THERMAL, PHOTORESPONSIVE AND CONDUCTIVITY STUDIES OF NITROAZOBENZENE POLYMER

Nur Afiqah Mohamad Iskandar, Sakinah Mohd Alauddin

Faculty of Chemical Engineering, University Technology MARA

***Abstract*—The thermal properties, photoresponsive and conductivity studies of nitroazobenzene polymers of both homopolymer and terpolymer are studied. The poly[6-(4-nitro-4-oxyazobenzene) hexylmethacrylate] (AzoN6) homopolymer and terpolymer consisting of sulfonic acid (AMPS) and methyl methacrylate (MMA) were synthesized by radical polymerization. Both of the samples were characterized by Differential Scaning Calorimetry (DSC), thermogravimetric analysis (TGA), UV-Visible spectrophotometry and electrochemical impedance spectroscopy (EIS). The azobenzene group that attached with –NO_2 in the polymers revealed that the homopolymer and terpolymer have light responsive properties and exhibit glass transition at considerably low temperature. Detailed conductivity showed that the ionic conductivity for both polymers is in the range of 10^{-9}-10^{-7} S.cm^{-1} and increasing with increase temperature.**

Keywords*—Liquid crystal polymers, side chain liquid crystal polymers, nitroazobenzene polymers, terpolymer.

I. INTRODUCTION

Liquid crystal polymers (LCP) are one of the unique materials that associate with liquid crystals and polymers. A side chain liquid crystal polymer consist of three structural components: a liquid crystal or mesogenic group, polymer backbone and a flexible alkyl spacers. In this research, the mesogenic group of the polymer is the azobenzene group. The azobenzene derivatives are well-known as photosensitive material for their ability to undergo photoactive movement when excited to light which leads to an anisotropy moieties[1].

The liquid crystalline materials have been greatly used in the application of fuel cell membrane. With generating the liquid crystallinity to the membrane, their morphology and diffusion properties can be externally controlled. The fuel cell membrane are now being developed and demonstrated for power conversion system and the most frequently used electrolyte membrane is the perfluorinated polymer Nafion[2]. The performance of a high quality electrolyte membrane, however, depends on the pole-dipole intermolecular interaction which grant to the stability of the mesophase thus making it difficult for the ion transport in the membrane[3]. Recently, self-assembled of sulfonated polyethylene crystallization[4], sulfonated polyaryls (sulfonated polyetherketones)[5] and polyamide based polymer with acid groups[6] have been explored to aid proton conductivity in fuel cell membrane.

Thermal enhancement of the photoinduced anisotropy that reported in liquid crystalline polymers which contain azobenzene chromophores either in homopolymer or terpolymer, providing a new way to increase and stabilize molecular orientation. It was identified that azobenzene molecule in *cis*-state has the capability to store energy and thus releasing it in the form of heat.

It has been reported that a side-chain containing azobenzene with an addition of methyl methacrylate, sulfonic acid have light responsive properties and exhibit liquid crystallinilty and possess ionic conductivity[7]. Thus in order to establish this is to study the thermal, photoresponsive and conductivity characteristic of nitroazobenzene polymer. This paper deals with photo-induced switching of ionic conductivity in a polymer with nitroazobenzene, as a third non-mesogonic component for both homopolymer and terpolymer.

II. METHODOLOGY

A. *Preparation of polymers*

The structure of homopolymer poly[6-(4-nitro-4oxyazobenzene) hexylmethacrylate] (AzoN6) and terpolymer poly[6-(4-nitro-4oxyazobenzene) hexylmethacrylate with sulfonic acid (AMPS) and methymethacrylate (MMA) are shown in Figure 1. They were synthesized by radical polymerization. The properties of polymers are summarized in Table 1.

