Study on the Photo-alignment Performance of Liquid Crystalline Polymers with Photosensitive Groups

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Abstract

The liquid crystalline polymers with photosensitive groups can self-assemble like the low-molar-mass liquid crystals. Also when the polymer film is exposed to linearly polarized (LP) light, it can react a polarization-axis selective photoreaction. Upon irradiating, a small negative optical anisotropy results from an axis-selective photoreaction of the photosensitive groups, while annealing in the LC temperature range leads a large positive optical anisotropic change of the polymer film. Photo-alignment in polymeric film is a promising technique applicable to the photo-alignment layer of liquid crystal displays, birefringent optical devices, information records and holographic data storage devices.

In this paper, a series of liquid crystalline polymers with photosensitive group were synthesized and photo-alignment performance was systematically investigated. The results showed that the photo-induced optical anisotropy ΔA increase with the exposure dose increase, and then became stable quickly, though $A_{/\!/}$ and $A_{\perp}$ continued increasing. What's more, the photo-induced optical anisotropy ΔA was thermally enhanced after annealing. The stability of coumain-containing polymers was better than cinnamate-containing polymers, because the former polymer materials only undergo an [2+2] photo-cross-linking reaction.

Key words: liquid crystal polymer; photosensitive groups; photo-alignment

Introduction

Liquid crystal is a transition state between solid and liquid. At the same time, it has the property of phase-ordering like amorphous material, as well as fluidity like liquid material. It renders optical anisotropic in physics [1]. Based on the found of the photoelectric effect of liquid crystal materials, liquid crystal materials obtain the rapid development in near 20 years. So it has become a hot area of scientific research and widely used in physics, materials science and life sciences [2]. Besides, because of the unique property of optical chemistry, optical physics and second order nonlinear, Coumarone and its derivatives get great attention from researchers. The orientation of liquid crystal is the key technology of manufacturing LCD devices. The traditional friction orientation technology has been widely used. Optical orientation technology is earliest brought forward by Gibbons in 1991 in Nature as a different method of non-contact orientation compared with friction method [3]. It overcomes electrostatic, friction dust, narrow Angle in the traditional orientation method and has low cost compared with tilt over steaming method. Although this method has lack of molecular orientation and its stability, but in fact, the development of optical orientation and related materials of physical and chemical has just started. But the work is viewed as "the highest research value and application prospects of the development of LCD technology ". Therefore, it has an application prospect in optical records, record information, electric orientation and so on [4].

Based on the structure of the side chain polymer, functional side chain polymer has functional groups of photosensitive units. So far, there are many photosensitive groups like the material of photo-isomerization (azo), photo-crosslink (cinnamic acid), photo-degradation (PI). However, among them, the material of photo-cross-linked is widely used [5]. On the irradiation of linear polarized UV light, the polymer containing photosensitive group will occur optical reaction along the direction of vibration of linear polarized UV light and produce anchoring force, which has a single orientation direction. When the liquid crystal molecules is in the self-assembly conditions, that is heated to liquid crystal temperature, liquid crystal molecules will orient in accordance with the direction of anchoring force. However, in the non-exposure areas, liquid crystal molecules did not have photochemical reactions and no anchoring forced, it still keeps the arrangement of the disorder. Therefore it produces the different orientation in exposure and non-exposure areas and forms the visual difference. It can be used in information recording.

The research is to design and synthesis liquid crystal polymer containing photosensitive group, which has relatively independent mesogenic unit and photosensitive group. So we can use it into optical orientation. At the same time, we preliminary study the optical orientation performance of these polymers. This containing photosensitive polymer can be homo-polymer as well as copolymer. Side chain polymer is made up of main chain, mesogenic unit, terminal group and flexible chain between main chain and mesogenic unit. According to this, we design the polymer, whose main chain is acrylic ester and flexible chain is six methylene groups, respectively containing chalcone, coumarin and cinnamic acid groups.

Experimental

Reagents and Methods

Acryloyl chloride, 7-Hydroxycoumarin and 6-Bromo-1-hexanol were purchased from Beijing Ouhe technology Co., LTDN. N'-Dicyclohexylcarbodiimide(DCC) and N, N'-Dimethylaminopyridine (DMAP) were supplied by Beijing Ann Ricky chemical technology Co., LTD. AIBN . Methyl p-hydroxycinnamate, and p-Hydroxybenzoic acid were purchased from Aladdin Reagent Database Inc. All other solvents and reagents were analytical-grade and were made in China. Most reagents were purified and dehydrated before used.

