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A new kind of azo polymeric LB film for reversible optical storage

Hongbin Li[1], Li Zhang[1], Xi Zhang[1,*], Jiacong Shen[1], Yanqiang Yang[2], Haosheng Fei[2]

[1] Key Laboratory of Supramolecular Structure and Spectroscopy, Department of Chemistry,
Jilin University, Changchun 130023, P. R. China
[2] Department of Physics, Jilin University, Changchun 130023, P. R. China

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Summary

A Reversed Duckweed polymeric LB film was fabricated by a new kind of amphiphilic polymer which was composed of hexanediamine- epichlorohydrin hydrophilic network and hydrophobic chains containing p-nitroazobenzene groups. Reversible optical birefringence and dichroism have been demonstrated in this polymeric LB film, and this reversible birefringence and dichroism can be cycled many times without appearance of any fatigue and show very good stability.

Introduction

Azo polymers are receiving increasing attention as materials for nonlinear and photoelectronic applications, especially in optical information storage. This could be used in erasable optical memory disks and tapes, erasable holographic information storage and optical sensors and so on (1). It has been demonstrated that stable optically induced dichroism and birefringence can be produced and used to record images. Since Wendorff reported reversible optical storage properties on some liquid crystalline azo polymers films in 1987, up to now, the optical induced dichroism and birefringence have been demonstrated on liquid crystalline homopolymers, liquid crystalline copolymers, amorphous high Tg polyacrylate derivatives (2-3).

Different from the method of optical storage based on photo-induced trans-cis isomerization(4), the origin of this photoinduced dichroism is attributed to trans-cis photoisomerization of the azo group followed by a cis-trans thermal or photoisomerization. When azo groups are excited by linearly polarized light of wavelength close to the azo's absorbance, the trans isomers will isomerize to cis states. The cis isomers can undergo some reorientation and then rapidly isomerized to trans isomers either by the thermal or photo isomerization process. The trans-cis-trans process for orientation of molecules will continue until the molecule's dipole moments lies in the direction which is perpendicular to the polarized direction of the writing beam. In this way, a net macroscopic optical anisotropy can be induced in the film. Because we need not to find any way to stabilize the cis-isomer of azo compound, the optical storage based on photo-induced dichroism and birefringence is less complicated, and the stability of this storage is obviously better than that of the method based on the photo-induced trans-cis isomerization of the azo groups.

Induced optical birefringence has been also demonstrated on LB films of small azo dyes (5). However, there are some drawbacks in this system. In order to ensure that the azo compounds have enough free volume for isomerization, the film was often transferred at very low surface pressure, hence, the density of azo groups is very low and the stability of induced birefringence is poor due to the film relaxation. Furthermore, these LB films are often subject to optical inhomogeneous due to the dye's aggregation.

In our previous work, we developed a new kind of polymeric LB film: namely "Duckweed" and "Reversed Duckweed" polymeric LB films (6). These polymeric LB film are fabricated by using

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* Corresponding author

a new kind of amphiphilic polymer which was composed of hydrophobic microgel cores and hydrophilic chains, or vice versa. This kind of amphiphilic polymer can self-rearrange at the air/water interface and are readily transferable as so-called “Duckweed “ or “Reversed Duckweed” polymeric Langmuir-Blodgett films to solid substrates. The so called “Duckweed” term means that the hydrohobic microgels are floating onto the surface of the water, and the hydrophilic grafting chains are projected into the water; “Reversed Duckweed” means that the hydrophilic networks extended downward into water and the hydrophobic grafting chains are upward packing away from the surface of water. Their film forming process is a process of assembling. Their unique feature is the combination of order and stability.In our recent work, functional groups – azo group was incorporated into this kind polymer. Here, we’ll report this new kind of azo polymeric LB film for reversible optical storage. This amphiphilic polymer is composed of a hexanediamine-epichlorohydrin hydrophilic network and grafting hydrophobic chains containing azo groups. This LB film combine the order and mobility, which has a well-established layer structure and azo-chromphore are in an isotropic state in each layer. Optical birefringence and dichroism can be laser ‘induced and erased, and the reversible birefringence and dichroism can be cycled many times without appearance of any fatigue and show very good stability.

Experimental

IR spectra were recorded on a ISF-66V spectrometer as thin films on KBr plates.^{1}H NMR were recorded with CDCL$_3$ solutions on a UNITY400 spectrometer using TMS proton signal as an internal standard. The GPC were abtained on WATERS GPC instrument (DMF as eluent). Element analysis was carried on 240C type element auto analyser (PE company ,American).

