superabsorbant polymers are partially neutralized ionic polymers (Figure 3.4) and the neutralized chains contain charges that repel each other. Negative charges associated with carboxylate groups are neutralized by positively charged sodium ions. When the superabsorbant polymers come in contact with water, it diffuses into the polymer and hydrates the sodium ions. The attraction of sodium ions to carboxylate ions is thus reduced by hydration allowing sodium ions to move freely inside the network. This creates an osmotic pressure inside the gel. Because of the weak attraction to the carboxylate ions, the hydrated sodium ions cannot leave the network. Therefore, the difference between the osmotic pressure inside and outside the gel drives swelling. Hence, these kinds of polymers swell better in de-ionized water than in normal water.  

3.5 APPLICATIONS AND RECENT DEVELOPMENTS

Hydrogels and superabsorbant polymers embrace numerous applications in biomedical fields, pharmaceutical fields, and as personal hygiene products because of their high water content and the consequent biocompatibility. Soft contact lenses made of hydrogels are popular because of their comfort, ease of use, disposability, and relatively low cost. Tissue engineering, molecular imprinting, wound dressing materials, immunoisolation, drug delivery are among many medical applications of hydrogels. Immunoisolation is the process of protecting implanted material such as biopolymers, cells, or drug release carriers from an immune reaction. Microencapsulation of these implanted cells with hydrogel based capsules is common to protect them from the immune system. Alginate, chitosan, agarose, and polyethylene glycol have been using for encapsulation. These hydrogels are non-interfering with cellular functions of the inside cells, encapsulation can be done under physiological conditions, and provide microenvironment for the trapped cell survival for longer time.
The soft and hydrophilic nature of hydrogels makes them particularly suitable as novel drug delivery systems. Kamada and coworkers have developed a pH sensitive polymeric drug carrier consists of a poly(vinylpyrrolidine-co-dimethyl maleic anhydride) conjugated doxorubicin. Doxorubicin is a drug used in cancer chemotherapy. The drug release was controlled by controlling the pH. As the pH decreases from neutral to acidic, the drug gradually released. The largest applications are of personal hygiene products such as baby diapers, adult protective underwear, and as sanitary napkins.

Superabsorbent polymers are important in treating waste water. The waste water, solidified/gelled with the use of superabsorbant polymers, can be treated as solid waste, removed from a plant without pumping out into the environment. Superabsorbant polymers play a vital role in agriculture; for example erosion protection, urban horticulture, and desert vegetation protection by increasing water holding capacity of soil. Therefore these polymers can increase plant growth rates, increase survival rate of seedlings, and lead to a better overall harvest. There are many other applications that have been developed for hydrogels and superabsorbant polymers such as floor protection pads, filtration applications, sustained-release delivery systems, wire and cable water blocking, fire retardation, grow in water toys, fragrance carriers, spill control, artificial snow, and so on.

Various polymerization techniques have been employed for the synthesis of hydrogels such as solution polymerization, bulk polymerization, graft polymerization, and suspension polymerization. Attempts have been made to improve water absorption in hydrogels. Fast water absorption was achieved by introducing porosity to the polymer. This can be achieved using different strategies. The phase separation method, in which the porous
hydrogels are synthesized at temperatures higher than the lower critical solution temperature (LCST) of the base polymer, is a method usually employed to synthesize poly($N$-isopropylacrylamide) gels.\textsuperscript{25} Adding a pore generator (eg. sodium chloride, sucrose) to the polymerization mixture, followed by extraction using a suitable solvent, is yet another method. When the hydrogel is kept in the extracting medium, the incorporated porogens diffuse out of the polymer network and pores remain unaltered. Foaming agents such as carbonates (magnesium carbonate, calcium carbonate and sodium bicarbonate) and organic solvents (n-pentane, hexane, dichloromethane, acetone and methanol) have been employed to generate porosity.

Another approach used to synthesize fast responding hydrogels is to reduce the gel dimensions. According to Tanaks and Fillimore’s theory of gel swelling,\textsuperscript{26} the characteristic time of gel swelling is proportional to the square of the linear dimension of the gel. However, only spherical shaped gels are considered in the above theory: Suspension polymerization can be employed to prepare spherical shaped gels. Moreover, reducing cross-linking density also improves the water absorbing capacity. However, the gel strength is lowered when the cross-linking density is reduced. Introduction of surface cross-linking in the preparation of hydrogels enhances water absorption as well as prevents deformation under heavy loads.

Incorporation of functionalities that can respond to external stimulus, such as pH, light, and temperature, to control the water absorption/desorption have been studied over the past few decades. It is also possible to improve the controlling ability by incorporating functionalities which can respond to multiple stimuli.\textsuperscript{27-33} Sumaru \textit{et. al} investigated reversible phase transitions of a polymer with response to light, temperature, and pH.\textsuperscript{34} The polymer was consisted of a poly($N$-isopropylacrylamide) backbone with spirobenzopyran pendants. Thermo-
and light-controllable phase transitions of oligo(ethylene glycol) methyl ether methacrylate (OEGMA) containing azobenzene end groups were tested by scientists.\textsuperscript{35} The lower critical solution temperature of this polymer solution shifted following UV irradiation. Thus the water absorption/desorption is controlled by the change of both UV light and temperature.

