Thermal, Photoresponsive and Conducting Properties of Polyoxyazobenzene Hexylmethacrylate Homopolymers and Terpolymers.

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***Abstract*— The liquid crystal polymer in this study, Polyoxyazobenzene hexylmethacrylate homopolymers and terpolymers were characterized by using the DSC, TGA UV–visible spectrophotometry and EIS. The polymers can be used in wide range of temperature and they showed low Tg value which is under 60°C and the terpolymers is said to be in smectic phase at 148°C. Thus, polymer is said to be thermally stable. Photoresponsive properties shown clearly as both polymers performed thermal relaxation under same duration in range of 24 to 48 hours. Lastly, the terpolymers showed highest conducting properties at 110°C with dc conductivity measured, 1.69x10e-¹¹ S/cm which comparable with other studies.**

Keywords*— Side-chain, liquid crystal polymers, thermal stability, phase behavior, light responsive material, thermal conductivity.

I. INTRODUCTION

Throughout the recent years, the liquid crystalline polymers (LCPs) have gathers attention and interest in academic and industrial purpose [1]. There are two types of LCPs, main-chain and side-chain LCPs. While mesogens incorporated at the backbone of polymer in main-chain LCPs, the side-chain LCPs is where mesogens are attached to the backbone through flexible spacer [2].

The morphology of polymer does affecting the performance of the polymer itself [3][4][5]. By improving the structure of LCPs such as addition of sulfonic acids group [6] , it can give higher conductivity for polymers. This kind of research has been an interest for further study as it can provide more room for conducting properties of LCPs [7].

Other than that, various study on azobenzene containing polymers successfully shows an excellent photocontrol molecular alignment [8],[9]. One of LCP's properties is the ability to self-assemble its molecular structure. By having aromatic compound that can change due to lights exposure, the molecular alignment of LCPs can be used to give wide range on application in photonic materials. The sunlight switchable light shutter does proved that azobenzene in liquid crystal can change the molecular structure of the compound [10].

Therefore, LCPs can still be improved by addition or modification on its structure that can be used in wide range of temperature which used in various application in conducting and photonic materials. In this study, analysis on specific LCPs namely Polyoxyazobenzene hexylmethacrylate are expected to give excellent results for research purpose and further studies.

II. METHODOLOGY

A. Materials

The Polyoxyazobenzene hexylmethacrylate homopolymers and terpolymers were prepared through free radical polymerization under an inert atmosphere.

As shown in Table 1, the homopolymers consist of mesogenic side chains while the terpolymer having two additional compound, polar group for solvating ions, acrylamido-2-methyl-1-propanesulfonic acids, AMPS, and methyl(methacrylate) groups, MMA, as non-mesogenic/non-ionic structure modifying units.

Table 1: Liquid crystal polymer

Sample	Name	Compound	Polymer Structure
1	Polyoxyazobenzene hexylmethacrylate homopolymers	Mesogenic side chain.	6PHH
2	Polyoxyazobenzene hexylmethacrylate terpolymers	Mesogenic side chain, AMPS, MMA.	6PHT

B. Characterisation techniques

Thermal transitions were determined by differential scanning calorimetry, DSC, using a Mettler Toledo DSC. The samples was weighted and heated from 25 °C to 200 °C and ran in 3 cycles.. All the scans were performed at 5 °C·min^{-1} under a nitrogen atmosphere and using liquid nitrogen as the coolant. The thermal stability of the samples was assessed by thermogravimetric analysis, TGA, using a Mettler Toledo TGA. Around 5 mg of sample in an Al_2O_3 pan containing a hole for gas release were heated from room temperature to 750 °C, at 10 °C·min^{-1}, under inert argon atmosphere with a flow rate of 200 ml·min^{-1}.

The light-responsive properties of the polymers were determined using UV–visible spectrophotometry Carry 60, by measuring the UV–visible absorption spectra at room temperature in solution and films. 0.003 wt.% of the samples were diluted using THF solution in 10ml volumetric flask and 80 wt.% of each samples diluted using 20 wt.% of dichloromethane to be cast on quartz slides. Ionic conductivity was measured using the electrochemical impedance spectroscopy, EIS, Hioki 3532-50 LCR Hi. The polymers were placed between two stainless steel disc separated by a Teflon ring and melted to be attached together before cool down to room temperature. Then, samples were heated from 25°C to 150°C and proceeding to cooling and heating again at same temperature.

III. RESULTS AND DISCUSSION

A. Thermal Stability

The thermogravimetric analysis is used to assess the thermal stability polymers which provide the range temperature of the polymer can be used. By knowing the temperature of polymer start to degrade, several precaution and modification can be made on further thermal properties. Thus, the polymer degradation due to high temperature exposure can be avoided [11].

