IONOMERS AZOBENZENE CRYSTALLINES LIQUIDES PHOTOACTIVE

PAR

Mitko Iotov

Présenté au D épartement de Chimie

FACULTE DES SCIENCES
UNIVERSITE DE SHERBROOKE

Sherbrooke, Quebec, Canada, May, 2006
NOTICE:
The author has granted a non-exclusive license allowing Library and Archives Canada to reproduce, publish, archive, preserve, conserve, communicate to the public by telecommunication or on the Internet, loan, distribute and sell theses worldwide, for commercial or non-commercial purposes, in microform, paper, electronic and/or any other formats.

The author retains copyright ownership and moral rights in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

In compliance with the Canadian Privacy Act some supporting forms may have been removed from this thesis.

While these forms may be included in the document page count, their removal does not represent any loss of content from the thesis.

AVIS:
L'auteur a accordé une licence non exclusive permettant à la Bibliothèque et Archives Canada de reproduire, publier, archiver, sauvegarder, conserver, transmettre au public par télécommunication ou par l'Internet, prêter, distribuer et vendre des thèses partout dans le monde, à des fins commerciales ou autres, sur support microforme, papier, électronique et/ou autres formats.

L'auteur conserve la propriété du droit d'auteur et des droits moraux qui protège cette thèse. Ni la thèse ni les extraits substantiels de celle-ci ne doivent être imprimées ou autrement reproduits sans son autorisation.

Conformément à la loi canadienne sur la protection de la vie privée, quelques formulaires secondaires ont été enlevés de cette thèse.

Bien que ces formulaires aient inclus dans la pagination, il n'y aura aucun contenu manquant.
Le 5 juin 2006

le jury a accepté le mémoire de M. Mitko Iotov dans sa version finale.

Membres du jury

M. Yue Zhao
Directeur
Département de chimie

M. Yves Dory
Membre
Département de chimie

M. Armand Soldera
Président-rapporteur
Département de chimie
SUMMARY

Azobenzene chemistry is an intensive area of exploration because it continues to surprise us with totally unforeseen phenomena some of which are still not totally explained. If the azobenzene chromophore is attached to a polymer chain or even if it is introduced in a polymer matrix without bonding, the photoisomerization of the chromophore can initiate a series of motions. The applications of the photo-induced motions of liquid crystalline polymers can be numerous. The use of the active photo-function where the reversibility of the photo-induced alignment is achieved can be used in erasable optical recordings, image processing etc. On the other hand when the passive function is put into use, long-lasting molecular orientations can be achieved with high optical anisotropy. This can be used in liquid crystalline aligning layers that are required for LC display devices.

In the present work we had synthesized a new type of liquid crystalline polymers: namely, azobenzene liquid crystalline ionomers. In order to do so, first the azobenzene monomer was co-polymerized with methacrylic acid. Then, the acid group of the random copolymers was partially neutralized by reaction with metal acetate, which introduced metal ions in the liquid crystalline azobenzene polymer

If the azobenzene chromophore can initiate a series of motions it must be due to its photoisomerization property. Irradiating them with UV light at 360nm performed a test for photoisomerization of the new materials synthesized and their UV-vis spectrum showed that the trans-cis isomerization took place. This gave us the green light for possible motion of the azobenzene chromophore on the azobenzene ionomers and we irradiated our samples with UV light and then with linearly polarized visible light to produce a desired orientation. Knowing that the chemistry of the azobenzene varies with its environment, we investigated the effects of ionic aggregates, which are characteristic of ionomers, on the photo-induced orientation of azobenzene mesogens. We then studied the effect on the photo orientation by introducing the sample into the oven at a particular temperature. This gave different results for the different ionomers. Another experiment,
which was of interest, was to study the different aggregations and their relative populations at different temperatures. Finally, the photochemical phase transitions from nematic to isotropic state at different reduced temperatures were examined for the different ionomers. The hypothesis assumed was that because of the different ionic aggregates that the different ionomers can adopt there will be differences in the rate of disappearing and in the rate of recovering of the nematic phase. A special set-up was constructed for this last experiment where a sample was irradiated with UV light and the luminosity of the phase, between crossed polarizers, was monitored by an oscilloscope.

We found that the presence of metal ions can either increase or decrease the thermal stability of the Liquid Crystalline phase formed by the azobenzene mesogens, which in turns can enhance or reduce the degree of photo-induced orientation of the azobenzene mesogens.
SOMMAIRE

La chimie des groupes Azobenzène est un secteur intensif d’exploration parce qu’elle continue à nous étonner par des phénomènes totalement imprévisibles, certains ne sont toujours pas totalement expliqués. Si le chromophore azobenzène est attaché à une chaîne de polymère ou même s’il est introduit dans une matrice de polymère, sans lien effectif, la photoisomérisation du chromophore peut initier une série de mouvements. Les applications des mouvements photo-induits de polymères cristallins liquides peuvent être nombreuses. L’alignement photo induit, peut être utilisé dans les enregistrements optiques effaçables. D’autre part quand la fonction passive est utilisée, les orientations moléculaires de longue durée peuvent être atteintes avec une haute anisotropie optique. Ce procédé peut être utilisé pour aligner les couches cristallines liquides qui sont exigées pour les organes de visualisation de CL.

Dans le présent travail nous avons synthétisé de nouveaux polymères cristallins liquides: tels que des ionomères azobenzènes cristallins liquides. Afin de procéder, premièrement le monomère d’azobenzène a été copolymerisé avec de l’acide méthacrylique. Après, les groupes acides des polymères ont été partiellement neutralisés par la réaction avec de l’acétate métallique pour introduire des ions métalliques dans le polymère cristallin liquide azobenzène.

L’azobenzène chromophore peut générer des mouvements, grâce à sa propriété de photoisomérisation bien connue. Nous avons donc irradié des nouveaux matériaux synthétisés, avec la lumière UV à 360nm pour tester leur photoisomérisation et leurs spectres UV-vis ont démontré que l’isomérisation de trans-cis a bien eu lieu. Ceci nous a donné la lumière verte pour le mouvement possible de l’azobenzène chromophore sur l’azobenzène ionomère et nous avons irradié nos échantillons avec la lumière UV suivie d’une irradiation avec la lumière visible linéairement polarisée qui a produit l’orientation désirée. Sachant que la chimie de l’azobenzène change selon son environnement, nous avons examiné l’effet d’agrégation ionique, qui est caractéristique des ionomères, sur
l'orientation photo-induite des mesogènes azobenzènes. Nous avons aussi étudié l'effet sur l'orientation induite en introduisant l'échantillon dans le four à une température spécifique. Ceci a donné des résultats différents pour les différents ionomers. Une autre expérience, qui fut intéressante, était d'étudier les différentes agrégations et leurs populations relatives à différentes températures. En toute fin, la transition de phase photochimique de l'état nématicque à l'état isotropique à différentes températures réduites a été examinée pour les différents ionomères. L'hypothèse est qu'à cause des agrégations ioniques différentes, qui peuvent être adoptées par les différents ionomères il y aurait des différences dans le taux de disparition et dans le taux de retour de la phase nématique. Un montage spécial a été construit pour cette dernière expérience où un échantillon a été irradié avec la lumière UV et la luminosité de la phase entre deux polariseurs croisés a été mesurée.

Nous avons trouvé que la présence d'ions métalliques peut augmenter ou diminuer la stabilité thermique de la phase cristalline liquide formée par les azobenzène mésogènes, qui à leurs tours peuvent améliorer ou peuvent réduire le degré d'orientation photo-induite de l'azobenzène.
ACKNOWLEDGMENT

I would like to thank my research advisor professor Yue Zhao for allowing me to do this very interesting project in his lab and for being helpful in assisting my research during my entire journey here at the University of Sherbrooke. I would like also to express special thanks to Mr. Qi Bo (Ph.D student in professor Yue Zhao Lab) for the synthesis part of this project.

I would like also to thank my colleagues from the lab for the technical support they gave to me and for the moral conditioning of the lab environment, and also for all the interesting conversations we had on the subject.

Finally, the project would have not been able to see daylight without the financial support of FQRNT (Le Fonds québécois de la recherche sur la nature et les technologies) and NSERC (Natural Sciences and Engineering Research Council of Canada).
TABLE OF MATTER

SUMMARY ................................................................. II
SOMMAIRE ................................................................. IV
ACKNOWLEDGMENT ...................................................... VI
TABLE OF MATTER......................................................... VII
LIST OF FIGURES............................................................ IX
LIST OF TABLES............................................................... XII
INTRODUCTION............................................................. 1
CHAPTER 1 A brief introduction to azobenzene-containing polymers .......... ...3
  1.1 Azobenzene ........................................................... 3
  1.2 Azobenzene-containing Polymers .................................. 5
  1.3 Metal-containing liquid crystalline polymers ....................... 11
CHAPTER 2 Synthesis and characterizations ................................ 17
  2.1 Materials ............................................................... 17
  2.2 Synthesis ............................................................... 17
    2.2.1 Synthesis of 4'-hydroxy-(4'-methoxy) azobenzene (1) ........... 18
    2.2.2 Synthesis of 4'-hexyloxy-4'-methoxyazobenzene (2) ............. 19
    2.2.3 Synthesis of 6-[4-(4-methoxyphenylazo)phenoxy] hexyl
       methacrylate (3) ..................................................... 19
    2.2.4 Synthesis of Azobenzene Copolymer with Methacrylic Acid ....... 21
    2.2.5 Synthesis of Azobenzene Liquid Crystalline Ionomers ........... 21
  2.3 Characterization ...................................................... 21
  2.4 Spin cast films ....................................................... 27
  2.5 UV-vis spectroscopy ................................................ 28
  2.6 Other instrumentations ............................................. 30
  2.7 Textures of liquid crystal materials ................................ 31
CHAPTER 3 Results and discussion ....................................... 35
  3.1 Photoisomerization .................................................. 35
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2</td>
<td>Photo-induced alignment and thermally enhanced orientation</td>
<td>38</td>
</tr>
<tr>
<td>3.3</td>
<td>Thermochromic Behavior</td>
<td>50</td>
</tr>
<tr>
<td>3.4</td>
<td>Photochemical Phase Transition</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>CONCLUSION</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>REFERENCE</td>
<td>61</td>
</tr>
</tbody>
</table>
**LIST OF FIGURES**