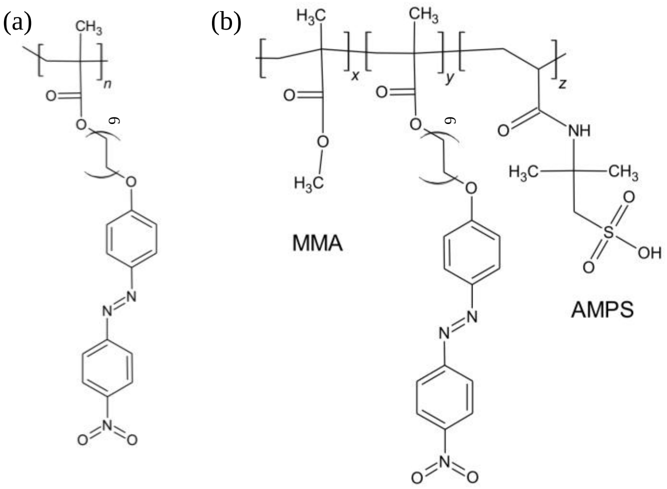


Figure 1. (a) Chemical Structure of AzoN6 homopolymer and (b) terpolymer consisting AzoN6, AMPS and MMA

Table 1. Properties of polymers

Polymers	M_n	M_w	PDI
AzoN6 homopolymer	12000	20000	1.75
AzoN6/AMPS/MMA terpolymer	1000	15000	16

B. Characterisation techniques

Differential scanning calorimetry, DSC using a Mettler Toledo DSC 1 was used to determine the thermal transition of the polymers. Samples of about 5mg were heated from 25°C to 200°C. All scans were operated at 10°C.min^{-1} under a nitrogen atmosphere and using liquid nitrogen as the coolant.

Thermogravimetric analysis, TGA thermograms were recorded on a Mettler Toledo TGA/SDTA 851 modulus under a nitrogen atmosphere. The heating rate for TGA was 10°C.min^{-1} and were heated from room temperature to 600°C to determine the stability and degradation of polymers

.The light responsive character of the AzoN6 homopolymer and polymerized AzoN6/AMPS/MMA terpolymer were assessed by UV-Vis absorption spectra at room temperature in both solution and films. Thin film of the polymers were obtained by casting solutions of the polymers in tetrahydrofuran (THF) onto quartz slides and subsequently dried.

Ionic conductivity was measured using electrochemical impedance spectroscopy (EIS) of Hioki 3532-50 LCR Hi tester in the range of frequency from 50 Hz to 5MHz, between 303 and 423 K. The samples were melted on electrode steel and were separated by a teflon ring.

III. RESULTS AND DISCUSSION

A. Light Responsive Behavior in solutions and films

The UV-Vis spectrum of AzoN6 homopolymer and terpolymer were dissolved in THF solutions and on film cast on quartz slides in Figure 3. Figure 2 shows the transformation of the *trans-cis* isomerization that occurred in the azobenzene ring. The solution for homopolymer exhibit two bands centered at around 374 nm and 470 nm. The former refer to the $\pi-\pi^*$ strong electronic transition of the *trans*-azobenzene chromophore and latter attributed to $n-\pi^*$ transition, which is weaker[8]. Upon irradiation with UV light for 10 minutes, the UV-Vis spectra displayed that the $\pi-\pi^*$ absorption band gradually decreases whereas the $n-\pi^*$ transition increases. With an interval of 30s, 1 minute, 5 minutes, 10 minutes, 2 hours and 5 hours after irradiation with UV light, the sample back relaxation was achieved by monitoring the $\pi-\pi^*$ absorbtion band which occurred as the sample were kept in the dark. The photostationary state of photoisomerization of the homopolymer was reached after 2 hours. As for the terpolymer in solution, it showed similar spectra to the homopolymer, indicating that the azobenzene moieties react correspondingly to light exposure.

