Conductivity, Light Responsive and Thermal Behavior of 4-methoxy-4-oxyazobenzene Decyl Methacrylate Polymer Membrane

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Abstract—The new ionically polymers have designed containing azobenzenes, sulfonic acid groups and methyl methacrylate. The 4-methoxy-4-oxy azobenzene decyl methacrylate and 4-methoxy-4-oxy azobenzene decyl methacrylate-co-poly[2-acrylamido-2-methyl-propane sulphonic acid]-co-poly[methyl methacrylate] were characterized by DSC,TGA,EIS and UV-VIS. The polymers have light responsive properties and liquid crystalline properties when characterized. P10 exhibit conductivities in range of $10^{-6.5}$S·cm^{-1} to 10^{-7}S·cm^{-1} whereas p10h conductivities in range of $10^{-9.5}$ S·cm^{-1} to $10^{-10.5}$ S·cm^{-1}. Higher conductivities due to AMPS content hence the disappearance of the anisotropic interactions between the mesogenic units at the clearing temperature may further enhance the conductivity of the p10 by an increase in their local mobility.

***Keywords*— 4-methoxy-4oxyazobenzene, light responsive, side chain liquid crystal polymers**

INTRODUCTION

Several new liquid crystals have been designed to contain ion such as alkali and transition metals and ionogens such as sulfonic acid group to improve its properties. The mesogen is important part of a side chain polymer liquid crystal, can also incorporated directly into the chain. The basic components of LC polymers are polymer backbone, mesogenic core and the length of the flexible spacer group.[1] The decoupling (flexible) spacer concept opened the way to the whole variety of SCLCP materials with a wide range of structural design and synthetic methods, which in many cases undergo a dramatic change.[3] The attempts of synthesizing of the LC polymers with the mesogenic units in side-chain were stimulated by the fast progress of low molecular LC investigations. It seemed to be very attractive to create the polymer systems, which combine in one material the unique properties of the low molecular LC and macromolecular compounds with their ability to create films, tissues and covers.[4] The stearic hindrance provided by the sulfonic group in AMPS is expected to control potential degradation of the polymer backbone, enhance thermal stability, and improve the polymer's resistance to precipitation by limiting hydrolysis aromatic side chain in both polymers. Aromatic side chain in both polymers used to absorb UV light because it is more stable so the reaction is quicker. Here we want to compare the properties of p10 and p10h, with the presence of MMA/AMPS based on few factor which are conductivity, light responsive , thermal stability and phase behavior. Light responsive is to determine the reaction of both polymers towards light. Photo-responsive polymers undergo a change in their properties in response to a light stimulus which azobenzene in the chain polymer is responsible for this as azobenzene is photoresponsive linkers. Also,to detect phase transitions of the polymers and liquid crystal behaviours, DSC measurements were carried out systematically.[12] Thermal stability is the stability of the polymers at high temperatures. Side-chain liquid crystalline polymers have been described as presenting first-order transitions between mesophases and the isotropic melt, and also glass transitions frequently occurring in the temperature range of the mesomorphic phases. Then, glass transition temperature also will be observed to as a polymer with long chains (high molecular mass) has less free volume than one with short chains. Thus, low molecular mass gives lower values of (T_g's) and higher molecular mass.[8]

METHODOLOGY

A. Materials

Tetrahydrofuran (THF), Dichloromethane, and the sample used are 4-methoxy-4-oxy azobenzene decyl methacrylate refer as p10h whereas another sample is 4 methoxy-*4-azo*benze-co-2-poly[methyl methacrylate]-co-poly[2-arylamido-2-methyl propane sulphonic acid] which refer to as p10. The sulphonic acid in p10 is to determine the phase behavior of the polymer. 2-acrylamido-2-methylpropane sulphonic acid (AMPS) has the potential to improve main chain stability in harsh environments.