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1</td>
<td>Congo Red photodichroism</td>
<td>2</td>
</tr>
<tr>
<td>Figure 2</td>
<td>Azobenzene trans-cis isomerization</td>
<td>3</td>
</tr>
<tr>
<td>Figure 3</td>
<td>Liquid crystal polymer G43S₄₉₄N104I</td>
<td>6</td>
</tr>
<tr>
<td>Figure 4</td>
<td>Azobenzene liquid crystalline and amorphous polymer systems</td>
<td>8</td>
</tr>
<tr>
<td>Figure 5</td>
<td>Types of molecular orientation of photochromic LC copolymers containing a non-photoactive moiety when radiated with linearly polarized light. A) No-photo-orientation B) Photo-orientation only of the photochromic moiety C) cooperative photo-orientation of both mesogens</td>
<td>9</td>
</tr>
<tr>
<td>Figure 6</td>
<td>Photoisomerization of azobenzene on the surface of a dendrimer</td>
<td>10</td>
</tr>
<tr>
<td>Figure 7</td>
<td>Lyotropic polymer containing two different metal atoms</td>
<td>13</td>
</tr>
<tr>
<td>Figure 8</td>
<td>Lyotropic side-chain polymer</td>
<td>14</td>
</tr>
<tr>
<td>Figure 9</td>
<td>Azobenzene monomer</td>
<td>17</td>
</tr>
<tr>
<td>Figure 10</td>
<td>Structure of azobenzene copolymer</td>
<td>18</td>
</tr>
<tr>
<td>Figure 11</td>
<td>Synthesis scheme of azobenzene monomer</td>
<td>20</td>
</tr>
<tr>
<td>Figure 12</td>
<td>Ionomer’s structure</td>
<td>22</td>
</tr>
<tr>
<td>Figure 13</td>
<td>FTIR spectra in the 1600-1800 cm⁻¹ region for polymers P0-P3 and PMA showing the stretching vibrations of the two carbonyl groups of the ester of azobenzene at 1730 cm⁻¹ and PMA at 1700 cm⁻¹</td>
<td>23</td>
</tr>
<tr>
<td>Figure 14</td>
<td>Nmr spectra of P1 copolymer in D-chloroform showing the absence of the vinyl protons in the region of 5-6 ppm</td>
<td>24</td>
</tr>
<tr>
<td>Figure 15</td>
<td>FTIR spectra of the copolymer of P1, Cu ionomer at 3% molar concentration and 6% molar concentration around 1700 cm⁻¹</td>
<td>26</td>
</tr>
<tr>
<td>Figure 16</td>
<td>DSC curves of parent P1 and its associated ionomers</td>
<td>27</td>
</tr>
<tr>
<td>Figure 17</td>
<td>400-500nm broad filter radiation spectrum</td>
<td>29</td>
</tr>
<tr>
<td>Figure 18</td>
<td>Photochemical phase transition set-up</td>
<td>30</td>
</tr>
</tbody>
</table>
Figure 19  Characteristic polymer liquid crystal texture of a) P1 b) P1-Zn3% c) P1-Cu3% d) P1-Mn3% e) P0 (nematic phase) f) P0 (smectic) .......................... 34

Figure 20  Photoisomerization of polymer P0 in solution with UV irradiation intensity of 2.5 mW/cm². The maximum absorption spectrum is prior to irradiation (0 sec), and the subsequent times shown on the right portion of the spectra are the irradiation times ............................................ 36

Figure 21  Photoisomerization of spin-cast film of polymer P1 on quartz with UV irradiation intensity of 2.5 mW/cm². The maximum absorption spectrum is prior to irradiation (0 sec), and the subsequent times shown on the right portion of the spectra are the irradiation times ............................................ 37

Figure 22  Thermal relaxation of spin-cast film of polymer P4-Zn3% on quartz with UV irradiation intensity of 2.5 mW/cm² prior to relaxation. The subsequent times shown on the right portion of the spectra are the relaxation times ............................................ 38

Figure 23  Polarized UV-vis spectra of a thin film of polymer P1 recorded with the spectrophotometer’s beam polarized parallel and perpendicular to the reference direction after linearly polarized 440nm irradiation ... 40

Figure 24  Order parameter vs. time of visible light irradiation for P1 and its ionomers, and their curve fitting with an exponential rise by Sigma Plot .................................................. 41

Figure 25  Extreme case of oriented azobenzene groups absorption of different light polarization direction .................................................. 43

Figure 26  Order parameter vs. time of visible light irradiation for P1 and P1-Zn3% at two different intensities. The curve fitting using an exponential rise is also shown .................................................. 44

Figure 27  Order parameter vs. time of visible light irradiation for P4, P4-Zn3% and P4-Zn4.5% at two different intensities of radiation. The curve fitting using an exponential rise is also shown .................................................. 46

Figure 28  Polarized UV-vis spectra of a) a photoaligned P1 film (15 min of irradiation of linearly polarized visible light) and b) the same film after annealing at 100° C for 10 min .................................................. 47
| Figure 29 | Changes in order parameter of azobenzene as a function of annealing temperature. | 48 |
| Figure 30 | Thermal stability influence on trans azobenzene orientation in P1 and his Cu and Zn ionomers. | 49 |
| Figure 31 | UV-vis spectra of a thin film and of a dilute solution in THF of P1 | 51 |
| Figure 32 | Schematic illustration of J and H aggregates formed by azobenzene moiety in the same plane. | 52 |
| Figure 33 | An example of curve fitting used to determine the relative amount of free azobenzene (centered at the middle), H-aggregated azobenzene (centered on the left) and J-aggregated azobenzene (centered on the right). | 52 |
| Figure 34 | Population changes of the azobenzene chromophore in the different aggregation states for P1 copolymer and P1-Zn3% a) non-associate b) H- and J-aggregates. | 53 |
| Figure 35 | Photochemical nematic-isotropic phase transition illustration for P1 and its ionomers on radiation with 360 nm UV light. | 56 |
| Figure 36 | Photochemical nematic-isotropic phase transition switch-on times' vs reduced temperature for P1 and its metal analogs. | 57 |
| Figure 37 | Photochemical isotropic-nematic phase transition switch-off times' vs reduced temperature for P1 and its metal analogs. | 58 |
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Characterization of copolymers of azobenzene with methacrylic acid...</th>
<th>23</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 2</td>
<td>Phase transitions of different ionomers used in this study</td>
<td>25</td>
</tr>
<tr>
<td>Table 3</td>
<td>Parameters obtained from the curve fitting of P1 and its inomers</td>
<td>42</td>
</tr>
<tr>
<td>Table 4</td>
<td>Parameters obtained from the curve fitting of P1 and P1-Zn3% at low and high dosage of irradiation</td>
<td>45</td>
</tr>
<tr>
<td>Table 5</td>
<td>% cis isomer at the photo-stationary state</td>
<td>46</td>
</tr>
</tbody>
</table>
INTRODUCTION

Azobenzene chemistry is a very absorbing area of exploration because it is quite well known and on the other hand because it continues to surprise us with totally unforeseen phenomena some of which are still not totally explained. To our knowledge Teitel(1) in 1957 was the first to notice, with the aid of a polarized microscope, that illumination with linearly polarized light of a sample containing azo aromatic compound (Congo Red) and benzopurpurine become dichroic when left to dry out. The explanation proposed for the phenomenon was that the polarized light’s mechanical action act on the chromophore; chemical group (as an azo group) that absorbs light at a specific frequency.

The search continued with Neporent et al.(2), who believed that studying photodichroism could provided them with vital information on the electronic properties of the molecules as well on characteristics of molecule-solvent systems such as viscosity, relaxation time of the photo-induced orientation of molecule etc. They studied films prepared by evaporating an aqueous solution of Congo red and then irradiated with polarized light in the region of 450-550 μm; the films acquired dichroism properties. The observations made were cleared: linearly polarized light parallel to the irradiating beam had a lower absorption on the irradiated sample and linearly polarized light perpendicular to the irradiating beam had a greater absorption on the irradiated sample. They also successfully got an inverse photodichroism by irradiating a solution of congo red in polyvinyl alcohol.

The film was heated to a particular temperature and switching of the polarized light on and off resulted into a development and vanishing of photodichroism. Neporent explained the phenomenon of photo-induced dichroism by rotation of the absorbing molecules to a favourite direction3.

Few years later Makushenko et al.(3) found on several simple azo compounds that on irradiation of polarized light not only the production of photodichroism, which was
observed early, but also reversible spectral changes indicative of photoisomerization of the molecules. The connection between dichroism and isomerization was finally made.

![Graph showing switching-on and switching-off time of the orienting light beam.]

**Example of a record of inverse orientation dichroism made with the photoelectric apparatus. 1--Switching-on time; 2--switching-off time of the orienting light beam.**

Figure 1. Congo Red photodichroism (4)

The use of the reversibility of the photo-induced alignment is in erasable optical recordings, such as optical computing devices, imaging processing etc. On the other hand the use of crystalline aligning layers with long-lasting molecular orientations with high optical anisotropy is for LC display devices.

The objective of this study is to design and synthesize a new type of polymer: azobenzene-containing liquid crystalline ionomers; and to investigate the azobenzene properties of this new type of material. Our hypothesis is that the properties of the azobenzene mesogen will vary according to its environment.
CHAPTER 1
A BRIEF INTRODUCTION TO AZOBENZENE CONTAINING POLYMERS

1.1 Azobenzene

Now it is well known that the azo aromatic group can be present into two conformations of different energies (5): the trans or "E" isomer of rod shape is more thermally stable than the V-shaped cis or "Z" isomer. Illustration of the two isomers is present in following figure 2.