Fig. 2 shows the weight loss curves and corresponding derivative curves for this study. It can be seen from Fig 2(a) that thermal degradation of homopolymer, 6PHH, consist of two main phase. The first phase, around 270°C to 370°C occurred due to breaking of labile group in side chains. Around 400°C to 500°C the second phase of homopolymer degradation happened as the polymer backbone reduction take places [6]. Degradation of terpolymer differs from homopolymer as it consist of three phase. From Fig 2(b), around 340°C to 450°C, degradation of terpolymer, 6PHT, in which the last phase occurred due to reduction of AMPS and MMA unit in polymer chain [6].

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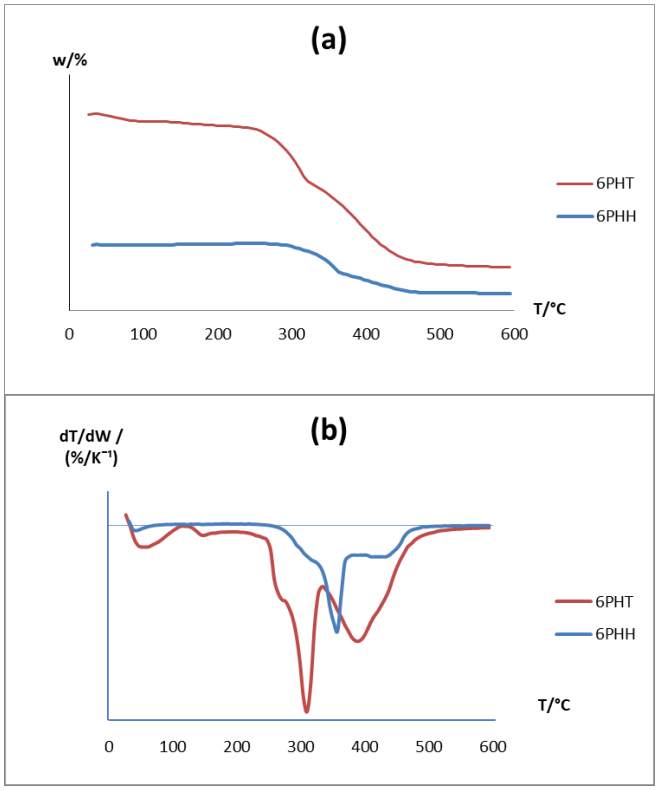

Fig. 1: (a) Thermogravimetric curves and (b) derivate thermogravimetric curves for homopolymer and terpolymer.

B. Phase Behavior

Through DSC method, the phase behavior of LCPs can be assessed. As the temperature rise, the LCPs will overcome the glass transition temperature (Tg) and the following structure will be either in smectic or nematic phase and finally the isotropic phase. The variation on LCPs structure can change glass transition temperature (Tg) [12]. Therefore, the modification of LCPs structure will be expected to give different results for phase behavior. The DSC traces obtained for the polymers at their first heating scans are shown in Fig 3. It can be seen that the terpolymer exhibit smectic phase because a peak exist at 148°C while homopolymer only shows Tg at 42°C.

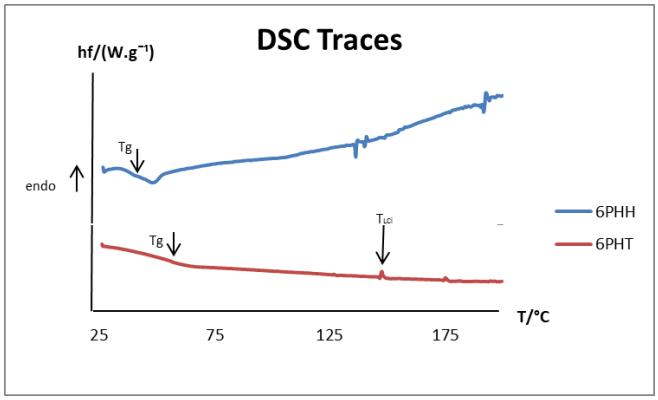

Fig. 2: DSC traces corresponding to the first heating scans of homopolymer and terpolymers.

The transition glass temperature (Tg) and a first order transition at higher temperatures, associated with the liquid crystal to isotropic transition, (T_{LCI}), can be observed and summarized in Table 2. The homopolymers only show Tg and much lower than terpolymers due to weaker structure which confirms that terpolymers more rigid than homopolymers structure where degradation at lower temperature is possible. Besides, the terpolymers reach stability in smectic phase which confirmed addition of AMPS and MMA change the behavior of liquid crystal in respect with certain range of temperature to optimize its properties in ionic conducting.