2.1 Preparation for conductivity

Conductivity was measured using a EIS in the frequency range of 50 Hz to 5 MHz, between 303 and 423 K. Each sample of the polymers were melted on a stainless steel electrode covered with another electrode, and then further cooled to room temperature. The electrodes were separated by a Teflon ring of internal diameter 12 mm.

2.2 Preparation for light responsive (UV-VIS)

Both of the polymers were tested using UV-VIS spectrometer. 2 methods were used for each sample which was film and solution method. For film method 4mg of p10 and p10h were measured. These samples will be filled by 1.0ml DCM. Then put a drop of the samples on film and let it dry in oven for 5 minutes. Using UV-VIS, the reading of the graph will be taken before shining the sample with UV light, 30 sec after shining, 1 min, 5 min, 2 hour, 24 hours and 48 hours. For solution, 0.25 mg of p10 and p10h were measured. Both will be filled by 1.0 ml of THF. Using UV-VIS, Repeat the same step like film method.

2.3 Preparation for DSC

Differential scanning calorimetry (DSC) is used to investigate the response of polymers to heating. DSC can be used to study the melting of a crystalline polymer or the glass transition. A typical heating rate used was around 5◦C/min under nitrogen gas. The samples taken are 5 mg each. The heating scan from 25◦C to 200◦C.

2.4 Preparation for TGA

Thermogravimetric Analysis (TGA) measures weight/mass change (loss or gain). It is to determine the composition and the thermal stability of the materials. The samples taken are 10 mg each, the heating scan from 25◦C to 600◦C at 10°C/min. Also under nitrogen gas. The samples taken are around 10 mg each.

II. RESULTS AND DISCUSSION

3.1 Conductivity

Electrochemical impedance spectroscopy (EIS) measurement was carried out for both of the samples at different temperatures. A close inspection of this figure shows that the real part of the conductivity of the samples were at the 150°C where the conductivity at **Figure 1** is between $10^{-6.5}$S·cm^{-1} to 10^{-7}S·cm^{-1}. The conductivity increases as temperature increases. Based from the observation, here is a decrease of the conductivity when frequency decreases. This can be explained as a Debye relaxation due to the macroscopic polarization of the charges as a consequence of the electric field applied. This relaxation is characterized by a relaxation time, which depends on the temperature, chemical structure of the samples and their thickness. This behavior may be due to the reorientation motion of dipoles and more likely to the motion of the localized charges, which dominate the dc-conductivity.[15] The presence of higher contents of AMPS groups in the side chains promotes the appearance of plateaus in the graph, indicative of long-range conductivity. AMPS itself have a good adsorption properties thus enhancing the chain's ability to move the chain. AMPS also have a good complexation. The complexation is enhanced, and the columbic effect of the sulphonate ion is also available. For p10h in **Figure 2** on the other hand, we observe that the conductivity is practically scattered around between $10^{-9.5}$ S·cm^{-1} to $10^{-10.5}$ S·cm^{-1} over the whole range of frequencies. The frequency of p10h starts at 10 ^{4} Hz compared to p10 at 10^{5} Hz for temperature 150°C. The data shows that the conductivity for p10h is lower than p10. Polymers with low AMPS contents do not exhibit appreciable *dc* conductivity and this suggests that a minimum threshold concentration of these groups is required to achieve charge transfer across these electrolytes.