![Azobenzene trans-cis isomerization](image)

**Figure 2. Azobenzene trans-cis isomerization. (5)**

The ground states energy difference between the two isomers is about 50kJ/mol in the case of azobenzene. The inversion of the two isomers represented in figure 2 can be achieved either by light or by heat. When radiating an azobenzene group with light of 360 nm wavelength, which corresponds to its absorption, the
stable trans form can be isomerized to the less stable cis form. The absorption of light brings the molecules to an exited state, which corresponds to the electronic transition \((\pi \rightarrow \pi^*)\)\(^{(6)}\). The cis form can be very unstable and spontaneous relaxation can be observed which brings back the cis to the more stable trans form. On the other hand the cis form can be stable for a long period of time and there is a need for an external trigger for the backward isomerization (cis to trans). This can be achieved thermally or photochemically. It is just a question of providing the right amount of energy to the cis form to switch back to the more stable trans form. This time the energy furnished is not the same as the trans-cis isomerization but it corresponds to the cis absorption band \((n \rightarrow \pi^*)\).

The cis and trans isomers differ therefore by the \(\lambda_{\text{max}}\) of absorption. Usually the azo groups absorb in the UV region but some can also absorb in the visible region depending of the constituents present on the aromatic cycles. Earlier studies have verified the cis isomer geometry and as shown in figure 2 the phenyl rings are twisted perpendicular to the plane determined by the N=N axis. The distance between the 4 and 4’ position of the trans form is 1.0 nm and that of the cis-azobenzene is 0.56 nm. The E isomer possesses a transition dipole moment approximately in the same direction with its long molecular axis.

Depending if thermal or photo energy is imputed for the isomerization of azo compounds there are two mechanisms that have been elucidated to date. The first mechanism that was suggested is the one where the azo aromatic groups isomerise by rotating about the -N=N- bond. This mechanism was associated to both photo and thermal isomerization. The later mechanism stipulated that isomerization takes place via the inversion of both or only one of the nitrogens through a linear sp-hybridized transition state with retention of the double bond (figure 2). This mechanism is generally accepted for the thermal isomerization.

As mentioned earlier azo molecules can create optical anisotropy on a thin layer with radiation of linearly polarized light through photochemical trans-cis-trans isomerization
cycles. Only those azo molecules which transition dipole moment is perpendicular to the direction of the electric field vector of the incident linearly polarized light will be inactive and will not undergo photochemical trans-cis isomerization. The others which transition dipole moment is not perpendicular to the electric field vector will undergo isomerization accompanied with a minor motion of their transition dipole moment until they are perpendicular to the direction of the electric field. This results in optical anisotropy, which is created by the photo alignment of the azobenzene molecule. Two mechanisms are proposed for the creation of optical anisotropy the first being the one described above and the second being the one with a stable cis form where optical anisotropy is created by the inactive trans isomers. In other words, the molecules are radiated with linearly polarized light and only those molecules that absorb (which transition dipole moment is not perpendicular to the linearly polarized light) undergo trans to cis isomerization. The back isomerization, cis to trans, doesn’t take place because of the cis form being stable for a long period of time. The activated molecules stay in their exited state having a v-shape and the anisotropy is created only from the inactive trans molecules, which have the rod shape.

1.2 Azo-containing Polymers

If the azobenzene chromophore is attached to a polymer chain or even if it is introduced in a polymer matrix without bonding, the photoisomerization of the chromophore can initiate a series of motions. We can summarize these motions into three categories (7). The first level of motion is the chromophore’s motion that is influenced by the light polarization. The second level of motion is the "domain" level, which is in the nanoscale level. This motion can be seen as the motion of the chromophore under some restraint. A liquid crystalline domain can represent the restraint for example. So what happens is that when the azobenzene chromophore orients itself it drives the whole domain to orient. This is the so-called cooperative effect motion, because the whole domain reorient to the preferred direction. The third type of motion is at the macroscopic level. The driving force here is the same as the previous level of motion or it can have a different mechanism. The difference is that we have a massive motion of the polymer
material. The patterns produced on thin film surfaces are visible to the naked eye. We have three types of motions at the molecular, at the nanometer and at the micrometer level.

The first research on photo induced orientations was mainly done on liquid crystal polymers. Figure 3 displays the first used liquid crystal polymer for induced orientation.

Figure 3. (Liquid crystal polymer G43S494N104I)(8)

So basically what they have done with this polymer is that they have filled a few μm thick cell with this polymer and preoriented with an electric field above the Tg for some time until the liquid crystal monodomains were developed. Then linearly polarized light was used with certain intensity for a short period of time and a stable photoalignment was produced. By heating above the isotropic temperature the photoalignment was erased. Afterwards, different liquid crystalline systems were used in copolymers with azo and ester type mesogens with the azo being the chromophore. During radiation with polarized
light the ester just moved along the azo groups and a much better photalignment was obtained with lower dosage of intensity. After this point Tredgold et al. (9) synthesized few copolymers of styrene with different constituent concentration of maleic anhydride and hydrolyzed maleic anhydride functionalised with alkyl azo chromophores. One of the series of copolymers containing 50% azo was amorphous and another serie containing 90% azo was semi-crystalline. This team was the first to notice a difference of much higher birefringence in ordered materials than in amorphous materials. The team also notice an increase in birefringence with heating the sample for a certain time after photoalignment. So the difference in orientation and reorientation must be explained. The term orientation or photo-induced orientation is used when the initial sample is amorphous, that is the mesogens or the azo groups are in different direction; in other words the sample is disordered. The term reorientation or photo-induced reorientation is used when the sample has an initial orientation usually obtained in liquid crystal polymers films by generating monodomains using electric or magnetic fields. At the same time Wiesner et al. (10) did some studies on relaxation of the photo-induced optical anisotropy on liquid crystalline copolymers containing azobenzene and also on amorphous copolymers containing azobenzene. They reported that under the same conditions the amorphous copolymers relax entirely while the liquid crystalline copolymers preserve the photoalignment for longer times.

Even though some examples of photo-orientation were produced on amorphous polymers like in the work of Todorov et al. it was believed that liquid crystals play a central task in the reorientation. So liquid crystal side-chain polymers had to be conceived with a suitable spacer between the mesogenic group and the main chain in order to introduce some free volume concept and to allow for independent motion of the mesogens for the possibility of alignment. So then from the work of Wiesner it was understood that photo-induced reorientation, usually obtained in L.C. polymers, is not stable in amorphous systems, not due to the fact of their amorphous state but to their low Tg.

For the liquid crystal polymer 2 on figure 4 the Tg is 31°C and for the amorphous polymer 3 the Tg is 30°C. The Tg of these polymers is close to room temperature. The
photo-induced reorientation is more stable at room temperature for the liquid crystalline polymer than for the amorphous polymer even though the two polymers have a similar Tg. For the liquid crystalline polymer, a possible liquid crystalline phase is present and the relaxation of the reorientation is stable due to the ordered domain of the liquid crystalline material. Since 1992, many studies on amorphous polymer showing polarization photochromism have appeared and the comparison with liquid crystalline polymers started to come into sight. In amorphous systems, the photo-chromatic units that are covalently bound to the polymer backbones resulted in enhanced stabilization of the molecular orientation induced by linearly polarized light. On the other hand if bigger optical anisotropy and superior thermal stability of the photo-induced alignment generated by linearly polarized light want to be achieved, liquid crystal polymers with azobenzene side chains is the key to success.

Figure 4. Azobenzene Liquid Crystalline and Amorphous polymer systems(9)

Super-molecular assemblies are produced from LC with unidirectional orientations of the molecular axis purely to give emergence of optical anisotropy. As one can imagine, the
interest of combining LC systems with photochromic systems is huge because of their amplification effect which is triggered by light, coming from their molecular order, resulting in noteworthy alterations of optical properties. Azobenzene chromophores in a radiated liquid crystal polymer matrix exhibit for example order parameter (S = 0.56) greater than those of amorphous polymers (S = 0.03). Temperature effects are very impressive. Optical anisotropy is only slightly influenced for LC photo-chromic polymer below the Tg but strong expansion of the order parameter is observed above the Tg. This is due to the self-aggregation of mesogenic azobenzene. If an amorphous polymer system is treated with heat above the Tg, the optical anisotropy is removed. This is due to thermal randomization of the molecular orientations.

Copolymers composed of photochromic moiety as azobenzene and non photo-chromic moiety shows photo-induced orientation of both mesogenic groups. This is the so called cooperative effect and is illustrated in figure 5C.

(11)

Figure 5. Types of molecular orientation of photochromic LC copolymers containing a non-photoactive moiety when radiated with linearly polarized light. A) No-photo-orientation B) Photo-orientation only of the photochromic moiety C) cooperative photo-orientation of both mesogens(9).
In the first case of the above picture the orientation is totally undeveloped due to the stable orientation order of the polymer matrix mesophase. In case B only the chromophore orient. The cooperative effect, observed in case C, is due either to dipolar interactions of the photoactive and non-photoactive moieties or steric effects or both or other intermolecular forces that can be present.

Light has also been used to photo-induce changes of liquid crystalline phases. When azobenzene undergo photoisomerization (E/Z) and is doped in nematic LC, the result is a change of mesophases from nematic to isotropic(10). This is explained by the change of molecular shape of the rod shape E isomer to the bent shape Z isomer that destroys the ordered mesophases. It acts as an impurity and photo-phase transition occurs. Applications of this use of light may be found in information storage and optical switching.