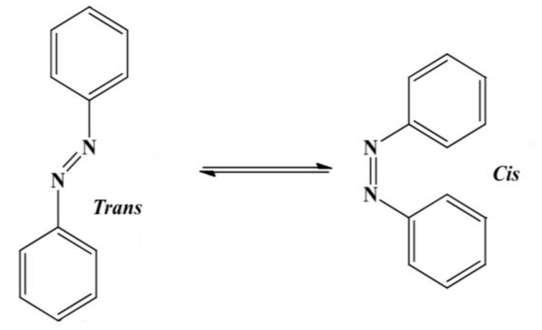


Figure 2. Rotation and inversion mechanism for the *trans-cis* isomerizations of nitro-substituted azobenzene[9]

The photoisomerization of AzoN6 homopolyer on film also display two absorption bands. As observed, when exposed to UV light, there is a decrease in $\pi-\pi^*$ band and at the same time an increase in $n-\pi^*$ band at ~361nm and ~490nm respectively. The photostationary state of the photoisomerization of AzoN6 was reached after 4 hours. This is due to the thermal relaxation of the cis-isomer[10]. Although it takes a longer time than in the solutions due to the inter- and intramolecular aggregation of the azobenzene units, this indicates that the trans-cis isomerization of the azobenzene group is also occurring in the films.