IR spectra were measured with SHIMADZU FTIR-8400 spectrophotometer, DSC spectra were recorded with NETZSCH DSC 200PC, TG spectra were recorded with NETZSCH TG209, 1H NMR spectra were recorded with A NMR-ARX400 spectrometer, POM photograph were recorded with POM- LEICA DM4500P.

Preparation of liquid crystal monomer

According to the literatures, the monomers containing the photosensitive groups of chalcone, coumarin and cinnamic acid were synthesized. Optimize the synthetic route, through the UV-vis spectra, IR, NMR we confirm the structure of monomer, and through the thermal analysis, polarizing microscope, we study the performance. Figure 1 is the structure of liquid crystal monomer containing photosensitive groups.

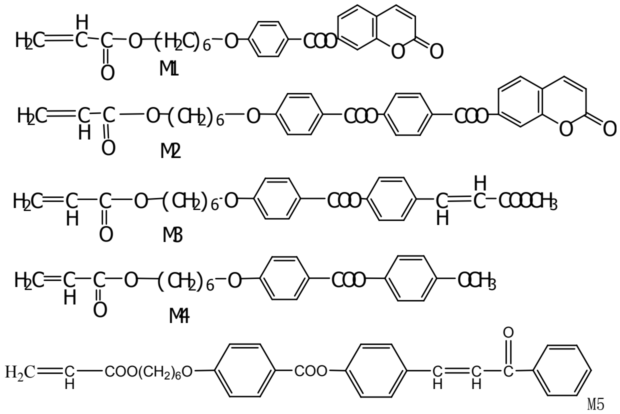

***Figure 1**: Structure of liquid crystal monomer*

Table1 is the property of liquid crystal monomer. From the table, we can see that there are 4 kinds of liquid crystal rendering liquid crystal property.

Table1: property of liquid crystal monomer

Name	Thermodynamic performance	liquid crystal properties
M1	Cr100.9°C	NO
M2	Cr140.7oCN164.2°C	YES
M3	Cr83.6oCS105.9oCN115.3°C	YES
M4	Cr47.75oCN61.5°C	YES
M5	Cr25oCS61.5°C	YES

Cr•Crystal• S•Smetic•N•Nematic

Preparation of liquid crystal polymer

According to the literature, The synthetic monomers were used to synthesis into polymers and copolymers. Through the UV-vis spectra, IR, NMR, we confirm the structure of monomer, and through the thermal analysis, polarizing microscope, we study the performance.

As showed in table 2, among the liquid crystal polymer, only polymer P4 has the liquid crystal properties and the others have no liquid crystal properties. But the copolymers had liquid crystal properties.

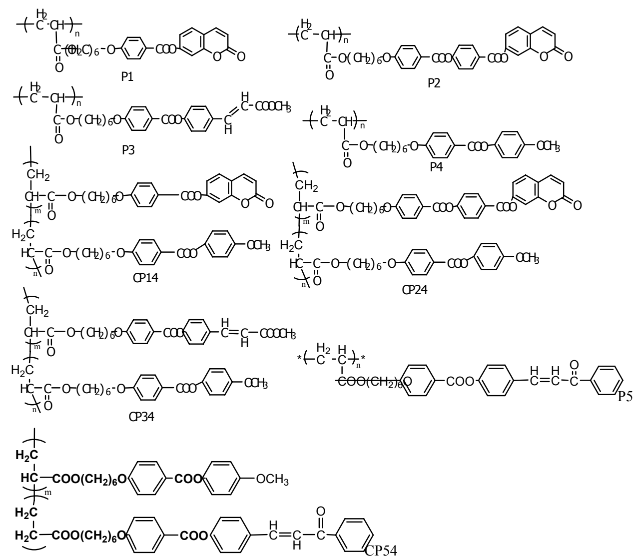

***Figure 2**: Structure of liquid crystal polymer*

Table2: the properties of homopolymer

Name	Mw*10^4	Mn/Mw	Temperature of mesogenic phase
CP14	3.13	1.98	90.5oC --105.3°C
CP24	1.52	1.71	135.7oC--154.1°C
CP34	3.54	2.70	50.8--59.6 °C
CP54	1.90	1.20	40--102 °C

The preparation of polymer film of liquid crystal

Under continuous agitation, the liquid crystal polymers were completely dissolved in purified solvent, giving a transparent solution. The coating solution was applied to an quartz substrate by using a modified spin-coater. The sample was dried in an open-air oven at 100 °C for 10min.