\textbf{3.6 THE PROJECT}

Hydrogels\textsuperscript{36,37} can respond to external stimuli by changing their microstructures from collapsed to expanded as well as by reversibly to return to their initial state with or without the presence of stimuli.

Poly(\textit{N}-isopropylacrylamide) [PNIPAAm] gels are typical thermoresponsive polymers with a lower critical solution temperature (LCST) (31–32 \textdegree C) close to the physiological temperature. These polymeric systems swell in water below the LCST and collapse above it.\textsuperscript{38-47} Because of this characteristic, PNIPAAm gels have been widely used for drug delivery, as sensors and as media separators.\textsuperscript{48-50}

As photochromic compounds spironaphthoxazines have particular values because of their excellent coloring power and resistance to photofatigue.\textsuperscript{51} The spiro-pyranyl C-O bond dissociates following the absorption of UV radiation, converting it from the colorless closed form 1 in to the highly blue colored open merocyanine form 2 (Figure 3.2). The reverse reaction occurs both thermally and/or photochemically.
Herein, we focus on PNIPAAm hydrogels modified with spironaphthoxazines as pendent groups (PNIPAAm-MSp) that display dual sensitivity. The PNIPAAm backbone is sensitive to temperature changes while the spironaphthoxazine pendant group is sensitive to UV-light. As the temperature rises above the LCST of the PNIPAAm backbone, the polymer gels repel water and shrink. At temperatures below the LCST the polymer gels absorb water. Irradiation in the UV region induces formation of the open, charge separated moiety. As more water molecules diffuse into the polymer network, charges are stabilized by solvent-chromophore interactions. Consequently, light exposed polymer hydrogels swell more than non-irradiated polymer hydrogels and this is accompanied by a change in color.

### 3.7 EXPERIMENTAL SECTION

#### 3.7.1 Materials

2,7-Dihydroxynaphthalene was purchased from Acros Organics. All other chemicals were purchased from Aldrich. N-Isopropylacrylamide was purified by recrystallization from a
mixture of one part toluene and four parts petroleum ether. Other reagents were purified using conventional literature methods.

### 3.7.2 General Methods and Instrumentation

NMR spectra were recorded using a BRUKER Avance 300 MHz NMR spectrometer with TMS as the internal standard. A HP5880A GC-MS spectrometer was used to record the mass spectra. UV-Vis absorption spectra of MSp in ethanol were recorded using a Shimadzu Multispec–1501 spectrometer. IR spectra were obtained using ThermoNicolet IR 200 spectrometer. Irradiation was carried out using a Southern New England Ultraviolet Co. Rayonet reactor fitted RPR-3500 Å lamps in a 6 bulb array. The morphology of the PNIPAAm-MSp hydrogels that had absorbed water was observed after freeze-drying the swollen samples for 48 hours (Labconco, freeze dry system/ freezone 4.5). Scanning electron microscopy (SEM) (Hitachi S-2700 SEM) was used to study the surface morphology.

To measure the water absorption coefficient of the gels, a known weight of dry polymer sample was immersed in distilled water for 1 h at 23 °C. Readings were recorded in 10 minute intervals. At each time the swollen gels were filtered through an aluminum sieve to remove water and weighed. Water absorption \( Q_t \) was measured using equation (1)

\[
Q_t = \frac{(W_t - W_0)}{W_0} \quad \text{------------------- (1)}
\]

where \( W_t \) is the weight of the swollen polymer at time \( t \) and \( W_0 \) is the weight of the dry polymer. The procedure was repeated three times to get an accurate average \( Q \) value.
To study the effect of temperature, the water absorption of the hydrogels was studied at lower temperature (0 °C) and higher temperature (35 °C). A known weight of dry gel was immersed in distilled water at each temperature and the weight of the hydrogels recorded within 10 minute intervals for 1 h, after filtering through an aluminum sieve. To get accurate Q values the procedure was repeated three times and the mean water absorption ($Q_t$) calculated using (1).

The hydrogels were exposed to 350 nm light and water absorption was measured before and after the light exposure. A known weight of dry polymer sample was immersed in distilled water for 1 h with continuous illumination at 350 nm at 23 °C and the gel weights were measured in 10 minute intervals. Filtration through an aluminum sieve removed excess water prior to each measurement. The procedures were repeated three times and the mean value for Q was calculated. The photochromic effect on water absorption was studied at 0 °C and 35 °C.

### 3.7.3 Synthesis

The synthetic pathway of polymerizable photochromic monomer (MSp) is shown in Scheme 3.1.
**Scheme 3.1.** Schematic synthetic pathway of photochromic monomer (MSp). (i) 0.6 M NaOH, 0 °C, NaNO₂, and conc. H₂SO₄; (ii) 1,3,3-Trimethyl-2-methyleneindoline, 1 h reflux; (iii) Methacryloyl chloride.