An important aspect of producing surface relief gratings is the need of macroscopic motion of the polymeric material. This third type of motion can be achieved through the combination of dendrimers and photochromism. This is illustrated in the following figure:

Figure 6. Photoisomerization of azobenzene on the surface of a dendrimer.
It can be seen that bounding the azobenzenes on the periphery of the dendrimer and isomerizing them leads to different shape of the macromolecule, different surface polarities and different inclusion properties. Higher generation of macro dendrimers can be produced if for example the dendrimer periphery is amphiphilic(13). The dendrimers can form bilayers to produce supramolecular structures. Also different forms can be achieved with dendrimers such as spherical, hemispherical and cylindrical for different purposes.

The applications of the photo-induced motions of LC and amorphous polymers can be numerous. The use of the active photo-function where the reversibility of the photo-induced alignment is achieved can be used in erasable optical recordings (14), such as optical computing devices, image processing etc. Since, the polymer film birefringence can be altered and return to its original value millions of times the process is reversible. The main disadvantage is the write/erase time requirement. Some other applications consist of optical elements such as interference color filters. On the other hand when the passive function is put into use, long-lasting molecular orientations can be achieved with high optical anisotropy. This can be used in LC aligning layers (15) that are required for LC display devices. This technique is better than the previous rubbing technique because it doesn’t create static electricity on the polymer film that can attract dust and act as an impurity of the mesophases and worsen the device

1.3 Metal containing liquid crystalline polymers.

Metal containing polymer are one of the most potential materials in polymer chemistry (16) because the rare-earth and transition metals incorporated into the polymer matrix can bring additional functionality such as electric conductivity, magnetic activity, special optic properties, catalytic activities etc. The most important task of chemistry for metal containing polymer, is the progress in finding new efficient methods of incorporating the metals into the polymer matrix and examining its physico-chemical properties. Even more interesting is the approach of combining different functions to create supra-molecular smart materials as is the case of liquid crystalline metal containing polymer. In
this perspective the metal-containing polymers can be taken into account as hybrid materials where the physical properties of metal atoms, the anisotropic properties of LC and the processing properties of polymer material come together.

There are two big families: Polymer metallomesogens(17) and LC ionomers(18). The definition of metallomesogenic polymers as LC polymers, which contain metallic entities, is vague. There are a lot of cases where the metal atoms have been introduced in polymers matrices as additives in order to modify the physical properties of the polymers but are not directly related to the mesogenic properties. Metallomesogenic LC polymers are LC polymers in which metal atom is part of the pro-mesogenic unit. In other words, where metal complex is the main component of the forming structure of the mesogenic group. Metallomesogenic can be classified as the same structural criteria that are typically used for the classification of organic LC polymers. Classification between non-crosslinked and crosslinked polymers is appropriate also for metallomesogenic. Within these two groups a further sub-classification between main-chain and side-chain polymers can as well be made depending of the structural position of the pro-mesogenic building block with respect to the chain of the polymer. Additionally, depending of the mesogenic behavior the different types of polymeric structures may be classified as lyotropic and thermotropic.

The majority the metallomesogenic polymers reported to date in the literature are main chain metallomesogenic. This is due to geometric reasons of the metal complexes that are used. Because low molecular weight metallomesogens are symmetric compounds, it is easier, when polymeric materials are synthesized, to make the symmetrically monomeric complexes that are used for the preparation of main-chain LC polymers. Figure 7 below illustrates an example of a lyotropic system containing two different metal atoms as a main chain metallomesogenic polymer.

The tributylphosphine co-ligands acts as a stabilizer of the metal-carbon sigma bond and therefore decrease the intermolecular attractions. This allows for better solubility of the polymeric chains in common organic solvents such as dichloromethane,
tetrahydrofuran or trichloroethylene. Alternation of Pd, Ni or Pt increase further the stability and the solubility of the system, and the emergence of liquid crystalline mesophases in concentrated solutions is allowed. Thus, the choice of the right metal atom is of great importance to the stability of the complex and therefore to LC properties. In thermotropic systems for example, the metal coordination will influence the overall shape that is very important for promoting the appearance of mesophases. The following figure shows an example of a lyotropic side-chain polymer.

![Lyotropic polymer containing two different metal atoms](image)

Figure 7. Lyotropic polymer containing two different metal atoms (19).

The introduction of different structural possibilities and rich diversity of molecular geometry due to the coordination chemistry of metal atoms can explain the molecular architecture of LC polymers. Moreover, magnetic, electric, catalytic or non-linear optical properties, ionic transport, redox/oxidation reversible properties, photo-effects need to be further investigated.

Ionomers are polymers containing ions. Making ionomers is a way to introduce metal ions into polymers. Random ionomers have unique properties. The definition of liquid crystal ionomers is that metal atoms are bounded by coulombic interactions with LC polymers’ functional groups, and affect the mesophases by the formation of multiplets (ion associates)(18). Ion associates or multiplets can be quadruplets, sextuplets and
higher aggregates. In random ionomers, several factors influence the formation of multiplets some are governed by the ionic species, others by the character of the host polymer.(20)  

\[ \text{Figure 8. Lyotropic side-chain polymer (21).} \]
The strength of the electrostatic interaction between ion pairs, which is governed by the size of the ions and the partial covalent character of the ionic bond, is one of the most significant ionic parameter that governs multiplets formation. No multiplet formation would be possible if the electrostatic interactions between ion pairs were very weak. Also small highly polar ion pairs interact more strongly than largely diffuse ion pairs.

Ion concentration of the ionomer is also of great importance in influencing multiplet formation. Aggregation of ion pairs doesn’t happen if ion pairs are very dilute because the distance between them is too far for them to experience a considerable electrostatic attraction.

Just as mentioned, the nature of the host polymer is also an important factor in determining the extent of multiplets formation in random ionomers. Low Tg polymers lean towards formation of multiplets, while high Tg polymers tend to inhibit multiplets formation due to rigidity. Also, in the presence of plasticizers, intermolecular interaction may be present between the plasticizer, the backbone of the polymer and the ionic groups, which also influence the process of multiplets formation. Furthermore, the size of the aggregates is influenced by steric factors. If there is less steric hindrance to aggregation the result is large multiplets formation. The opposite is also true.

Magnetic properties had been reported by E.B. Barmatov et al.(18) They prepared a series of LC ionomers containing copper(II). The anti-ferromagnetic properties appeared at very low concentration of copper ions. Therefore a mean of controlling ion content in liquid crystal ionomers is critical. In ionomers, it is very easy to control ion content compared to metallomesogens. This has a direct consequence of their magnetic properties. In addition, metal atoms in ionomers are not bounded directly to the mesogenic group as in metallomesogens, which can permit to us to separately control the influence of metal atoms magnetism and supramolecular LC polymer structure in target substances.
The objective of this study is to synthesize and study a new photoactive material, namely: azobenzene LC ionomers. For that purpose we chose to use a simple approach to prepare the ionomers and we proceeded by incorporating methacrylic acid into a side chain liquid crystalline polymer and then neutralizing to a certain degree the acid group with different metal ions. The objective is to study photo-alignment, photo-induced phase transition, birefringence and ionic aggregations properties of the synthesized material in order to better understand and to contribute to the development of this still infant stage of new materials called ionomers. By incorporating a metal ion into the LC azobenzene polymer, the ionic aggregates may influence not only the LC phase of the polymer, but also the photo-induced orientation of the azobenzene mesogens.
CHAPTER 2
SYNTHESIS AND CHARACTERIZATION

2.1 Materials

P-Anisidine (99%), phenol (99%+), 6-chloro-1-hexanol (96%), methacryloyl chloride (97%), methacrylic acid (99%), copper (II) acetate (98%), zinc acetate dihydrate (98%+), manganese (II) acetate (98%), calcium hydride (90-95%) were used as received from Aldrich. Sodium nitrate (ACS norms), sodium hydroxide were purchased from Fisher Chemicals and used without further purification. Potassium iodide (Baker chemicals), potassium carbonate anhydrous (EMD), sodium sulfate anhydrous (ACS, Anachemia) were used as received. THF was refluxed with sodium and distilled before used. AIBN, was purchased from Polyscience, inc., crystallized from ethanol and dried under reduced pressure at room temperature before use. Triethylamine was refluxed with calcium hydride and distilled before use. All other solvents were commercially available and used as received.

2.2 Synthesis

The first step was the synthesis of the azobenzene monomer whose structure is shown in figure 9.(22) Afterwards, the homopolymer and copolymer of azobenzene with methacrylic acid were prepared by free radical polymerization.(23) Figure 10 shows the structural features of the copolymer.

![Figure 9. Azobenzene monomer](image-url)
Figure 10. Structure of Azobenzene copolymer. \[ \text{X and Y are the copolymer composition} \]

The third and final step was the synthesis of the different metal ion-containing ionomers.(24) The synthetic route to the azobenzene monomer is shown in Figure 11. More details are given below.

2.2.1 Synthesis of 4'-Hydroxy-(4'-methoxy) azobenzene (1)

P-anisidine (0.20 mol) was dissolved in 670.0ml of 10% dilute hydrochloric acid (12M) water solution. A solution of sodium nitrite (0.20mol) in 40ml water was added drop wise
at 0°C. A mixture of phenol (0.20mol) and sodium hydroxide (40.00g) in 125.0ml water was slowly added to the reaction flask over a period of 30 minutes at 0°C with vigorous stirring. The suspended solid was filtered and washed with water after the solution had been acidified with concentrated hydrochloric acid. Purification was performed by flash chromatography on silica gel using petroleum ether/ethyl acetate (3:1) as eluent. Dark brown crystals were obtained with a yield of 80%; mp: 136°C; $^1$H-NMR (300MHz, CDCl$_3$) $\delta$ 7.88-7.95 (m, 4H), 6.95-7.10 (m, 4H), 5.12 (s, H), 3.95 (s, 3H); Mass spectrum m/z (%) 228 (80), 107 (100); exact mass calculated for C$_{13}$H$_{12}$N$_2$O$_2$: 228.09.