Photochemical orientation test

The samples were exposed by the UV exposure system. In the optical path, we added an optical filter, whose center wavelength is 320 nm and half-wave width is 15nm. Besides, a polarizer for 240-320nm was also added and obtained Ultraviolet polarized light. The light intensity is measured by DR21600 digital light intensity instrument made by Gamma Scientific Company. The performance of photochemical orientation is measured by USB4000 miniature fiber spectrometer produced by Ocean optics.

The principle of Photochemical orientation test

The degree of photoreaction is calculated by the decreasing of UV absorbance directed with the vector direction of linear polarized light at 320nm. The equation is:

$$DP = (A0 - At) / (A0 - Ac)$$

In which: A_0 is the absorbance before exposure, A_t is the absorbance of after some exposure time. A_c is the absorbance that is not changing with the exposure energy. Figure 3 is schematic diagram.

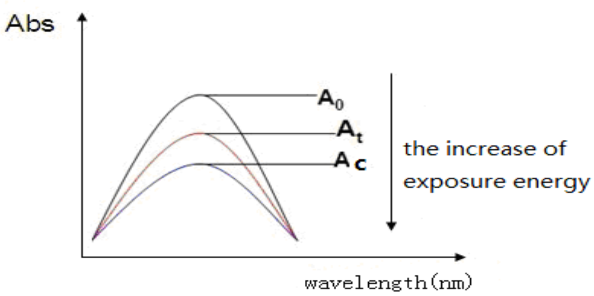

***Figure 3.** The relationship between the Abs and the exposure energy*

Liquid crystal is orderly. There are many methods to characterize the degree of liquid crystal orientation. In this article, the effect of orientation is measured by ΔA, which reflects the degree of molecule orientation.

$$\Delta A = A_{\perp} - A_{/\!/}$$

In which: $A_{\perp}$ is the absorbance of perpendicular to the vector of linear polarization. $A_{/\!/}$ is the absorbance of parallel to the vector of linear polarization. $\Delta A>0$ represent the orientation is perpendicular to the vector of linear polarization. $\Delta A<0$ represent the orientation is parallel to the vector of linear polarization. The large value indicates the more orderly molecular arrangement.

Results and discussion

Photochemical Reaction of Copolymer

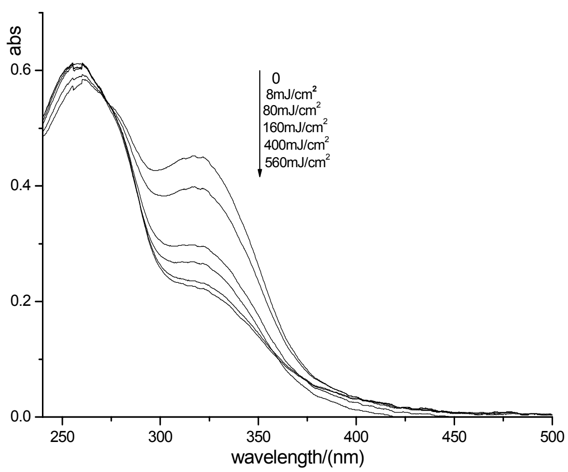

***Figure 4**: UV absorption spectra of copolymer P54 in different exposure energy*

Figure 4 is the UV absorbance spectrum of copolymer film P54 in different exposure energy. In this figure we can see that we can see that with the increase exposure energy, the rate of photoreaction gradually slow down in 320nm. When the exposure energy is up to 560 mJ/cm^2, the absorbance of P54 gets to minimum. After then, with the increasing of exposure energy, the Abs is constant, which indicate the photochemical reaction is finished. At the same time, we can see that there is isoabsorptive point in 265nm, which means under the irradiation of liner polarizer ultraviolet light in 320nm, the copolymer undergo [2+2] cycloaddition and no isomerization reaction.

Fig5 is the curve of photo-crosslink degree. From the figure, we can see that with the increase exposure energy, the rate of photoreaction is increasing. When increasing some extent, the rate of photoreaction is gradually slow down. When the exposure energy is low than 48 mJ/cm^2, the photoreaction speed is very fast because there are have many non-reaction molecule of polymer and the arrangement of molecule is very closely. When large exposure energy is given, the speed is slow down compared with 48mJ/cm^2 because the amount of orientate molecules is so many. When the exposure energy is high than 560 mJ/cm^2, the photochemical reaction is finished.