Table 2: Transition temperatures and a first order transition at higher temperatures, associated with the liquid crystal to isotropic transition, (TLCI) of homopolymers and terpolymers.

Sample	Name	Tg(°C)	T_{LCI}(°C)
1	6PHH	42	-
2	6PHT	54	148

C. Light Responsive Properties

Mesogenic side chains concentration in the polymers able to show light responsive behavior upon exposure of samples to UV lights which cause the trans to cis photoisomerization occurred [13]. Double bond in the azobenzene compound are said to be the reason of isomerization occurred. As the sample in this study consists of azobenzene compound, the sample are expected to shows photoresponsive properties [14].

From Fig. 3 (a) to (d), all samples are expected to shows trans to cis photoisomerization in range from 300 nm to 400 nm [15]. The E-Z transformation occurred as the UV lights caused the double bond changed position to make aromatic structure become less stable. This phenomenon proved that less stable structure are the significant from longer wavelengths of UV lights.

Homopolymer in solution required more time, 31 hours, compared to terpolymer, 24 hours to reach thermal cis to trans relaxation, see Fig. 3 (a) and (c), due to difference concentration of mesogenic side chains in the polymers. Difference in UV absorbance are to be expected as terpolymers have lower concentration in mesogenic side chains compared to homopolymers which make relaxation time faster [6].

Longer time required for thermal cis to trans relaxation in films occurred on same duration, 48 hours, see Fig. 3 (b) and (d) because it is more dependent on energy required for thermal relaxation in films than concentration of azobenzene compound in polymers.

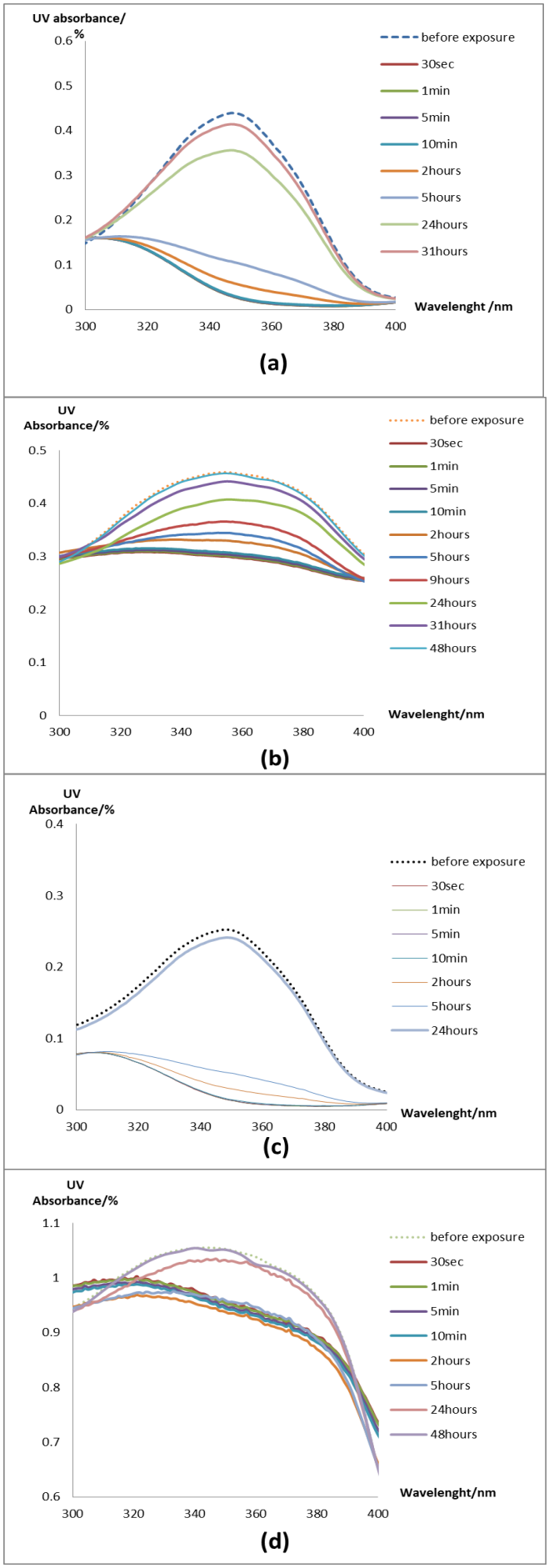

Fig. 3: UV visible spectra for; (a) homopolymer in solution, (b) homopolymer film cast on quartz slides, (c) terpolymer in solution, (d) terpolymer film cast on quartz slides.