2.2.2 Synthesis of 4'-hexyloxy-4'-methoxyazobenzene (2)

In a round-bottom flask equipped with a condenser, (0.090mol) of 6-chloro-1-hexanol, (1.35*10$^{-1}$mol) of potassium carbonate and (9mg) of potassium iodide were dissolved in dimethylsulphoxide (DMSO) and heated at 100°C for 24 h. The final mixture was poured into 10% aqueous sodium hydroxide. The precipitate was collected and washed with water. Recrystallization was performed in ethanol and the product obtained had an yellow color with and yield of 95%; mp: 124°C; $^1$H-NMR (300MHz, CDCl$_3$) $\delta$ 7.85-7.95 (m, 4H), 6.95-7.05 (m, 4H), 4.05 (t, 2H), 3.90 (s, 3H), 3.68 (t, 2H), 1.85 (m, 2H), 1.65 (m, 2H), 1.40-1.55 (m, 4H); Mass spectrum m/z (%) 328 (50), 107 (100), 77 (38); exact mass calculated for C$_{19}$H$_{24}$N$_2$O$_3$: 328.41.

2.2.3 Synthesis of 6-[4-(4-methoxyphenylazo)phenoxy] hexyl methacrylate (3)

Product 2 (9.00*10$^{-2}$mol) was dissolved in absolute tetrahydrofuran at 60°C, triethylamine (0.12mol) was added and methacryloyl chloride (0.12mol) in 10.0ml tetrahydrofuran was then added dropwise at 60°C. The reaction mixture was cooled and stirred at room temperature for 24 h. The solvent was removed and the resulting solid was collected and redissolved in chloroform. The solution was washed three times with
Figure 11. Synthesis scheme of azobenzene monomer

water, dried with anhydrous sodium sulfate. The crude product was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate (2:1) as eluent; then recrystallized twice in methanol; mp: 72-74°C; $^1$H-NMR (300MHz, CDCl$_3$) $\delta$ 7.85-7.95 (m, 4H), 6.95-7.05 (m, 4H), 6.12 (s, H), 5.58 (s, H), 4.18 (t, 2H), 4.05 (t, 2H), 3.88 (s, 3H), 1.95 (s, 3H), 1.85 (m, 2H), 1.70 (m, 2H), 1.40-1.60 (m, 4H); Mass spectrum m/z (%)

R$^1$ = OCH$_3$
396 (100), 345 (10), 135 (25) 107 (40), 77 (10); exact mass calculated for C_{23}H_{28}N_{2}O_{4}: 396.20

2.2.4 Synthesis of Azobenzene Copolymer with Methacrylic Acid.

Methacrylic acid (2.17*10^{-2} g, 0.26mmol), azobenzene monomer (0.50g, 1.30mmol) and AIBN (0.010g, 2 wt%) were dissolved in dried THF. After three freeze-thaw-vacuum cycles, the polymerization was carried out at 60-70°C for 24 h. The resulting polymer mixture was precipitated in cold methanol three times and dried under reduced pressure; the polymer yield was 50-60%.

2.2.5 Synthesis of Azobenzene Liquid Crystalline Ionomers

Figure 12 shows the general structure of the liquid crystalline ionomers. Azobenzene containing LC ionomers were obtained by the following method: 0.50 wt% ethanol solution of the metal acetate was added to a 1 wt% solution of copolymer in THF. The solution was filtered and evaporated and dried in vacuum at 110°C for 1h. Three different metal were used to produce azobenzene containing LC ionomers: Cu (II), Zn (II), and Mn (II). The substitution of protons of carboxyl groups by the metal atoms was proved by FTIR spectroscopy.

2.3 Characterization

Table 1 summarizes the different polymers and copolymers synthesized for the present study. It outlines the main characteristics of the materials such as mol % of azo composition, polymer polydispersity and also their phase transition temperatures. The pure azo polymer shows two distinctive LC phases. The azobenzene copolymer with methacrylic acid shows different results. At high azo content there is only one LC phase present and as the azo content decreases in the copolymer, the nematic LC phase disappears.
Figure 12. Ionomer’s structure

M: Cu
Zn
Mn
Table 1. Characterization of copolymers of azobenzene with methacrylic acid.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Feeding Composition (AZO: MAA mol%)</th>
<th>Molar Composition (1H-NMR)</th>
<th>Mn (GPC)</th>
<th>Mn/Mw (GPC)</th>
<th>Phase Transitions$^a$</th>
<th>HΔΣ-N (°C)</th>
<th>HΔN-I (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P0</td>
<td>100:00</td>
<td></td>
<td>2.2$\times$10$^4$</td>
<td>1.8</td>
<td>G62Σ89 N128I</td>
<td></td>
<td>1.91,1.50</td>
</tr>
<tr>
<td>P1</td>
<td>83:17</td>
<td>72:28</td>
<td>3.0$\times$10$^4$</td>
<td>2.1</td>
<td>G60N119I</td>
<td></td>
<td>2.52</td>
</tr>
<tr>
<td>P2</td>
<td>68:32</td>
<td>57:43</td>
<td>1.7$\times$10$^4$</td>
<td>2.3</td>
<td>G72N116I</td>
<td></td>
<td>1.09</td>
</tr>
<tr>
<td>P3</td>
<td>62:38</td>
<td>45:55</td>
<td>4.0$\times$10$^4$</td>
<td>1.5</td>
<td>G76</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P4</td>
<td>50:50</td>
<td></td>
<td></td>
<td></td>
<td>G81</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ G = glass phase; Σ = smectic A phase; N = nematic phase; I = isotropic phase

Figure 13. FTIR spectra in the 1600-1800 cm$^{-1}$ region for polymers P0-P3 and PMA showing the stretching vibrations of the two carbonyl groups of the ester of azobenzene at 1730 cm$^{-1}$ and PMA at 1700 cm$^{-1}$.
The structures of the different copolymers of azobenzene with methacrylic acid were confirmed by FTIR and $^1$H-NMR. FTIR spectra indicate two absorption bands around 1730 and 1705 cm$^{-1}$, which are assigned to the stretching vibrations of carbonyl groups in the ester of azobenzene and methacrylic acid, respectively (Figure 13). The absorption band centered at 1700 cm$^{-1}$ of PMA is assigned to the H-bonded dimers of COOH group. The relative intensity of the C=O bands of azobenzene and methacrylic acid is varied with respect to the change in the copolymer composition.

$^1$H-NMR was carried out to confirm the structure and composition of copolymers of azobenzene with methacrylic acid. The peaks located around 7.0 ppm and 8.0 ppm characterized eight protons of azobenzene unit. There are no protons of vinyl groups present in the copolymers. Copolymer (P4) with high MA composition was found not dissolved in chloroform just as MAA and when using Dimethyl sulfoxide-D6 as solvent, chemical shifts of the carboxylic group at 12.4ppm were indicated.

Figure 14. Nmr spectra of P1 copolymer in D-chloroform showing the absence of the vinyl protons in the region of 5-6 ppm.
The FTIR spectroscopy has been used to characterize the different ionomers (Figure 15). The appearance of COO\(^{-}\) ions is supported by the gradual decreasing of intensity at 1700cm\(^{-1}\) with increase in ion concentration. Table 2 summarizes the phase transitions of the different ionomers studied. The % mark indicates the total ion composition over the whole copolymer.

**Table 2. Phase transitions of different ionomers used in this study.**

<table>
<thead>
<tr>
<th>Ionomer</th>
<th>Phase Transitions(^a)</th>
<th>(\Delta H_{N-I}) (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>((^\circ)C)</td>
<td></td>
</tr>
<tr>
<td>(P_1)-Cu3%</td>
<td>G ↔ N ↔ I</td>
<td>1.76</td>
</tr>
<tr>
<td>(P_1)-Zn3%</td>
<td>47(^\circ)C 80(^\circ)C</td>
<td></td>
</tr>
<tr>
<td>(P_1)-Mn3%</td>
<td>59(^\circ)C 125(^\circ)C</td>
<td>1.88</td>
</tr>
<tr>
<td></td>
<td>G ↔ N ↔ I</td>
<td></td>
</tr>
<tr>
<td>(P_1)-Mn3%</td>
<td>78(^\circ)C 139(^\circ)C</td>
<td>1.41</td>
</tr>
<tr>
<td>(P_2)-Zn5%</td>
<td>67(^\circ)C</td>
<td></td>
</tr>
<tr>
<td>(P_4)-Zn3%</td>
<td>68(^\circ)C</td>
<td></td>
</tr>
<tr>
<td>(P_4)-Zn4.5%</td>
<td>G 44(^\circ)C</td>
<td></td>
</tr>
</tbody>
</table>

\(\Delta H_{N-I}\) is the enthalpy change associated with the transition from the nematic to the isotropic phase. The % mark indicates the total ion composition over the whole copolymer.

\(a\) G = glass transition; N = nematic phase; I = isotropic phase
Figure 15. FTIR spectra of the copolymer of P1, Cu ionomer at 3% molar concentration and 6% molar concentration around 1700 cm$^{-1}$.

DSC and optical polarization microscopy were used in the study of the phase state of parent copolymers and their related ionomers. Figure 16 shows the DSC curves of the parent LC copolymer (P1) and its related LC ionomers. It's obvious from the following figure that depending on the nature of the ion, the initial LC phase representative of the parent copolymer will be stabilized or destabilized to some extent in the ionomers.
Figure 16. DSC curves of parent P1 and its associated ionomers.