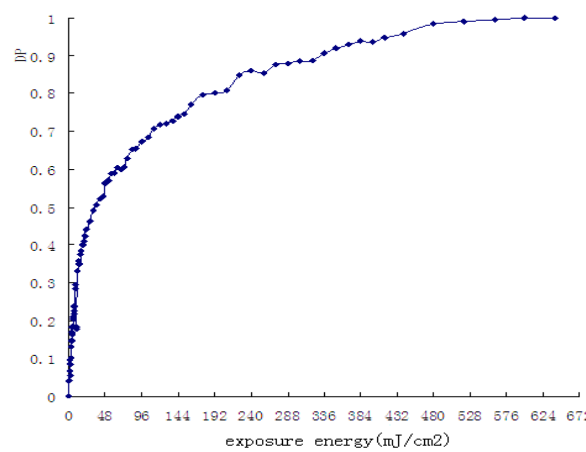

***Figure 5**. The curve of photo-crosslink degree of P54*

Photochemical orientation of Copolymer

Figure 6 is the relation curve between the exposure energy and degree of orientation of the liquid crystal polymer containing chalcone photosensitive groups. From the figure we can see that in room temperature, with the increase of exposure energy, the value of ΔA first increases to a certain value and then reduced and remain unchanged. When the exposure energy is 48 mJ/ cm^2, ΔA is up to 0.012. If increasing the exposure energy, the ΔA will decrease. When the exposure energy is 128 mJ/ cm^2, ΔA is decreasing to 0.009. If we continue increase the exposure energy, ΔA is constant. The effect of annealing has great relationship with exposure energy. When the exposure energy is 8 mJ/ cm^2, the degree of cross-linked is 12% that is the ΔA is 0.004 after exposure. However, after annealing, ΔA is 0.053, which indicates liquid crystal molecules arrange most orderly along the vertical direction of linear polarized UV light. It also means there are anchoring force in the photo-crosslink polymer and induce the orientation direction along the direction before annealing. When continue increasing the exposure energy to 32 mJ/ cm^2. △A will decrease. When the exposure energy is more than 32mJ/ cm^2 that is the degree of cross-linked is more than 21%. The value is changing from positive to negative, which means that there is a reversal after annealing and the direction of liquid crystal is changing from perpendicular to the vector of linear polarization to parallel to the vector of linear polarization. It illustrates that the photo-crosslink polymer act as impurities, which block the liquid crystal orientation along the direction before annealing. When the exposure energy is up to 80 mJ/ cm^2 and degree of photo-crosslink is 26%. △A gets to the minimum of -0.056, which indicates that liquid crystal arrange most orderly along the parallel to the vector of linear polarization. After that, if continue increase exposure energy, the value of △A will increase to a constant and the degree of ordering will decrease.

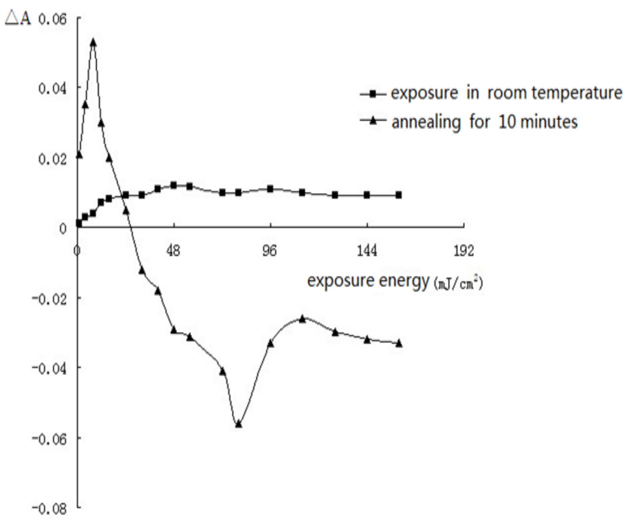

***Figure 6**: The relationship of orientation degree and exposure*

Conclusions

The copolymer p54 containing chalcone group was exposed with the liner polarize UV light and the photochemical reaction and orientation was investigated. Result showed that the P54 had photoreaction along the direction of parallel to the vector of linear polarization. Through the UV-visual spectrum, it was found that there was cross-linking reaction and no isomerization reaction. The degree of orientation had some relationship with exposure energy, which is the degree of photo-crosslink. If the degree of photo-crosslink is small, the annealing will promote the results and the arrangement will be reversal if degree of photo-crosslink is very large.

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Weimin Zhang, male, professor, graduated in East China University of Science & Technology in 1986. He is working in Lab.Printing & Packaging Material and Technology (Beijing area major laboratory), in Beijing Institute of Graphic Communication. His work is focused on organic information recording materials, especially organic photoreceptor, functional materials.

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