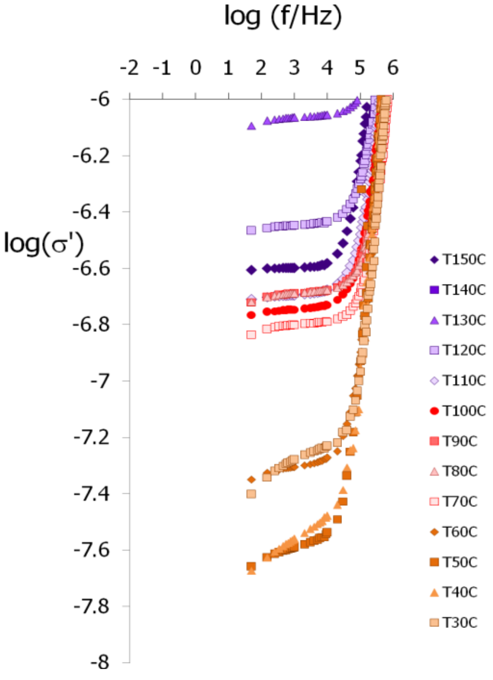

Fig. 1: The conductivity of p10

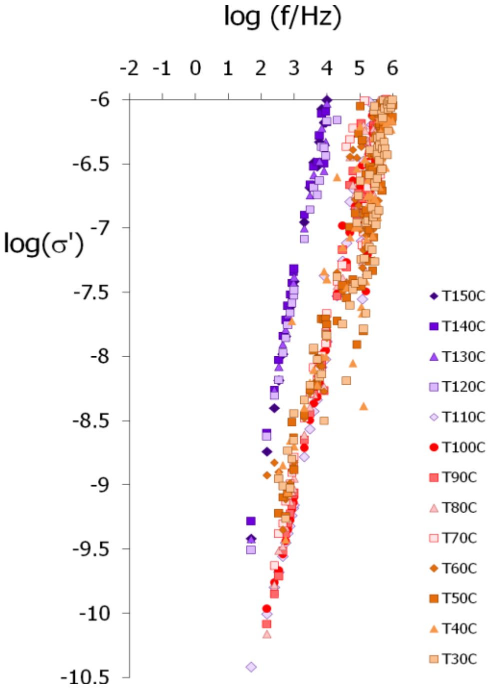

Fig. 2: The conductivity of p10h

3.2 Light Responsive

Based from **Figure 3, the** graph of p10 film display two main absorption which is increase of the π–π* band at 250 nm and increase of the *n*–π* band at 350 nm. This shows that *trans*-to-*cis* photoisomerisation of the azobenzene groups is occurring in the films. Once UV-light exposure decrease, the UV spectra recover to their original shapes. The relaxation rate of film is slower than solutions because in the solution the mobility is better thus the relaxation time can achieve faster. Azobenzene is photochemical responsive linkers that reducing it will weaken the UV signals for the polymers. Whereas in **Figure 4** shows graph of p10h film, generally, the absorption spectra show a low-intensity n–π* transition band located in the UV region and a relatively high-intensity π–π* transition band located in the visible region. Here, the position of the *n*–π* band is around 250 nm (UV region), and the π–π* band maximum absorption is near 350 nm (visible region).The relaxation occur at 24 hours. The original UV absorption spectra for all polymers are essentially recovered due to the thermally activated *cis*-to-*trans* relaxation**.** For p10 graph of solution, the exposures times to get a stationary state is faster in the solutions compared to films. In **Figure 5**, the relaxation is faster than film, thus it achieved the relaxation rate at 5 hours only. The sulphonic acid in the AMPS is the best mobility control agent thus the relaxation time is achieved faster. However, for p10h graph of solution in **Figure 6** , after 24 hours, the original UV absorption spectra for all polymers are essentially recovered due to the thermally activated *cis*-to-*trans* with increasing π–π* band.