**Synthesis of 2,7-Dihydroxy-1-nitrosonaphthalene.**

2,7-Dihydroxy-1-nitrosonaphthalene was synthesized according to the previously described procedure. 7-Dihydroxynaphthalene (3), 1.00g (6.25 mmol) was completely dissolved in 15 mL of 0.6M sodium hydroxide solution in a 100 mL round bottom flask. The mixture was cooled to 0 °C in an ice bath and 0.43 g (6.25 mmol) of sodium nitrite was added. While stirring, 1.4 mL of concentrated sulfuric acid was slowly added to the mixture such that the temperature does not exceed 0 °C. During the addition, 2,7-Dihydroxy-1-nitrosonaphthalene started precipitating. After the addition of sulfuric acid, the mixture was allowed to stir for 1 h at low temperature. The precipitate was suction-filtered and washed thoroughly with water, and dried under vacuo. The purple colored crude product was obtained as reasonably pure form as indicated by TLC analysis (CHCl₃: MeOH) and was used in the next step without further purification. Yield: 96 %. mp: 285-287 °C (lit. mp 285 °C). δH (300 MHz; DMSO; Me₄Si, ppm) 7.42 (d, 1H), 7.59 (d, 1H), 7.56 (d, 1H), 6.80 (d, 1H), 6.86 (d, 1H), 6.18 (OH s, 2H). IR (cm⁻¹): 3143 (O-H), 1301 (N=O).

**Synthesis of 1,3,3-Trimethyl-9'-hydroxyspiroindolinenaphthoxazine.**

1,3,3-Trimethyl-9'-hydroxyspiroindolinenaphthoxazine was synthesized according to the procedure of Dürr et al. While a suspension of 2,7-dihydroxy-1-nitrosonaphthalene (4) (1.88 g,
10mmol) in 50 mL of anhydrous methanol was under reflux, a solution of 1,3,3,-trimethyl-2-
methyleneindoline (5) (1.99 g, 10 mmol) in anhydrous methanol (5 mL) was added drop wise.  
After continuous refluxing under dry argon stream, a brown colored solution was obtained. The 
brown solution was stored at room temperature overnight. The formed solid product was 
collected by suction filtration. Product remains in the solvent collected by removing all the 
 solvent. The purification method was modified as follows. The formed brown color precipitate 
was purified by column chromatography with silica gel (ethanol) followed by silica gel (ethyl 
acetate: hexane 2:1) to yield very light yellowish-white crystals of pure 1,3,3-trimethyl-9’-
hydroxyspiroindolenaphthoxazine. [Yield: 2.3 g (66%)]. mp: 169-173 ℃ (lit. mp 167-173 ℃).  

\[ \delta_{H}(300 \text{ MHz; CDCl}_3; \text{Me}_4\text{Si, ppm) }: 7.69 \text{ (s, 1H), 6.84 \text{ (d, 1H), 7.58 \text{ (d, 1H), 7.65 \text{ (d, 1H), 7.02 \text{ (d, 1H), 7.84 \text{ (d, 1H), 7.09 \text{ (t, 1H), 7.23 \text{ t, 1H), 6.58 \text{ t, 1H), 2.77 \text{ (s, 3H), 1.37 \text{ (s, 3H), 1.35 \text{ (s, 3H).}} IR \text{ (cm}^{-1}) \text{: 3313 \text{ (O-H), 3065 \text{ (=C-H), 1627 \text{ (C=N), 1357 \text{ (C-O).}} MS \text{ (m/z) = 344 [M}^+\text{], 329 [M-CH}_3^+\text{], 314 [M-2CH}_3^+\text{].}}} \]

**Synthesis of 9’-Methacryloyloxy-1,3,3-trimethyl-spiro[indoline-2,3’- 
[3H]napth[2,1b][1,4]oxazine] (MSp).**

9’-Methacryloyloxy-1,3,3-trimethyl-spiro[indoline-2,3’-[3H]napth[2,1b][1,4]oxazine] (MSp) 
was synthesized according to previously described procedure. To a mixture of 3.00g (0.00872 
mol) of 1,3,3-Trimethyl-9’-hydroxyspiroindolenaphthoxazine (5) and 1.32 mL of triethylamine 
in 60 mL of dry dioxane, a mixture of 1.086 g of acryloyl chloride in 30 mL of dry dioxane was 
added dropwise in an ice bath. The mixture was stirred overnight at room temperature.  
Purification method of obtained yellowish white solid was modified as follows. Pure MSp was 
obtained as white crystals by column chromatography (alumina, ethyl acetate/hexane; 1/9).
[Yield: 1.4 g (39.8 %)]. mp: 139-140 °C. δH (300 MHz; CDCl3; Me4Si, ppm): 1.3 (s, 6H), 2.1 (s, 3H), 2.75 (s, 3H), 5.8 (s, 1H), 6.4 (s, 1H), 6.9 (t, 1H), 7.0 (d, 1H), 7.25 (t, 1H), 7.6-7.8 (m, 2H), 8.3 (s, 1H). IR (cm⁻¹): 3050 (=C-H), 1728 (C=O), 1629 (C=N), 1606 (C=C), 1166 (C-O). MS: m/z = 412 [M⁺], 397 [M – CH₃]⁺.

3.7.4 Polymerization

N-isopropylacrylamide (0.97 g, 8.58 mmol), N,N’-methylenebis(acrylamide) (BIS) (0.0097 g, 0.063 mmol), MSp (0.02 g, 0.048 mmol), and 2,2’-azobis(isobutyronitrile) (0.05 g, 0.30 mmol) were dissolved in anhydrous DMSO (1.0 mL). The copolymerization was carried out under argon at 60 °C for 12 h. A red colored polymer gel was obtained after completion of the polymerization. The polymer gel was immersed in a large amount of distilled water to remove any residual unbound materials and dried in a vacuum oven until a constant weight was achieved.