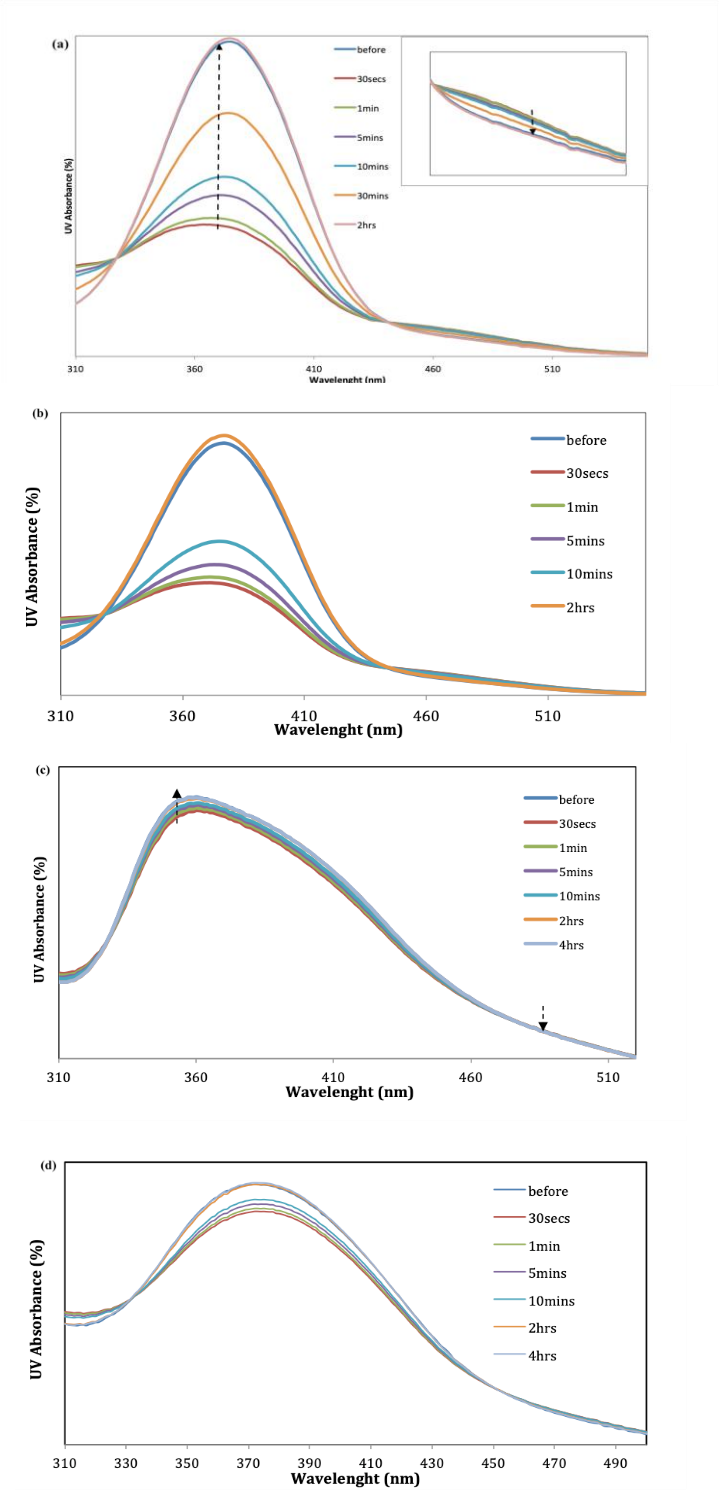


Figure 3. (a) UV-visible spectra of AzoN6 homopolymer in THF solution;(b) AzoN6/AMPS/MMA terpolymer in THF solution;(c) AzoN6 homopolymer on film;(d) AzoN6/AMPS/MMA terpolymer on film.

B. Phase behavior

The homopolymer and terpolymer were described as presenting first order transition between mesophases and the isotropic melt as well as glass transition temperature[11]. The DSC thermograms of polymers AzoN6 homopolymer and AzoN6/AMPS/MMA terpolymer during second heating scans are shown in Figure 3 and the summarized of the data is listed in Table 2. It can be observed that, both of the polymers exhibit two phase transition peaks. The first peak is the second order transition which associated with the glass transition temperature, T_g. The T_g of the polymers slightly increases with the presence of AMPS and MMA in terpolymer. The employment of the polymer with high T_g is one of the approaches to overcome the serious problem of the temporal stability of chromophore alignment at elevated temperatures[12].A relatively high T_g is useful in applications that demanded resistance at high temperatures. As for the second peak which associated with the melting temperature, T_m, it was observed that the melting of crystalline phase of the homopolymer was T_m = 162°C with enthalpy of 3.23 J/g. However, a lower energy was needed for the terpolymer to achieved its melting temperature. Similarly, the clearing point of the terpolymer also lessened due to the presence of AMPS. It is stated that the AMPS reduces a small amount of the T_{LCI} [13].

Table 2. Transition temperatures and associated enthalpy, ΔH_{LCI}

Sample	Name of Sample	T_g (°C)	T_{LCI} (°C)	ΔH_{LCI} (J.g^{-1})
1	AzoN6 homopolymer	60.1	162	3.23
2	AzoN6/AMPS/MMA terpolymer	61.2	153	2.97

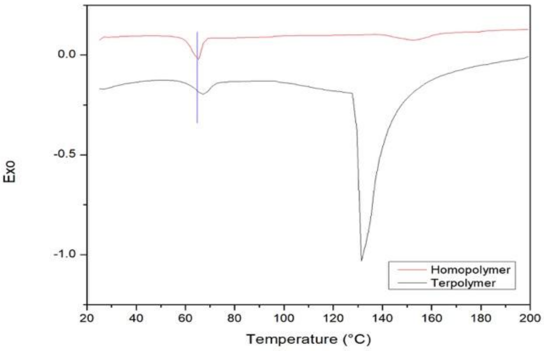


Figure 4. DSC traces corresponding to the second heating scans of the AzoN6 homopolymer and AzoN6/AMPS/MMA terpolymer