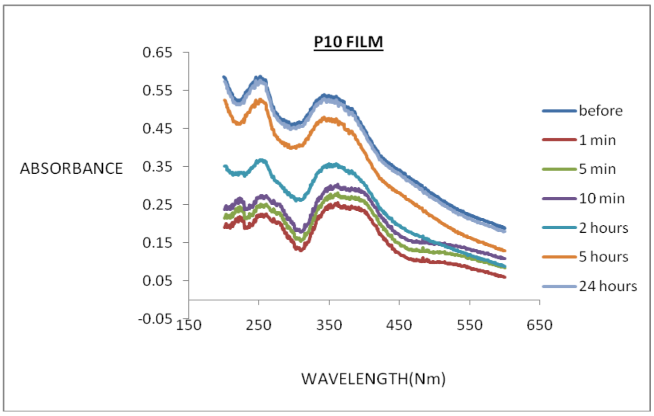

Fig. 3: UV-VIS graph for p10 film

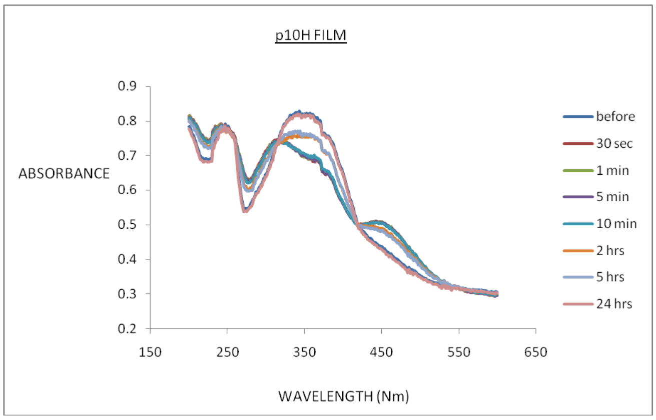

Fig. 4: UV-VIS graph for p10h film

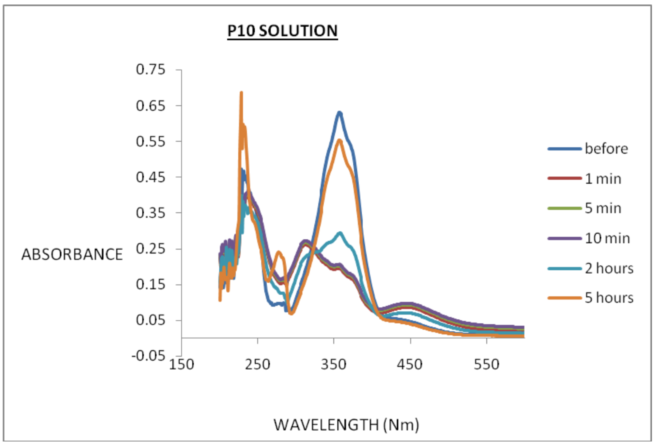

Fig. 5: UV-VIS graph for p10 solution

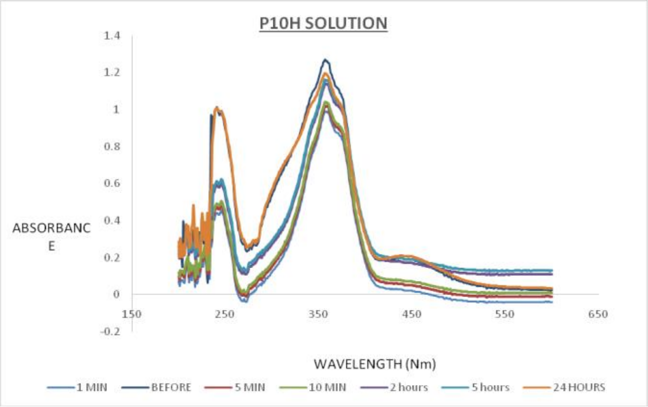

Fig. 6: UV-VIS graph for p10h solution

3.3 Phase Behavior

The DSC thermograms of p10 and p10h obtained on the second heating scan are collected in **Figure 7** . The p10 tend to show higher tg value around 50°C and the transition temperature, Tlci is between 150°C to 200°C. P10h on the other hand shows Tg value between 120°C to 150°C. The p10 tend to exhibit higher glass transitions than P10h presumably reflecting the less flexible poly(methyl methacrylate),PMMA (Tg > 100ºC) backbones. This increase is counteracted, at least to some extent, by a plasticizing effect of the flexible p10 side-chains. The lower the mesogenic unit the narrower the liquid crystal temperature ranges. Based on literature reading, The p10h and P10, exhibits enantiotropic smectic A and nematic behavior and vitrifies to form a smectic glass.[9] The nematic phase is observed over a very narrow temperature range on cooling from the isotropic melt, and prior to the formation of the smectic.[9,10]