3.8 RESULTS AND DISCUSSION

3.8.1 Photochromic Properties of the Monomer MSp

Isomerization of 9’-methacryloyloxy-1,3,3-trimethyl-spiro[indoline-2,3’-[3H]naphth[2,1b][1,4]oxazine] (MSp) was studied in ethanol as a result of exposure of 350 nm light (Figure 3.3). The colorless MSp solution converts to blue after 5 minute irradiation. Isomerization from the closed form (λmax = 323 nm) to the open form (λmax = 610 nm), takes place [Figure 3.4 (a)] with the peak at 610 nm increasing as the peak at 325 nm decreases. The photostationary state favors the open merocyanine form. Under room light, reverse isomerization
occurs and the equilibrium shifts to the closed spiro form, [Figure 3.4 (b)]. Because of the fast reversion at room temperature, the absorption spectra were taken at 0 °C.

**Figure 3.3.** The reversible color change of MSp.
Figure 3.4. (a) Forward reaction of MSp with time; Irradiation at $\lambda \sim 350$ nm (b) Reverse reaction of MSp with time under room light. Both reactions were carried at 0 °C in ethanol.
3.8.2 Dual Responsive PNIPAAm-MSp

Scheme 3.2. Cartoon of the dual responsiveness of the PNIPAAm-MSp hydrogel. The white oval shapes represent the closed spironaphthoxazine pendant groups before irradiation and the black lines show the PNIPAAm backbone. The ash oval shapes show the open merocyanine form of the spironaphthoxazine pendant groups after irradiation.

Scheme 3.2 is a cartoon of PNIPAAm hydrogels bearing spironaphthoxazine pendant groups which respond to light. The photochromic functionality (MSp) exists as the stable closed isomer under ambient conditions. Upon irradiation at 350 nm UV, this rearranges to a charge separated form capable of being stabilized by polar solvents including water. This enables more water molecules to diffuse into the polymer and the irradiated PNIPAAm-MSp absorbs more water than the non-irradiated polymer. The poly(N-isopropylacrylamide) backbone responds to changes in temperature but has a lower critical solution temperature (32-33 °C) because of the
hydrophilic amide and the hydrophobic isopropyl functionalities in the side chains. The polymer can only absorb water below the LCST. Above LCST, the polymer undergoes a phase transition becoming insoluble and water repellent.

IR spectra of the dry and the swollen PNIPAAm-MSp hydrogel are shown in Figure 3.5. Transmittances for PNIPAAm-MSp include frequencies expected for the NH stretching of the amide group at 3287 cm\(^{-1}\), and the carbonyl stretching of the amide and MSp at 1542 and 1626 cm\(^{-1}\) respectively. The swollen polymer shows a broad OH stretching at 3290 cm\(^{-1}\) due to absorbed water.
3.8.3 Effect of Temperature on the Swelling of PNIPAAm-MSp

Swelling of the polymer gels was measured quantitatively in distilled water at three different temperatures (0, 23, and 35 °C). The temperatures of measure selected were room temperature [23 °C], a temperature higher than the LCST [35 °C], and a temperature which can lower the rate of the reverse isomerization [0 °C]. Lower temperature slows the reverse photochemical reaction. The gels absorb only small amounts of water as the temperature rises above LCST. Below LCST the gels absorb twice their dry weight in water within one hour (Figure 3.6).
Though little difference could be observed in the Q values at 23 °C and 0 °C, Figure 4, the sample at 23 °C absorbs more water than the polymer held at 35 °C where the polymer is quite non-absorbent. At the latter temperature the polymer also no longer appears transparent because the PNIPAAm backbone is water repellant. These polymers shrink rather than swell while the heated hydrogels repel absorbed water.

3.8.4 Effect of Light and Temperature on the Swelling of PNIPAAm-MSp

Swelling following UV light exposure was also measured at three different temperatures (0, 23, and 35 °C). When irradiated at 350 nm, the polymer changes from red to blue because of the isomerization of the chromophore. Water absorption (Q) of irradiated polymers varied with temperature, Figure 3.7.
Figure 3.7. Swelling of the irradiated polymers at different temperatures 23, 0, and 35 °C during one hour.

Water absorption (Q) with and without irradiation was compared at different temperatures (Table 3.1). At lower temperatures the isomerization of the merocyanine to the closed spiro form proceeds more slowly allowing more water to diffuse into the polymer, stabilizing the charges. The result is that the irradiated polymer sample absorbs more water at 0 °C than does the irradiated polymer samples held at 23 and 35 °C respectively. Further a polymer sample held above the LCST at 35 °C did not swell.
Table 3. 1. Swelling of PNIPAAm-MSp at different temperatures with and without irradiation for one hour. PNIPAAm-MSp with 1.9% MSp was used to study the swelling.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Non-irradiated polymer hydrogel Q</th>
<th>Irradiated polymer hydrogel Q(Irr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.25</td>
<td>3.25</td>
</tr>
<tr>
<td>23</td>
<td>2.63</td>
<td>1.88</td>
</tr>
<tr>
<td>35</td>
<td>0.30</td>
<td>0.25</td>
</tr>
</tbody>
</table>

3.8.5 Effect of MSp content on the Swelling of PNIPAAm-MSp

Regardless of the percentage of MSp in the hydrogel, light exposed hydrogels absorb more water than do the hydrogels held in the dark. Therefore the Q values for light exposed polymer samples show higher water absorption than the non-irradiated polymer samples. Because of the water repelling organic photochromic functionality, higher percentages of it by weight in the polymer network lower the water absorption at 0 °C, Table 3.2. The best water absorption is obtained for the polymer that contains 1.9% organic photochrome functionality by weight.
Table 3.2. Swelling of PNIPAAm-MSp with different MSp percentages at 0 °C.