2.4 Spin cast films

The present study required the make up of thin films. For this reason a spin coater machine, model KW-4A, from Chemat Technology was used for the fabrication of spin cast film. The machine was equipped with two different timers and two different corresponding speeds. The material in question was dissolved in THF, deposited on quartz plate, and spins casted. The speed and timer knobs were arranged so to produce the desire film thickness and the same conditions were used for each spin cast film. After
letting the films to slowly evaporate under a THF environment for several hours, the quartz plates were dried under reduced pressure for 24 hours. For every new experiment the films were redone in order to eliminate any complications due to thermal history and memory effects. Spin cast film are supposed to be amorphous and their isotropic state was tested after each drying. The absorbance was controlled to be between 0.3 and 0.5.

2.5 UV-vis spectroscopy

The main tool of this study is UV-vis spectroscopy. Recording of UV-vis spectra were made with a HP 8452A spectrophotometer and a polarizer (Oriel). UV and visible irradiation was performed on the films using Novacure 2100 and Exfo Light systems combined with UV and Visible interference filters (10 nm bandwidth, Oriel) and a broad 400-500 nm bandwidth filter which spectral profile can be seen on Figure 17. For the photo-induced orientation experiment the intensity of irradiation of UV light at \( \lambda = 360 \text{nm} \) was about 10 mW/cm\(^2\) and two different intensity were used for the visible light at \( \lambda = 440 \text{nm} \); one at high intensity (around 4-4.5 mW/cm\(^2\) the other at low intensity around 1.5-2 mW/cm\(^2\)). This was done on purpose to study the effect of photo-alignment on different irradiation intensities.

To observe the change in optical transmittance associated with the photochemical phase transition, a set-up alike to that used in our lab (25) was employed figure 18. Essentially, the spin cast film was put inside a hot stage (Instec), which was placed between crossed polarizing optical microscopy. The microscopy light was used as the probe light with normal incidence, and high-speed photo-detector (Displaytech) connected to a digital oscilloscope (TekTronic, TDS 420A) was used to quantify the optical transmission. The UV irradiation beam was aimed at an angle to the normal of the cast film surface in order to avoid reflection entry of the excitation beam into the photo-detector.
Figure 17. 400-500nm broad filter radiation spectrum.
Figure 18. Photochemical Phase Transition Set-up.

2.6 Other instrumentations

A Bruker spectrometer (300 MHz, AC 300) was used for the recording of 1H NMR spectra. FTIR spectra were recorded on a Bomem MB-102 FTIR spectrometer. Gel permeation chromatography (GPC), a Waters systems, equipped with a refractive index and a photodiode array detector was used for the characterizations of polymers’ polydispersities. The eluent used was THF at a 0.5mL/min elution rate and calibration was performed with polystyrene standards. Textures were observed under a Leitz DMR-P polarizing optical microscope using an Instec hot stage. A Perkin-Elmer DSC-7 differential scanning calorimeter with heating and cooling rates of 10 °C/min was used for the measuring of phase transition temperatures.
2.7 Textures of liquid crystal materials

The interest was also to observe if there is a difference in LC phase morphology when the copolymer is combined with an ion. Textures of copolymer P1 and its metal analog P1-Zn3% were characterized with the polarizing optical microscopy (POM). The sample was prepared by spin cast film on a normal glass support. A second glass plate was introduced over the sample in order to sandwich it. This was done for the purpose of keeping the sample material in place even after isotropic temperatures is reached. The two glass plates with the sample between them were then introduced in the hot stage and the temperature was increased over the Tc of the polymer. After this the temperature was decreased in the appropriate LC zone of the material and left at that temperature until the texture developed. It can be seen from figure 19 that indeed the textures are different for the copolymer and its metal counterpart, which agrees with the different composition of the materials. The nematic liquid crystals are characterized by a marble texture. On the other hand the smectic phase is characterized by bright colors.

a)
Figure 19. Characteristic polymer liquid crystal texture of a) P1 b) P1-Zn3% c) P1-Cu3% d) P1-Mn3% e) P0 (nematic phase) f) P0 (smectic).

Figure 19 a) to 19 e) shows the nematic liquid crystal texture. Nematic liquid crystal is a common type and has a thread-like formation. The texture is characterized by a marble texture. In contrary, Figure 19 f) shows the smectic phase. The difference is that the Smectic liquid crystals have a soapy texture and are found at lower temperatures than the nematic. In the smectic phase fairly regular stripe pattern appear which is not present in the nematic phase.
CHAPTER 3
RESULTS AND DISCUSSION

3.1 Photoisomerization

As previously mentioned, the photo-alignment in our polymers is due to the photoisomerization of the azobenzene molecule. Therefore, first it was necessarily to observe if the polymers, copolymers and ionomers photoisomerize. The photo-isomerization of P0 is shown in the figure 20. A cell of P0 polymer dissolved in THF was radiated with UV light at 360nm for different times and the UV-vis spectrum was recorded after each radiation. After sufficient time of radiating the cell the absorbance at 360nm decreased to 0 indicating that trans-cis isomerization took place; a very high quantum yield was also obtained.

The photo-stationary state with maximum cis isomer content is not very stable in solution. After only few minutes the molecules return to the trans form. Photoisomerization followed by thermal relaxation was observed for all of our samples, which allowed us to proceed further in our study.

It was also necessary to observe the photoisomerization effect for thin film since all the following studies were performed on spin cast thin films. Figure 21 shows the photoisomerization of P1 on a spin cast quartz film. The higher trans population in the photo-stationary state explains less efficient trans-cis isomerization. It may be due to lower quantum yield to the isomerization because of both inter and intra molecular interactions present in solid films.

The photo-stationary state with maximum content of cis isomer is stable for several hours. The return to the trans form through thermal relaxation was observed for all of the samples. The time to complete the relaxation was around 24 hours. There was not any significant time difference to reach the photo-stationary state and for the return to maximum trans isomer for the samples. Figure 22 shows the thermal relaxation of \( P_4-Zn3\% \).
The spin-cast film was radiated with UV light until the photo stationary state was reached and then let to relax at room temperature. The UV-vis spectra at different relaxation times were recorded. The photo-stationary state with maximum cis isomer was reached after 220 sec.

![Absorbance vs Wavelength](image)

**Figure 20.** Photoisomerization of polymer P0 in solution with UV irradiation intensity of 2.5 mW/cm². The maximum absorption spectrum is prior to irradiation (0 sec), and the subsequent times shown on the right portion of the spectra are the irradiation times.
Figure 21. Photoisomerization of spin-cast film of polymer P1 on quartz with UV irradiation intensity of 2.5 mW/cm². The maximum absorption spectrum is prior to irradiation (0 sec), and the subsequent times shown on the right portion of the spectra are the irradiation times.
Figure 22. Thermal relaxation of spin-cast film of polymer P4-Zn3% on quartz with UV irradiation intensity of 2.5 mW/cm² prior to relaxation. The subsequent times shown on the right portion of the spectra are the relaxation times.

3.2 Photo-induced alignment and thermally enhanced orientation

Ichimura and Han(26) had successfully obtained a photo-alignment of a thin spin cast film on silica of a liquid crystalline azo polymer using linearly polarized 365nm light. This wavelength corresponds to the absorption of the azo LC polymer of the stable trans azo isomer. This procedure was followed in this study to obtain a photo-alignment of our molecules. Prior to irradiation, the UV-vis spectra of the different ionomers with their corresponding parent copolymers were taken to evaluate the wavelength of maximum absorption. It was found that the wavelength of maximum absorption is situated in the
vicinity of 360nm and no significant changes were observed for the different materials used. In order to get the maximum efficiency a monochromatic filter of 360nm was used. After several tries, irradiation with 360nm polarized UV light of the sample, the polarized UV spectra at different polarized angles were taken in order to examine the photo-induced alignment. There was not a significant difference in absorption observed between UV-vis polarized spectra at different polarization angles for the same sample. This led to the abandon of the following mechanism. A possible explanation may come from the fact that the irradiation intensity at 360 nm is high enough to produce a high population of cis isomers, which basically randomize the polymer sample.

The new procedure\textsuperscript{25} undertaken consisted in irradiating the sample with unpolarized UV light to arrive at the photo-stationary state with the highest concentration of cis isomers and then to irradiate with linearly polarized visible light to produce the orientation. After obtaining the photo-induced orientations, the samples were annealed at specific temperatures in order to study their induced orientation behaviour. The results are shown below. The plausible mechanism for alignment will be discussed later.

Figure 23 gives an example of photo-induced orientation by showing the UV-vis spectra of a thin film of polymer P1. The sample was first irradiated with 360.3nm non-polarized UV light for 20 min at a dosage of 7mW/cm\textsuperscript{2} in order to reach the photo-stationary state of maximum cis isomer content. No polarization dependant absorbance was observed for the \((\pi\rightarrow\pi^*)\) and for the \((n\rightarrow\pi^*)\) transition looking at the appropriate spectra, which clearly indicates the absence of a photo-alignment of the azobenzene groups. The sample was then irradiated with 440 nm linearly polarized visible light, which corresponds to the \((n\rightarrow\pi^*)\) or cis to trans transition, at a dosage of 4.5 mW/cm\textsuperscript{2} for 15 min. Looking at the polarized UV-vis spectra at 360nm corresponding to the trans group absorption, a clear indication of polarization-dependence is observed indicating a photo-induced orientation of the azobenzene groups (figure 23). The reference direction was taken as the direction perpendicular to the polarization of the visible light irradiation. It can be distinguished between the highest absorbance with the spectrophotometer’s beam polarized parallel to the reference direction \((A_{\parallel})\) and the lowest absorbance with the spectrophotometer’s
beam polarized perpendicular to the reference direction ($A_{\text{perpendicular}}$). This polarization dependent absorbance clearly indicates a photo-induced orientation of the azobenzene trans group in the direction perpendicular to the polarization of visible light radiation at 440nm. Comparable spectra effects, exhibiting a preferential orientation of the trans azobenzene groups after visible polarized irradiation were observed for the rest of our samples under investigation. The need to quantify this photo-induced orientation and to compare it for the different sample, turn out to be very appealing for this study because of unavailability of results in the literature. Photo-induced alignment was quantified, using the order parameter ($S$) from the dichroism through $S = (A_{\text{parallel}} - A_{\text{perpendicular}}) / (A_{\text{parallel}} + 2*A_{\text{perpendicular}})$.