C. Thermal Stability

The thermal stability of the polymers were assessed by thermogravimetric analysis,TGA and the weight loss curves, TG and corresponding derivative curves, DTG are shown in Figures 5(a) and 5(b) respectively. The thermal decomposition of analyzed both polymers occurs in two and three stages. In figure 5(a), the curve of thermal degradation for homopolymer occurs through two main weight loss processes, which starts around 300°C to 350°C and can be attributed to the decomposition of the side chain that present in the substituted azobenzene group[14]. The second stage of the decomposition of homopolymer occurs at about temperature of 410°C-470°C which attributed to the loss of polymer backbone. However, different case for the terpolymer, at around 160°C-200°C there was about 5% weight loss which probably due to the traces of the residual solvent and absorbed water[15]. The second stage(240°C-340°C) of decomposition maybe due the bond breaking and releasing of pendant groups and the third stage (400°C-470°C) is mainly the decomposition of the MMA and the AMPS unit in the polymer chain. The residue of carbon in the homopolymer and terpolymer at 600°C are about 20% and 60% respectively. It can be conclude that, the terpolymer is thermally suitable for use as a membrane in fuel cell membrane as the polymers did not degrade all and it is very important for a electrolyte membrane to have good mechanical properties to withstand high temperatures[16].

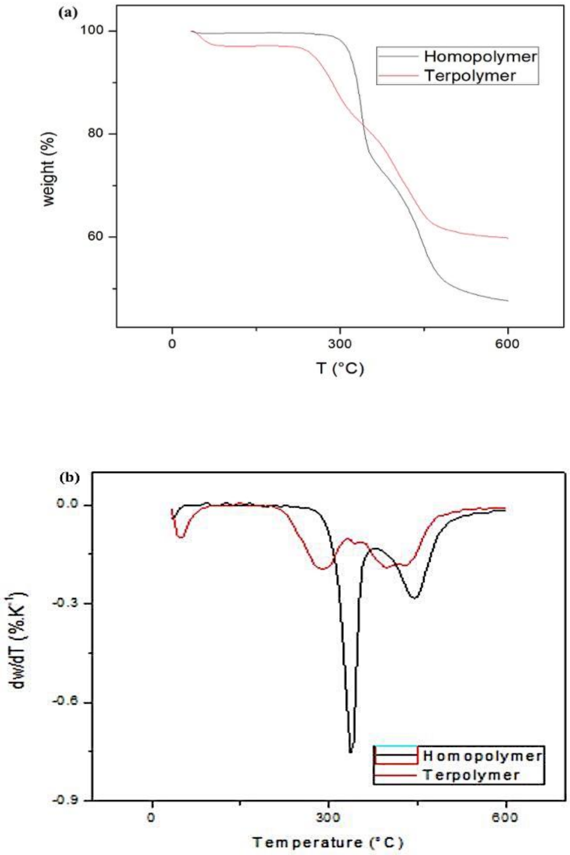


Figure 5. (a) Thermogravimetric curves, TG and (b) derivative thermogravimetric curves, DTG.

D. Temperature-dependent conductivity

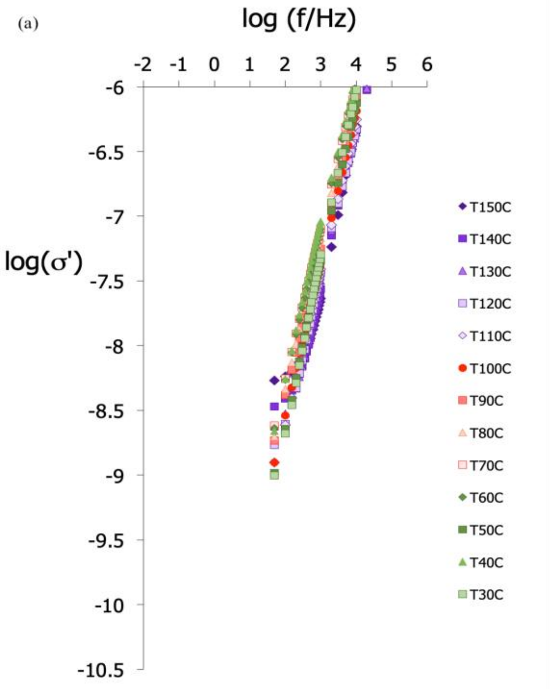
The conductivity of the polymers were investigated by using electrochemical impedance spectroscopy, EIS in the frequency range of 50 Hz to 5MHz. Figure 6 showed the temperature dependence of electrical conductivity of the polymers. The results of the conductivity for the polymers presented are only of the above glass transition. Based on the graph, there is no sign of conducting polymers in the AzoN6 homopolymer. However, the terpolymer illustrate rather high conductivity which in the range of 10^{-7} to 10^{-8} S.cm^{-1}. The existence of the AMPS in terpolymer promotes successive proton transfer through the anionic chain which contributes in major part in conductivity[17].