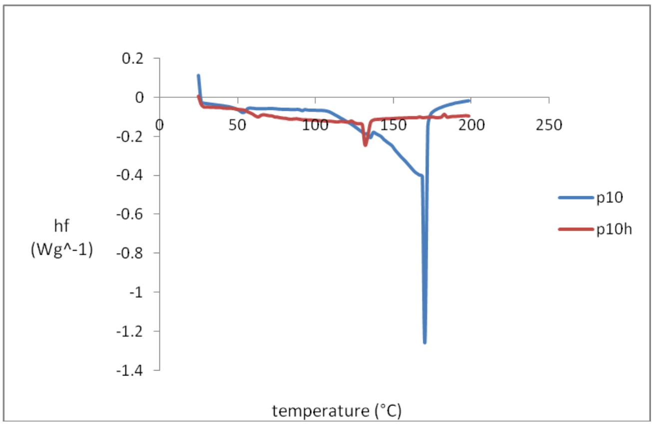

Fig. 7: DSC graph for p10 and p10h

3.4 Thermal stability

The thermal degradation behavior of p10 and p10h was investigated using TGA and the measurements were carried out under a nitrogen purge in the range of 25°C–600°C. The obtained TGA curves are shown in **Figure 8** whereas the corresponding derivative curves, DTG, are shown in **Figure 9** respectively. Thermal degradation of the P10h occurs through two main weight loss processes, between 300ºC and 400ºC while for p10 the weight loss start to occur around 400°C .The weight loss due to the production of the gaseous products like carbon monoxide, water vapor and carbon dioxide as the samples degrade. Then, followed by an additional process at about 300ºC, also the decomposition of the polymer backbone occurs between 400 ºC and 500ºC for p10h. P10 have AMPS contents which that are why it needs additional process to release the solvent in the polymer structure. The residual values after heating to 600ºC, falls within 2 mg, in weight, which higher compared to P10h, and these can be explained by the presence of the side chains.[9, 10]