![Graph](image)

**Figure 23.** Polarized UV-vis spectra of a thin film of polymer P1 recorded with the spectrophotometer’s beam polarized parallel and perpendicular to the reference direction after linearly polarized 440nm irradiation.
Figure 24 shows the rise in order parameter of azobenzene groups in the copolymer P1 and his metal ions (Mn, Zn and Cu) analogs. The intensity of polarized visible irradiation used was around 4 mW/cm². Besides, the growth of the photo-alignment is progressive in the first 10 minutes of irradiation and slowly attains a plateau at longer times with a maximum S value ($S_{\text{max}}$). An exponential rise by SigmaPlot was fitted with $S = (1 - \exp(-t/\tau)) \times S_{\text{max}}$, where $\tau$ is the characteristic time for the rate of orientation development. The curve fitting exposed in figure 24 gave us the following parameters that are shown in table 3.

![Figure 24. Order parameter vs. time of visible light irradiation for P1 and its ionomers, and their curve fitting with an exponential rise by SigmaPlot.](image-url)
Table 3. Parameters obtained from the curve fitting of P1 and its ionomers

<table>
<thead>
<tr>
<th></th>
<th>P1</th>
<th>P1-Mn3%</th>
<th>P1-Cu3%</th>
<th>P1-Zn3%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{\text{max}}$</td>
<td>0.17</td>
<td>0.16</td>
<td>0.14</td>
<td>0.17</td>
</tr>
<tr>
<td>$\tau$ (min)</td>
<td>5.48</td>
<td>5.03</td>
<td>4.32</td>
<td>5.77</td>
</tr>
</tbody>
</table>

It was suggested that there are two possible mechanisms for the birefringence of polymer thin films. Two identical solid thin films were used for the experiment where one of them was pretreated with 360 nm UV light for sufficient time to obtain its photo-stationary state. Then the two films were radiated with polarized light at 440nm. The results showed an exponential growth of the birefringence of the two samples, followed by a constant rate increase at longer time. The two samples reach eventually the same maximum birefringence at longer irradiation time only thought it took less time for the pretreated sample. The irradiation of the samples with 440nm light corresponds to the $(n\rightarrow\pi^*)$, or cis to trans transition. This promotes the cis molecules to isomerize and to orient perpendicular to the direction of the linearly polarized 440nm light. That is why a faster increase in birefringence, only of the pretreated sample, was observed at shorter times of irradiation. This was called mechanism # 2. On the other hand because irradiating with 440 nm activates fewer trans cis isomerization cycles, but eventually this will produce some cis-to-trans cycles also, which are responsible for the alignment of the molecules. That’s why the untreated sample takes longer time to reach maximum birefringence: mechanism # 1.

The comparison of the photo-induced alignment between the parent, copolymer P1, and its ionomers has been made. The different metal ionomers influence the photo-induced orientation at longer times thus influencing the maximum birefringence. The maximum photo-induced alignment is higher for the Zn ionomer and lowest for the Cu ionomer. For this experiment the thickness was very cautiously controlled to give a similar
thickness for all the spin cast films. This was done, by preparing spin cast films of similar absorbance (0.4). The order parameter that was determined from the dichroism characterizes the orientation of the trans azobenzene molecules. Figure 25 explains the phenomenon of dichroism.

![Diagram showing Y-direction polarized light and X-direction polarized light](image)

Figure 25. Extreme case of oriented azobenzene groups absorption of different light polarization direction.

A thin film whose azobenzene groups are oriented in the x direction will absorb little amount of linearly polarized light in the perpendicular direction and almost all of the polarized light in the same direction. This phenomenon is shown in figure 25. If the sample was in the liquid
or amorphous state, it will absorb linearly polarized light in the x and y direction equally because of the absence of any preferential orientation of trans azobenzene molecules. Figure 26 shows the effect of two different irradiation intensities used for the photo-induced alignment of P1 and P1-Zn3%. Two new spin-cast films were made for this experiment. Their absorbance is different than the previous films used for figure 24.

![Graph showing order parameter vs. time of visible light irradiation for P1 and P1-Zn3% at two different intensities. The curve fitting using an exponential rise is also shown.](image)

**Figure 26.** Order parameter vs. time of visible light irradiation for P1 and P1-Zn3% at two different intensities. The curve fitting using an exponential rise is also shown.

From figure 26 it can be seen that when irradiation of the sample with linearly polarized visible light at low dosage is used, the photo-alignment develops slower than if irradiated at high dosage. In other word the plateau is reached faster at high dosage irradiation.
The curve fitting shown in Figure 26 yielded the following parameters:

Table 4. Parameters obtained from the curve fitting of P1 and P1-Zn3% at low and high dosage of irradiation.

<table>
<thead>
<tr>
<th></th>
<th>P1</th>
<th>P1</th>
<th>P1-Zn3%</th>
<th>P1-Zn3%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I = high</td>
<td>I = low</td>
<td>I = high</td>
<td>I = low</td>
</tr>
<tr>
<td>$S_{\text{max}}$</td>
<td>0.15</td>
<td>0.17</td>
<td>0.17</td>
<td>0.20</td>
</tr>
<tr>
<td>$\tau$ (min)</td>
<td>3.74</td>
<td>6.79</td>
<td>2.07</td>
<td>4.22</td>
</tr>
</tbody>
</table>

It was interesting to observe the effect of photo-alignment of the parent copolymer and his ionomer with different metal ion concentration. For this purposes figure 27 shows this effect for P4, P4-Zn3% and P4-Zn4.5%.

The P4 and P4-Zn3% behaves as expected. In other words $S_{\text{max}}$ for the Zn ionomer seems to be slightly higher than its parent copolymer regardless of the intensity of irradiation. But with higher Zn content of the ionomer the maximum order parameter seems to have a significantly lower value.

Another parameter that was omitted in the discussion till now is the $\% \text{cis} = 100(\text{A}_0 - \text{A}_s)/\text{A}_0$, where $\text{A}_0$ and $\text{A}_s$ are the absorbance at 365 nm before and after irradiation, at the photo-stationary state. Just as found previously(27), the $\% \text{cis}$ seems to increase slightly
when the content of the azobenzene mesogene is decreased. The results are shown in table 5.

![Graph showing order parameter vs. time of visible light irradiation for P4, P4-Zn3% and P4-Zn4.5% at two different intensities of radiation. The curve fitting using an exponential rise is also shown.]

Figure 27. Order parameter vs. time of visible light irradiation for P4, P4-Zn3% and P4-Zn4.5% at two different intensities of radiation. The curve fitting using an exponential rise is also shown.

Table 5. % cis isomer at the photo-stationary state.

<table>
<thead>
<tr>
<th>Material</th>
<th>cis-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>P0</td>
<td>64</td>
</tr>
<tr>
<td>P1</td>
<td>60</td>
</tr>
<tr>
<td>P2</td>
<td>69</td>
</tr>
<tr>
<td>P4</td>
<td>69</td>
</tr>
</tbody>
</table>
As an example figure 28 shows the polarized UV-vis spectra of a) a photoaligned P1 film (15 min of irradiation of linearly polarized visible light) and b) the same film after annealing at 100° C for 10 min. The dichroism is increased drastically through thermal treatment.

Figure 28. Polarized UV-vis spectra of a) a photoaligned P1 film (15 min of irradiation of linearly polarized visible light) and b) the same film after annealing at 100° C for 10 min.
Once the azobenzene has been aligned with polarized visible light, the photo-alignment can be boosted or decreased by thermal treatment. This depends on the nature of the polymer. P0, P1, and P2 all had their initial photo-alignment enhanced by thermal treatment. On the other hand P4 did show a decrease of photo-alignment when heated. This is illustrated in figure 29. The thermal treatment was performed by introducing the film after initial photo-alignment in the oven at fixed temperature for 10 min, and then cooled to room temperature for the acquiring of the UV-vis polarized spectra.

Figure 29. Changes in order parameter of azobenzene as a function of annealing temperature.
It can be remarked from the above figure that all LC polymers have their azobenzene alignment boost after thermal treatment. This is due as already described to self-aggregation of mesogenic azobenzene above the Tg. For the P4 that is not LC the opposite effect is observed above the Tg, due to thermal randomization of the molecular orientations of the azobenzene molecules. After reaching the maximum azobenzene orientation for the LC copolymers the order parameter drops down at higher temperatures. This drop corresponds roughly to the clearing temperatures of the materials.

![Graph showing the thermal stability influence on trans azobenzene orientation in P1 and its Cu and Zn ionomers.](image)

**Figure 30.** Thermal stability influence on trans azobenzene orientation in P1 and its Cu and Zn ionomers.

The same thermal treatment enhancement orientation shown in figure 30 was observed for the LC copolymer and LC ionomer of Barmatov et al(24). They have reported a
growth in clearing temperature and glass transition of all their LC ionomers as compared to their parent copolymer. For figure 30, different spin cast films were produced with different absorbance than figure 29. They associated this to the mutiplet formation structures, which exhibit a stabilization of the LC phase. Indeed, two of the ionomers P1-Zn3% and P1-Mn3% exhibit the same features. But the P1-Cu3% ionomer has the opposite effect. This is probably due to mutiplet formations that create more disordered structures, structure defects, and have an effect of distorting the LC phase. Transition metal ions want to fill their empty coordination orbital in order to reach a coordination number of 4-6. Oxygen in the ester and ether groups can act as ligands to the metal ions. Unfavorable dispositions of the aggregates may thus lead to reduction of the clearing temperature and the glass transition. Figure 28 reveals these features. It can be seen that for the Zn ionomer the trans azobenzene orientation in the LC phase is stabilized and also shifted at higher temperatures compare to P1. The opposite effect is observed for the Cu ionomer. The trans azobenzene orientation is destabilized and shifted to lower temperatures.