Figure 7 shows the Arrhenius plot for homopolymer and terpolymer. Based on the plot, the samples show linear trend as the temperature increases from 100°C to 150°C. The activation energy, E_a for ionic conductivity was calculated giving the E_a in the range of 0.006-0.05 kJ.mol^{-1}. The magnitude of activation energy depends on the number of π-electrons present in the polymers as the more number of π-bonds, the lower the magnitude of activation energy and vice versa[18].

Table 3. Conductivity values of polymers at temperature of

Sample	Conductivity (S.cm^{-1})
AzoN6 Homopolymer	$No\ conductivity$
AzoN6/AMPS/MMA Terpolymer	8.7×10^{-7}

150°C



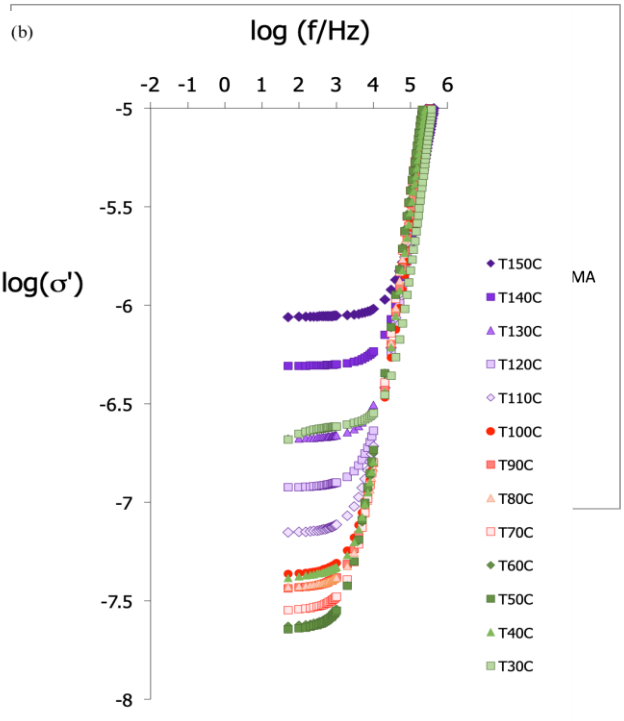
Logarithmic plots of the real component of the complex conductivity of AzoN6 homopolymer

Figure 7. Arrhenius plots of conductivity measured for AzoN6 homopolymer and AzoN6/AMPS/MMA terpolymer.

IV. CONCLUSION

In summary, upon UV radiation, photoinduced morphological changes of the nitroazobenzene were observed and both polymers have a light-switching properties. The light-induced was mainly caused by the *trans-to-cis* isomerization of the azobenzene. From experimental results, it took 2 hours for the solution to achieved its relaxation state of the photoisomerization. The thermal behavior for the homopolymer exhibit good thermal stability up until 300°C which is higher than terpolymer. The maximum proton conductivity achieved in the sample was 8.7×10^{-7}S.cm^{-1}. The design of nitroazobenzene terpolymer based on the liquid crystals has a potential to develop novel anhydrous proton conducting electrolytes for medium temperature of fuel cell

Figure 6. (a) Logarithmic plots of the real component, σ' of the complex conductivity of AzoN6 homopolymer and (b) AzoN6/AMPS/MMA terpolymer



Logarithmic plot of the real component of the complex conductivity of AzoN6/MMA/AMPS terpolymer

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