<table>
<thead>
<tr>
<th>MSp percentage (%)</th>
<th>Non-irradiated polymer hydrogel</th>
<th>Irradiated polymer hydrogel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Q</td>
<td>Q (Irr)</td>
</tr>
<tr>
<td>Q2%</td>
<td>2.61</td>
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</tr>
<tr>
<td>Q4%</td>
<td>1.26</td>
<td>2.29</td>
</tr>
<tr>
<td>Q9%</td>
<td>1.12</td>
<td>2.53</td>
</tr>
</tbody>
</table>

3.8.6 Swelling of PNIPAAm-MSp in Tap Water

As expected, distilled water is more readily absorbed than tap water because the latter has a higher ion density (Figure 3.8).

Figure 3.8. Water absorption of PNIPAAm-MSp in distilled water and tap water at (a) 23 °C and (b) 0 °C.
3.8.7 Morphology of PNIPAAm-MSp Hydrogel

SEM images of swollen hydrogels with irradiation and without irradiation were obtained. As can be seen (Figure 3.9) the surface of the swollen PNIPAAm-MSp hydrogels has been disturbed by light exposure.

![Image](attachment:swollen_hydrogel_images.png)

**Figure 3.9.** The swollen hydrogel samples; (a) Non-irradiated (red color), (b) Irradiated, (blue color), and their corresponding SEM images.

This change in surface morphology occurred because of the ring opening of the pendant MSp during UV irradiation. This photo-stimulated isomerization has induced a change in polymer structure, such that more water molecules can diffuse into it and the polymer swells more. The SEM image of the non-irradiated hydrogel showed a closed-like surface, but the irradiated hydrogel surface shows a much open surface which more water molecules can penetrate through the surface. Therefore more water absorption can be observed with the irradiated hydrogel.
3.9 CONCLUSIONS

We have developed an efficient dual responsive hydrogel in which swelling can be controlled by applying two external stimuli; heat and light. A series of new dual responsive poly(N-isopropylacrylamide) hydrogels having spironaphthoxazine pendent groups has been synthesized via free radical polymerization. These red polymers are responsive both to temperature and light. Thermoresponsive poly(N-isopropylacrylamide) swells reversibly shrinking both below and above its LCST. Spironaphthoxazine pendants make the polymers photoresponsive in that the dissociation of the spiro C-O bond causes a color change during UV irradiation. Lower temperatures as well as irradiation with UV light each induce the hydrogels to absorb more water. The PNIPAAm-MSp polymer swells with UV irradiation and deswells with heat.

3.10 REFERENCES

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CHAPTER 4
ELECTRO AND LIGHT RESPONSIVE HYDROGELS
PHOTOACTUATED BENDING OF POLYMERS

4.1 ELECTRORESPONSIVE POLYMERS

Among many stimuli-responsive hydrogels, electric field responsive hydrogels are important because electric fields are one of the most conventional and convenient stimuli as far as signal control is concerned. Electroresponsive deformations, such as volume changes or bending of polyelectrolyte hydrogels, transform the chemical free energy directly into mechanical work to give isothermal energy conversion. Such reactions are termed chemomechanical systems. Therefore electroresponsive hydrogels can be used as actuators, artificial muscles, chemical valves, and controlled drug delivery systems.

Considering the electroresponse of gels in water, hydrogen is released at the negative electrode whereas oxygen is released at the positive electrode. Because of the electrolysis, the region of the positive electrode becomes more acidic as oxygen is released and H ions are formed in solution. Similarly, the region near the negative electrode becomes more basic. This electrolytic process of the solvent changes the electroresponse of the gels. For example, poly(vinyl alcohol)/poly(acrylic acid) hydrogel fibers bend quickly around a pH of 9.0 (weakly basic) in the presence of an electric field, while the extent of bending is decreased at pH levels above or below this 9.0.

Electroresponsive hydrogels are normally comprised of polyelectrolytes, polymer networks containing ionic functional groups (carboxylic acids, amides and alcohols). The
response is manifested as swelling/shrinking or bending, depending on the shape and gel alignment with the electric field. Several mechanisms have been reported to explain such gel deformations. When the water/solution swollen polyelectrolyte gel is inserted between a pair of electrodes and the DC voltage is supplied, a contractile behavior of the gel is observed. Osada and Gong have reported electroresponsive contractile behavior of water swollen poly(2-acrylamido-2-methyl-1-propanesulfonic acid) in 1998 (Figure 4.1).  

![Figure 4.1](image_url)

**Figure 4.1.** Electroresponsive contractile behavior of water swollen poly(2-acrylamido-2-methyl-1-propanesulfonic acid): (a) before and (b) after applying the electric field. (Adapted from reference 4).