3.3 Thermochromic Behavior

Figure 31 shows the UV-vis spectra of a thin film and of a dilute solution in THF of P2. It is evident that when a spin cast film is made aggregates become present. In solution the aggregates hardly develop and the absorbance that is observed at 360 nm is free from aggregation. It is going to be referred to 45as the non-associate or free absorbance. In the solid state the azobenzene molecules are known to form aggregates. In the aggregates the transition dipoles of the azobenzene molecules are coplanar (28). Figure 32 shows the two different aggregates present; the H-aggregates that make a blue shift and the J-aggregates that make a red shift in the UV-vis spectrum of the spin cast film. Therefore the thermochromic behavior of azobenzene has its origin from the changes in the wavelength of absorption of the azobenzene moiety due to the different azobenzene aggregations. Quite important changes in the absorption wavelengths of the chromophore of previously investigated azobenzene LC polymers have been reported in the literature (29) compared to the present results. In order to know whether or not the presence of
metal ions or their ionic aggregates affect significantly the aggregation state of azobenzene mesogens, we investigated the thermochromic behaviour of P1 and its ionomers. For this experiment, thin spin cast films were prepared and drying conditions at room temperature under vacuum were used for 24 hours. Intentionally, the films were not subjected to any heat, UV and visible light prior to the experiment. By using a curve fitting technique available to us in Grams/32 (from Galactic Corporations) the separation of the absorptions into the three types of aggregates absorptions can be made. This is ultimately done to obtain more information about the different aggregates. Figure 33 gives an example of the separate absorptions.

Figure 31. UV-vis spectra of a thin film and of a dilute solution in THF of P1.
Figure 32. Schematic illustration of J and H aggregates formed by azobenzene moiety in the same plane.

Figure 33. An example of curve fitting used to determine the relative amount of free azobenzene (centered at the middle), H-aggregated azobenzene (centered on the left), and J-aggregated azobenzene (centered on the right).
Figure 34. Population changes of the azobenzene chromophore in the different aggregation states for P1 copolymer and P1-Zn3% a) non-associate b) H- and J-aggregates.
The UV-vis spectra were taken at different temperatures on heating the films at a rate of 2°C/min. Using the procedure of curve fitting the relative populations of azobenzene groups in the three aggregation states could be established from the areas under the curves. Figure 34 shows the thermochromic effect by plotting the areas under the curves as a function of temperature. For P1 and for P1-Zn3% ionomer change in the aggregation states of azobenzene chromophores with temperature are clear. For copolymer P1 the free or non-associated azobenzene group population starts to decrease after the Tg. The decrease in free azobenzene population is accompanied by the increase in the H-aggregate population. Above 95°C the further decrease in free of aggregation azobenzene population is associated with the increase of both H- and J-aggregation populations. The two aggregations do not reach their maximum value at the same temperature. The thermochromic effect that is observed for P1 is fitting the thermally induced augmentation of the self-organization of the mesogens in the LC phase. On the other hand for P1-Zn3% the free azobenzene population decreases also after the Tg but reaches a minimum faster than its parent copolymer P1. In this case both the H- and J-aggregate populations increase after the Tg compensating for the free azobenzene decrease. Their respective maximum values are also reached at different temperature but at lower temperatures that P1. This may account for the induced self-organization of the mesogens in the LC phase at lower temperatures. The smaller changes in population of P1-Zn3% accounts for the lower thermal induced augmentation of the self-organization of the azobenzene groups in the LC phase compared to the P1. This may be due to metal ions or their ionic aggregates that hamper the ordering of azobenzene mesogens.

3.4 Photochemical Phase Transition

The study of the photo-induced alignment of the parent copolymer and its ionomers showed the effect of ionic aggregates. This motivated us to proceed with a study on the photochemical phase transition of the materials that is initiated by the azobenzene photoisomerization. First, thin films were prepared in order to investigate the process using the apparatus set-up described in section 2.5. Then it was noticed that the birefringence of the LC state was not high enough and there was not a significant change
in the optical transmission signal between the LC state and the isotropic state. Even though when a second glass plate was introduced over the film and sheared, there was no significant difference that could have been measured. Therefore the films were made by solution deposition and, after drying, brought to a temperature higher than the isotropic temperature for 10 minutes. Then the films were annealed at $T < T_{NI}$ for suitably long time to allow development of the LC phase. When the film with the developed LC phase was placed between crossed polarizers, the microscope light was detected. Once the film was radiated with UV light, the trans-cis isomerization destabilized the LC phase, which led to the isotropic state and, as a result, to a drop in the transmission of the light. Low intensity UV light was used in order to keep some concentration of trans azobenzene chromophore in the photostationary state when irradiated with UV light. This condition allows for some time for the cis isomer to bring disorder to the LC phase into the isotropic phase. The rate of transition between the LC phase and the isotropic phase is related to the decay of the optical transmission on irradiation with UV light.

Figure 35 gives an example of the changes in optical transmission for P1 and its ionomers when radiated with 360nm UV light. In order for the results to be comparable the same reduced temperature was used $T_{\text{red}} = T/T_{NI} = 0.988$ for the four samples. Because of the uncontrollable thickness parameter the sample had different birefringence when brought to the LC phase and obviously showed higher or smaller optical transmission changes when radiated with UV light. This is obvious from figure 35. Also it takes a threshold time radiation in order for the phase transition to be triggered depending on the thickness of the films. From the figure 35 it is clear that the drop in optical transmission takes longer time to complete for the ionomers. The trigger on of the UV Light is located at 0 sec, and the trigger off is located at around 17 sec ±3sec.

The switch-on time was defined as the characteristic time for the signal to drop from 90% to 10% of the initial level. Several measurements of photochemical phase transitions were performed for each sample at different reduced temperatures and it was interesting to observe how the switch-on times varied. Figure 36 shows the variation of switch-on time at different reduced temperatures for P1 and its ionomers. It can be seen that the
photochemical phase transition of the azobenzene mesogens is delayed by ionic aggregates and that this delay is more and more important below 0.988 reduced temperature.

Figure 35. Photochemical nematic-isotropic phase transition illustration for P1 and its ionomers on radiation with 360 nm UV light.
Figure 36. Photochemical nematic-isotropic phase transition switch-on times' vs reduced temperature for P1 and his metal analogs.

After UV radiation, the trans-cis isomerization of the azobenzene mesogens takes place and a nematic-isotropic phase transition is observed. Once the UV radiation is stopped, the nematic phase is recovered due to the thermal relaxation of the unstable cis isomer. As soon as the UV is stopped thermal cis-trans relaxation occurs and the LC phase of trans mesogens starts to recover. In figure 35, the recovery of the nematic phase can be observed for P1 and its metal analog with exception of P1-Cu3%. It can be remarked that the return signal is almost the same for P1, P1-Mn3% and P1-Zn3%. If a plot of the switch-off times, defined as the characteristic time for the signal to rise from 10% to 90% of the initial level (see figure 35), vs. reduced temperature defined by $T_{\text{red}} = T/T_{\text{ni}}$ is plot
it will give figure 37. It is clear that the switch-off times at reduced temperatures above 0.988 are increasing significantly for the ionomers. This suggests the inability of the mesogenic groups to reorganize in the LC phase due to the metal ions.

![Graph showing switch-off times vs reduced temperature for different ionomers.](image)

**Figure 37.** Photochemical isotropic-nematic phase transition switch-off times' vs reduced temperature for P1 and his metal analogs.
CONCLUSION

We succeeded in designing, synthesizing and characterizing a new type of polymeric material, Azobenzene LC ionomer. Ionomers, metal-containing polymers, were investigated as new materials by introducing an azobenzene derivative as the mesogen. More than that, our hypothesis turned out to be true. The azobenzene properties used in the photo-induced alignment, the thermally enhanced orientation, the thermochromic behavior and the photo-chemical phase transition from nematic to isotropic depends to a great extend to the environment of the azobenzene chromophore. This dependence was first established by irradiating a sample with UV light and then irradiating with linearly polarized visible light, which resulted in a desired photo-induced orientation of the azobenzene mesogens. The presence of metal ions either increased the photo-induced orientation; such is the case of the magnesium ionomers, or decreased the photo-induced orientation in the case of the Cu and Zn ionomers, compared to the parent copolymer free of metal ions. When increasing the metal concentration of the ionomer we observed that the material loses its potential of photo orienting, and the photo-induced orientation is obtained to lower degree. Then we had a very elegant way of testing our materials for liquid crystalline properties. A pre-oriented sample was introduced in the oven and the temperature was increased. This resulted in a boost of the alignment of the mesogens for those LC materials. We associated this phenomenon to self-aggregation of mesogenic azobenzene above the Tg. An opposite effect, erasing of the alignment, was observed for one of the material that was not LC. This was associated to thermal randomization of the mesogenic groups above the Tg. By comparing again the metal ionomers with its parent copolymer, we discovered that a growth in clearing temperature and a stabilization of the LC phase for the Mn 3% ionomer and Zn 3% ionomer. But a decrease in clearing temperature and a destabilization of the LC phase was observed for the Cu 3% ionomer. This could be associated to multiplet formations, which created structure defects. A possible prolongation of this project could be the elucidation of the exact structures of the metal aggregates using a model on computer where parameters such as multiplet
formations, transition metal ions coordination numbers and the results from this study are taken into considerations.

We found that the presence of metal ions can either increase or decrease the thermal stability of the liquid crystalline phases formed by the azobenzene mesogens, which in turns can enhance or reduce the degree of photo-induced orientation of the azobenzene mesogens.
REFERENCE

1. TEITEL, Naturwissenschaften, 44, 370 (1957)
11. ICHIMURA KUNIHIRO Chemical Review, 100, 5 (200)