D. Ionic conductivity

Temperature dependence of ionic conductivity for the polymers was measured using electrochemical impedance spectroscopy, EIS, and it is given by Arrhenius Equation [16];

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{k_\beta T}\right)$$

where Ea denotes the thermal activation energy of electrical conduction that depends on the nature of the conductor, σ_0 denotes the conductivity value when the reciprocal of T tends to zero and kβ is the Boltzmann constant.

Fig 4 shows the conductivity plotted against frequency for each temperature. It can be seen that the terpolymer have higher conductivity compared to homopolymer due to the addition of AMPS. The modification on terpolymer by adding AMPS allowed the proton transfer along the polymer achieved.

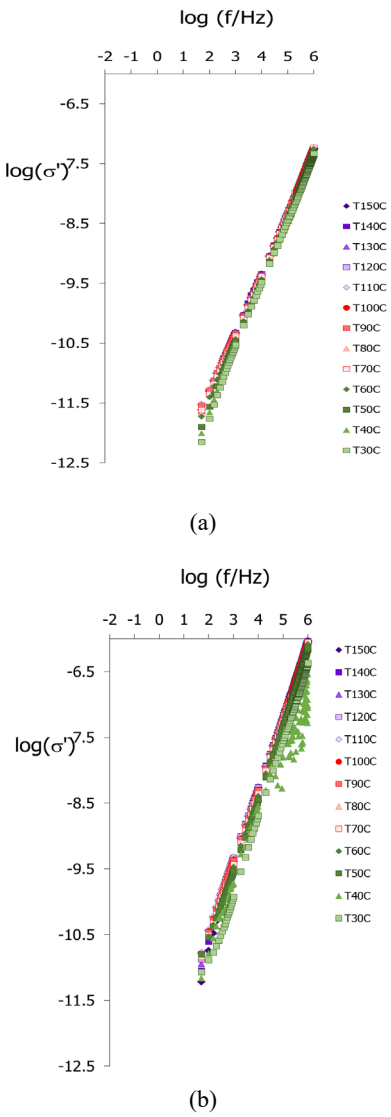

Fig. 4: Double logarithmic plots of the real component, σ′, of the complex conductivity of (a) homopolymer and (b) terpolymer as a function of the frequency.

The terpolymers show a higher conductivity at 110°C where it lies in the range of temperature of the polymers to exhibit liquid crystal properties. Fig 4 shows the Arrhenius plot for homopolymer and terpolymer, and the activation energy for the sample is summarized in Table 3. Based on results, this study proved that the terpolymer analyzed in this study is potential LCPs for conducting purpose.

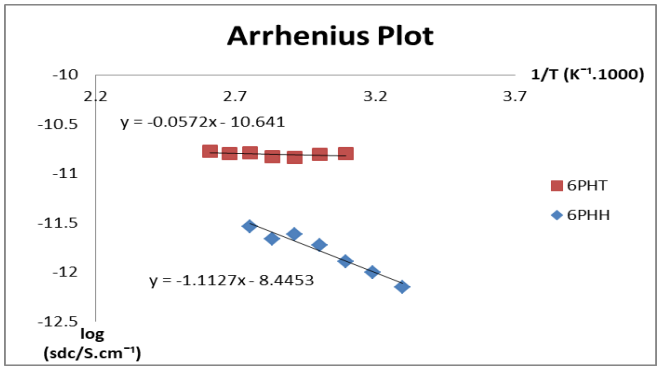

Fig. 5: Arrhenius plots for the dc conductivity measured.

Table 3: Activation energies for dc conductivity for the samples, Ea (σdc), calculated in smectic ranges.

Sample	Name	Ea energy (J/mol)
1	6PHH	0.2526
2	6PHT	2.2241

The activation energy decrease as the ionic conductivity increased [6]. This behavior is shown by the polymers as higher energy required for terpolymer to show its ionic conducting properties. Ionic conductivity measured in this study can be comparable with other previous studies, see Table 4. Different dc conductivity measured obtained proved that modification on the polymers structure does affecting the ability of polymer to exhibit conducting properties [17].

Table 4: Dc conductivity measured comparison studies.

Sample	Dc conductivity measured (S/cm)	Source
6PHT	1.69x10E-11	This Study
5% wt. ZnO in 5CB	3.98x10E-8	[16]
6OSCl	3.21x10E-9	[18]

IV. Conclusion

LCPs have become an interest in further studies due to its potential in improving the arrangement in order to improve other physical properties. This study proved that the homopolymers and terpolymers can be used in wide range temperature and both show low Tg value which is under 60°C. Besides, due to azobenzene contained in the LCPs, they showed photoresponsive properties. Lastly, the terpolymers which contained AMPS do exhibit conducting properties at 110°C with dc conductivity measured; 1.69x10e-11 S/cm. The results obtained clearly shows that the LCPs still can be improved through proper modification to exhibit ionic conducting properties.

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