The contraction may be caused by the transport of hydrated ions and water in the gel network. When an external electric field is applied across the gel, the macro- (stationary ions) and micro-ions (counter ions) encounter electric forces in the opposite direction. The macro-ions are stationary because they are chemically fixed to the polymer network, whereas the micro-ions are mobile as they serve as counter ions. Therefore, evolution of the counter ions along the
electric field pulls out water molecules. The contraction efficiency is inversely proportional to the charge density of the gel, and directly proportional to the swelling capacity. Moreover, the contraction only depends on the amount of electric current passed through the gel.\textsuperscript{6}

When the gel is kept inbetween two parallel electrodes without any contact with the electrodes, a bending behaviour is observed. When a DC electric field is applied on a negatively charged hydrogel in an aqueous solution, micro- ions (counter ions) move towards the negative electrode and macro- ions (stationary ions) remain motionless. The free ions in the surrounding solution also move towards the counter-electrodes and come in to the hydrogel. Therefore the osmotic pressure near the positive electrode increases and becomes larger than that of the negative electrode region. The resulting osmotic pressure difference in the hydrogel causes it to bend towards the negative electrode. Similarly, positively charged hydrogels bend towards the positive electrode.\textsuperscript{1}

In general, electroresponses can be influenced by many factors, such as the experimental set up itself, formulation of the gel (charge density, degree of swelling, nature of the cross-links, monomers and pendant groups), nature of the aqueous medium, and presence of electrolytes.\textsuperscript{7} Both electroresponsive deformations, namely bending and contracting, are favorable for various applications. Electroresponsive bending of hydrogels has been studied mostly for the fabrication of mechanical devices such as artificial muscles, valves, and switches.\textsuperscript{6-8} Electroresponsive contractile behavior (or shrinking) of hydrogels is mainly investigated for potential applications in controlled drug release.\textsuperscript{9}
4.2 RECENT DEVELOPMENTS OF ELECTRORESPONSIVE HYDROGELS

In 1982, Tanaka observed contraction and a phase transition in partially hydrolized polyacrylamide gels in contact with platinum electrodes under a DC potential. He attributed deswelling to the electrophoretic pressure gradient.\textsuperscript{10} Osada and Hasebe also reported similar findings in water swollen poly(2-acrylamido-2-methyl-1-propanesulfonic acid) under a DC electric current. They observed an increase in deswelling rate with higher electric fields, addition of sodium chloride, as well as the presence of organic solvents.\textsuperscript{8} After finding the electroresponsive contractile behavior of the above gels, many scientists have widely studied electroresponsive behavior of different hydrogels.\textsuperscript{1,4,5,7,9,11-16} An electroresponsive contraction of a chitosan/poly(hydroxy ethyl methacrylate) hydrogel was studied by Kim and coworkers.\textsuperscript{17} The hydrogel was placed in deionized water, and parallel to two carbon electrodes with no contact with the electrodes. As the hydrogel consists of biocompatible and non-toxic material, namely chitosan and poly(hydroxy ethyl methacrylate), it can be used in electroresponsive drug delivery.

The mechanical response of hydrogels stimulated by an applied electric field is favorable for controlled drug release applications.\textsuperscript{7,9,18} Gels incubated in drug solutions absorb drugs by diffusion. Applying an electric field, releases the drugs in different methods. (1) Ejection of the drug from the gel with shrinking, (2) Drug diffusion out of the gel (electric stimuli inhibit drug release), and (3) Drug electrophoresis (ionic drugs can be released towards the electrode bearing an opposite charge.\textsuperscript{7}

Many developments of hydrogel based artificial muscles activated by electrical change have been reported.\textsuperscript{10,19-21} The first model of electrically driven artificial muscles was the
“chemical valve” membrane developed by Osada and Hasebe, which reversibly contracts and expands its micro-pores with the application of an electric field.\textsuperscript{8} Under a DC voltage of 6.3 V/cm (or 0.7 mA/cm\textsuperscript{2}) the water swollen poly(2-acrylamido-2-methyl-1-propanesulfonic acid) was reduced 70\% by of its weight in 20 minutes.\textsuperscript{8} Toyota Central R&D laboratories constructed a finger-shaped gel actuator to perform elementary grasping functions under electric control.\textsuperscript{10} Moschou \textit{et. al.} reported a voltage switchable artificial muscle consisting of an acrylamide, polypyrrole composite with carbon black.\textsuperscript{19,20} The gel responded to a 3 V potential for 2 minutes and bent towards the cathode. When the electroactuation is reversed, the bending direction switched with the polarity. The gel also relaxed to its original position with the removal of the external electric field.

All the above-mentioned electroresponsive hydrogels were polyelectrolytes, partially hydrolyzed hydrogels or polymers containing conducting materials inside. The first polymers photoactuated in the presence of an electric field were prepared by Irie in 1986 who reported the bending of rod-shaped poly(acrylamide) gels possessing triphenylimethane leucocyanide groups in the presence of an electric field and light.\textsuperscript{22} Upon exposure to UV light ($\lambda > 270$ nm), the leuconitrile groups dissociated producing mobile cyanide ions. Thus, bending of the polymer was observed in the presence of an electric field and the bending direction could be controlled by changing the polarity of the external field. After removal of the UV light, the bent polymer straightend to its original position.\textsuperscript{22}
4.3 THE PROJECT

Herein we report photoresponsive bending of rod-shaped hydrogels made of poly(N-isopropylacrylamide) containing modified spironaphthoxazine pendent groups (PNIPAAm-MSp) in an electric field. The charges being generated on the spironaphthoxazine upon irradiation induce reversible bending of the gel. The synthesis and characterization of PNIPAAm gels containing modified spironaphthoxazine groups (PNIPAAm-MSp) was previously reported. The PNIPAAm-MSp gels absorb more water in the presence of UV light. A closed isomeric form of spironaphthoxazine rearranges to a charge-separated form upon UV irradiation (λ ~ 350 nm). The latter is capable of being stabilized by polar solvents including water. This enables more water to diffuse into the polymer, and the irradiated PNIPAAm-MSp absorbs more water than the non-irradiated polymer.