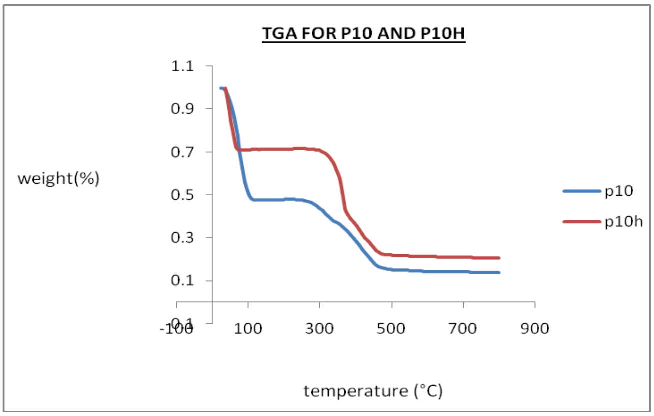

Fig. 8: TGA for p10 and p10h

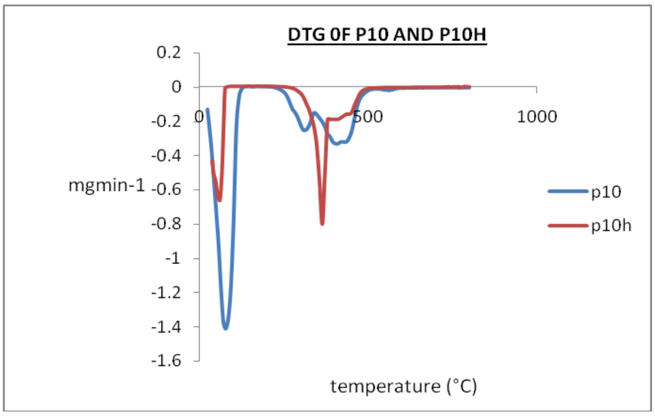

Fig. 9: DTG for p10 and p10h

III. CONCLUSION

Side chain liquid crystal polymers containing azobenzene-based mesogenic side chains and mesogenic units containing sulphonic acid groups have been characterized. Both sample prepared exhibit light responsive properties while the p10 result in conductivity, DSC and TGA is always higher than p10h result except the Tcl value. This is because the presence of AMPS and MMA reduces the liquid crystal-isotropic transition temperature and liquid crystal range by diluting the anisotropic interactions between p10 side-chains and by increasing Tg value respectively. Their presence, however, may also reduce the interactions between AMPS groups and increase free volume around the backbone thus increase the local mobility.[9, 10]

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References

1 C. T. Imrie, F. E. Karasz & G. S. Attard . (1994). The Effect of Molecular Weight on the Thermal Properties of Polystyrene-Based Sidechain Liquid-Crystalline Polymers. *Journal of Macromolecular Science, .*

2 D, J. (2005). Studies on arylidene and azobenzene Based photochromic liquid Crystalline polymers. *a reservoir of indian thesis .*

3 Ewa Wagner-WysieckaEmail authorNatalia ŁukasikJan F. BiernatElżbieta Luboch. (2018). Azo group(s) in selected macrocyclic compounds. *Journal of Inclusion Phenomena and Macrocylic Chemistry .*

4 George W. Gray, Hans W. Spiess, Volkmar Vill. (2008). *Handbook of Liquid Crystals, Volume 3: High Molecular Weight Liquid Crystals.* John Wiley & Sons.

5 GROENEWOUD, W. (2001). Characterisation of Polymers by Thermal Analysis. *sciencedirect .*

6 J. CUI and A. DEL CAMPO. (2014). Photo-responsive polymers: properties,synthesis and applications. *Institute of Polmer Research .*

7 Kai Wang,‡ Lu Yin,‡ Tengfei Miu, Meng Liu, Yin Zhao, Yang Chen, Nianchen Zhou,. (2018). Design and synthesis of a novel azobenzene containing polymer both in the main and side chain towards unique photocontrolled isomerization properties. *materials chemistry frontier .*

8 L. J. Francisca Mary P. Kannan. (2000). Studies on the odd-even effect of methylene spacers in poly(pyromellitimide-ester)s. *journal of polymer science .*

9 Laura Vanti, Sakinah Mohd Alauddin, Daniel Zaton, Nurul ipin, Marco Giacinti-Baschetti, Corrie T. Imrie, Amparo Ribes-Greus,. (2018). Ionically conducting and photoresponsive liquid crystalline terpolymers: towards multifunctional polymer electrolytes. *Europian Polymer Journal .*

10 Martinez-Felipe. (2011). Liquid crystal polymers and ionomers for membrane applications. *liquid crystals .*

11 Muhammad Tariq, Shahid Hameed,Rachel F. Magnago, Ivan H. Bechtold,Aloir A. Merlo. (2014). Side-chain liquid-crystalline polymer tetrazoles: synthesis and characterization. *journal of the brazillian chemical society .*

12 R. Duran, D. Guillon, Ph. Gramain and A. Skoulios. (1998). Thermal properties of a series of side-chain liquid crystalline poly(methacrylate). *journal de physique .*

13 Roxana M. del Castillo, Luis F. del Castillo, Alipio G. Callesa and Compan˜ Vicente. (2018). Experimental and computational conductivity study of multilayer graphene in polypropylene. *Journal of Materials Chemistry .*

14 Shibaev, V. P. (2017). Liquid Crystal Polymers. *Reference Module in Materials Science and Materials Engineering .*

15 Terekhov, M. (2003). Orientation, structure and dynamics of main chain in liquid cristalline side-chain polysiloxanes studied by 29Si NMR.

16 Tomasz Ganicz and Włodzimierz Stańczyk . (2009). Side-chain Liquid Crystal Polymers (SCLCP): Methods and overview. *Centre of Molecular and Macromolecular Studies .*

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