4.4 EXPERIMENTAL SECTION

4.4.1 Materials.

2,7-Dihydroxynaphthalene was purchased from Acros Organics. All other chemicals were purchased from Aldrich. N-isopropylacrylamide was purified by recrystallization from a mixture of one part toluene and four parts petroleum ether. Other reagents were purified using conventional literature methods.

4.4.2 Synthesis of Rod Shaped PNIPAAm-MSp.

Synthesis of modified spironaphthoxazine, (9’-Methacryloyloxy-1,3,3-trimethylspiro[indoline-2,3’-3H]naphth[2,1b][1,4]oxazine) (MSp), was reported in chapter 3.23,24
Rod shaped PNIPAAm-MSp was prepared in capillary tubes by free radical copolymerization of N-isopropylacrylamide (NIPAAm) [0.97g] and MSp (0.0291 g; 3% wt of NIPAAm) in the presence of N,N’-methylenebis(acrylamide) (BIS) [0.0194 g; 2% wt of NIPAAm) in dimethyl sulfoxide. After removal from the capillary tubes, the red colored, rod-shaped gels were soaked in dimethyl sulfoxide and water to remove all residual monomers and initiator.

Before studying the bending, the gels were swollen to an equilibrium condition by allowing them to stand in water/salt solution overnight.

4.5 RESULTS AND DISCUSSION

4.5.1 Photoresponsive Bending of PNIPAAm-MSp Gels.

Rod-shaped PNIPAAm-MSp gel with dimensions of 1 mm in diameter and 25 mm in length was placed in a small water pool (Nylon, 36×19×4 mm), between two parallel platinum electrodes (Figure 4.2).

Figure 4.2. Schematic representation of; (a) the water pool used for measurement; (b) position of the polymer gel in the water pool.
The gel did not change shape in a 17 V/cm electric field in the dark. Upon UV light irradiation ($\lambda \sim 350$ nm), the gel was completely bent in 15 minutes in the same electric field. The ends of the gel moved towards the negative electrode during bending. The gel reverted to its original straight conformation following removal of the UV light (Figure 4.3).

**Figure 4.3.** Reversible bending of the rod-shaped PNIPAAm-MSp gel (25 mm length and 1 mm cross-section diameter) in an electric field.

This bending behavior can be explained by the inhomogeneous expansion of the gel in the electric field. The positively charged portion of the gel expands more than the negatively charged region. Upon UV irradiation, the spironaphthoxazine pendant groups isomerize to its zwitterionic form (Figure 4.4), in which the negative ion side of the pendant is fixed to the gel network.
Figure 4.4. Reversible isomerization of spironaphthoxazine moiety in the gel network.

The positively charged region thus has the mobility to attract to the negatively charged electrode region of the gel in the presence of an electric field aligned perpendicular to the gel axis. Fixed negative charges on the other side of the gel induce internal repulsion causing the expansion of the positive side of the gel (Figure 4.5).

Figure 4.5. Schematic representation of the alignment of charges on spironaphthoxazine pendant groups upon UV irradiation in the electric field.
Relative to the bending rate of the gel studied previously, the bending of PNIPAAm-MSp was slow. This is because the charges formed exist as zwitterions, wherein the mobility is limited compared to that of singly charged free ions. In water, no bending due to the change of polarity is observed. This is explained by the lower mobility of the charges on the zwitter ion. Instead of moving to the other side of the gel, the charges of the pendant groups rearrange within the electric field and the shape remained the same (Figure 4.5).

In order to determine the response time of the motion quantitatively, the distance traveled by the ends of the polymer was measured (Figure 4.6).

![Figure 4.6](image)

**Figure 4.6.** (a) Schematic representation of the distance travelled by the ends of the gel; (b) Bending of the gel with time.

The gel ends travel 6 mm from the equilibrium point in 15 minutes, the maximum distance. Bending was slow during first 8 minutes and then increased quickly to the maximum.
At the beginning few charges were formed on the gel. Over time and with increased UV irradiation more charges formed on the gel. Thus the slower bending at the beginning and faster bending after 8 minutes was observed, Figure 4.6.

![Graph showing distance travelled by gel ends vs time](image)

**Figure 4.7.** Straightening of the gel after removal of the UV light. (a) Distance travelled by the gel ends with time; (b) Photographs of gel straightening with time.

As soon as the UV light is switched off, the charge separated merocyanine isomerizes to the uncharged spironaphthoxazine. Therefore the gel slowly relaxes to its original position. In the
absence of UV light, the gels straighten after 175 minutes. Quantitative straightening of the gels after removal of UV light is shown in Figure 4.7. During bending and straightening, the gel did not move towards the electrodes thus the gels were not in contact with the electrodes. Therefore deswelling was not observed.

4.5.2 Actuation with the MSp Content

To study the effect of MSp content on the bending, cylindrical shaped gels consisting of 1% MSp and 3% MSp were investigated (Figure 4.8).
The bending with an increase in the MSp is faster. Gels with 1% Msp content only showed 5 mm maximum bending, while the 3% MSp containing polymers showed up to 6 mm bending. This can be explained by the formation of more zwitter ions on the gel containing higher MSp content following UV irradiation. As more charges form, both faster and higher bending distances were observed.

4.5.3 Bending as a Function of the Cross-linking Density

Bending was studied as a function of the content of the cross-linker (BIS) percentage. Gels with higher BIS content (5%) bent slower to their maximum in one hour, while the gels with lower BIS content (2%) bent to the maximum within 15 minutes. A decrease in cross-linker
percentage allowed the gel to easily deform easily as compared to the gel with higher cross-linking density (Figure 4.9).

Figure 4.9. Gel bending with Cross-linking density. (a) Distance travelled by gel ends as a function of time; (b) Photographs of gel bending with time.
4.5.4. Bending in Salt Solutions

A faster bending of the rod-shaped PNIPAAm-MSp gels was obtained in a 0.01 M sodium chloride solution. The gel bent completely in 44 seconds and bent to the opposite direction after changing the polarity of the electric field (Figure 4.10). This bending behavior according to the change of polarity could be repeated many times under UV irradiation.

![Figure 4.10. Bending of PNIPAAm-MSp rod-shaped gels in 0.01 M NaCl solution.](image)

A charged electrolyte solution (NaCl) increases the actuation. In both cases, in water and in salt solution, the bending speed is lowered if the magnitude of the electric field is reduced.

4.6 CONCLUSION

We have developed photo- and electro- responsive hydrogels based on poly(N-isopropylacrylamide) containing modified spironphthoxazine pendant groups. This shows reversible electroacuation upon UV irradiation ($\lambda \sim 350$ nm) under an applied electric field. In salt solutions, gel bends quickly to the opposite side upon changes in the polarity of the electric field. Since the electric field was applied perpendicular to the gel, bending was observed. Deswelling was not seen because the gel was not in contact with the electrodes.
4.7 REFERENCES


APPENDIX

LIST OF ABBREVIATIONS:

AA  Acrylic acid
AIBN Azobisisobutyronitrile
A  Angstrom
ASTM American Society for Testing and Materials
BIS N,N'-Methylenebisacrylamide
BMA Butylmethacrylate
BPO Benzoyl peroxide
C  Degree Celcius
cm  Centimeter
δ  Chemical shift
d (for NMR) Doublet
Δ  Heat
DC  Direct current
DCM Dichloromethane
DIP Direct Ionization Probe
DVB Divinylbenzene
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tr>
<td>EPDM</td>
<td>Ethylene propylene diene</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatography</td>
</tr>
<tr>
<td>h</td>
<td>Hour</td>
</tr>
<tr>
<td>H₂O</td>
<td>Water</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>Sulfuric acid</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric acid</td>
</tr>
<tr>
<td>HEMA</td>
<td>Hydroxyethyl methacrylate</td>
</tr>
<tr>
<td>Hν</td>
<td>Photon</td>
</tr>
<tr>
<td>IDA</td>
<td>Isodecylacrylate</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>λ</td>
<td>Wavelength</td>
</tr>
<tr>
<td>LA</td>
<td>Lauryl acrylate</td>
</tr>
<tr>
<td>LCST</td>
<td>Lower critical Solution Temperature</td>
</tr>
<tr>
<td>m</td>
<td>Meter</td>
</tr>
<tr>
<td>m (for NMR)</td>
<td>Multiplet</td>
</tr>
<tr>
<td>M</td>
<td>Moles per liter</td>
</tr>
<tr>
<td>MHz</td>
<td>Mega Hertz</td>
</tr>
<tr>
<td>ml</td>
<td>Milliliter</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
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<tr>
<td>--------------</td>
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<tr>
<td>mm</td>
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</tr>
<tr>
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<td>Mass Spectrometry</td>
</tr>
<tr>
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<td>Sodium Chloride</td>
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<tr>
<td>NaOH</td>
<td>Sodium Hydroxide</td>
</tr>
<tr>
<td>NIPAAm</td>
<td>N-Isopropylacrylamide</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>OEGMA</td>
<td>Oligo(ethyleneglycol) methyl ether methacrylate</td>
</tr>
<tr>
<td></td>
<td>poly(N-(DL)-(1-hydroxymethyl))</td>
</tr>
<tr>
<td>P(DL)-HMPMA</td>
<td>propylmethacrylamide)</td>
</tr>
<tr>
<td>PDEAAM</td>
<td>poly(N,N'-diethacrylamide)</td>
</tr>
<tr>
<td>PEG</td>
<td>Polyethylene glycol</td>
</tr>
<tr>
<td>PMMA</td>
<td>Polymethyl methacrylate</td>
</tr>
<tr>
<td>PNIPAAm</td>
<td>Poly(N-isopropylacrylamide)</td>
</tr>
<tr>
<td>PPO</td>
<td>Polypropylene glycol</td>
</tr>
<tr>
<td>PVCL</td>
<td>poly(N-vinylcaprolactone)</td>
</tr>
<tr>
<td>rpm</td>
<td>Rounds per minute</td>
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<td>Abbreviation</td>
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<td>--------------</td>
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