Synthesis

The synthesis of grafting chain containing azo group:

1) N-methyl-N-6-hydroxyhexyl aniline (**I**)(8)

27.9g 6-bromide-hexanol (0. 154mol) and 16.2ml (0.15mol) freshly distilled N-methylaniline dissolved in 80ml n-butanol, 20.73g potassium carbonate was added into the solution then refluxed with stirring for 48hr. After cooling to room temperature, the white precipitate was filtered, then distilled under vacuum to give a colorless oil. Yield: 14.7g (71%). b. p. 168-171°C (5-6mmHg)

2) 4-nitro-4’-(N-methyl-N-hydroxyhexyl)azobenzene (**II**)

0.9g p-Nitroaniline was diazotized, then 1.5ml (**I**) in 5ml (1:1 CH_3OH/H_2O was carefully added with stirring at temperature below 5°C. The dark-red precipitate was collected with a Bunchner funnel and washed with water, recrystallization from CH_3OH/H_2O (1:1) yield a dark-red powder. Yield: 1.8g(78%). ^{1}H NMR($CDCl_3$): δ=1.415 (m, 8H), 3.097 (s, 3H), 3.405 (t, 2H), 3.662(t, 2H), 6.745 (d, 2H), 7.905 (d, 2H), 8.310-8.333 (AB, 4H); IR: 3411.4 cm^{-1}; 3100.6 cm^{-1}; 2929.4 cm^{-1}; 2855.4 cm^{-1}1601.7 cm^{-1}; 1587.2 cm^{-1}; 1512.4 cm^{-1}; 1446.0 cm^{-1}; 1421.4 cm^{-1}; 1335.7 cm^{-1}; 1257. 7 cm^{-1}; 861.9 cm^{-1}; 822.6 cm^{-1}; 756.0 cm^{-1}; $C_{19}H_{24}N_4O_3$: Cal C:64.03 H:6.79 N:15.72; Found C:61.59 H:6.13 N:14.96

3)4-nitro-4’-N-(6-(2-hydroxy-3-chloride-propoxy)hexane)-N’-methyl-azobenzene (**III**)

0.23g (0.01mol) sodium was added to 60ml refined dioxane, when the sodium had melted into small balls, 1.79g (**II**) was added and refluxed for 5hr, after cooling to room temperature, the unreacted sodium was carefully removed. Then 1.2ml (0.015mol) epichlorohydrin was added then refluxed again for 2hr, precipitate was collected with a Bunchner funnel and washed with water, dried under vacuum. Yield: 1.4 (62%). IR: 3378.4 cm^{-1}; 2926.4 cm^{-1}; 2778.3 cm^{-1}; 1597.7 cm^{-1}; 1514.4 cm^{-1} 1445.5 cm^{-1}; 1369.1 cm^{-1}; 1354.1 cm^{-1}; 1249.7 cm^{-1}; 1133.2 cm^{-1}; 879.7 cm^{-1}; 832.6 cm^{-1}; 765.9 cm^{-1} $C_{22}H_{29}N_4O_4Cl$: Cal. C: 58.86 H: 6.51 N: 12.48; Found C: 58.70 H: 7.09 N: 12.00

4) synthesis of amphiphilic polymer

The approach for synthesizing the amphiphilic polymer PazoNE and the schematic structure of PazoNE were shown is Fig. 1.

0.83g (2mmol) (**III**) and 0.464g (4mmol) hexanediamine dissolved in 4mL refined N,N-dimethylformamide (DMF), then 0.3ml (4mmol) epichlorohydrin was added, the polymerization reaction was carried out at 150°C for 2 hours with vigorous stirring. After cooling to room temperature, the polymer was precipitated in methanol and washed with water and THF, dried in vacuum at room temperature. Yield: 0.85g (65%). The GPC indicated an equivalent molecular weight of 18700 (relative to polystyrene, DMF as eluent). Assuming the molar absorbance index of azobeneze chromophore in the polymer equal to that in the monomer, we determined the grafting degree of polymer was 10.6 using UV-Vis spectra. IR: 3340.1 cm^{-1}; 2926.4 cm^{-1}; 2855.3 cm^{-1}; 1596.1 cm^{-1}; 1513.2 cm^{-1}; 1451.3 cm^{-1}; 1377.5 cm^{-1}; 1339.2 cm^{-1}; 1249.8 cm^{-1}; 1130.4 cm^{-1}; 821.5 cm^{-1}; 776.2 cm^{-1}

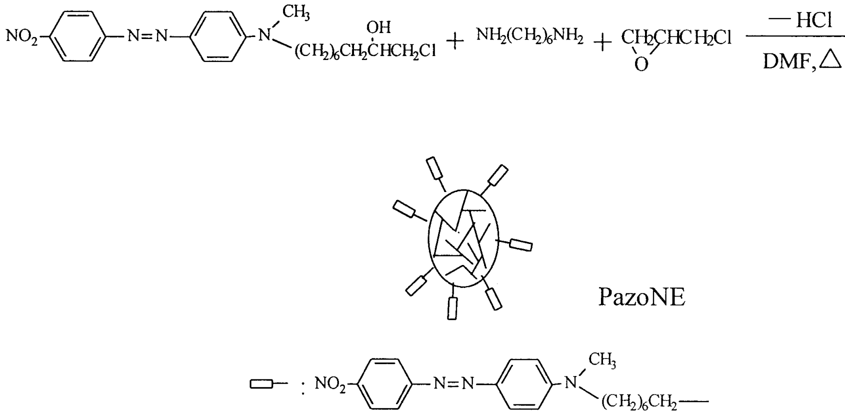

Fig. 1 Approach for synthesizing of the amphiphilic polymer (PazoNE) and the schematic structure of PazoNE

Spreading experiments, LB films transfer and characterization

The monolayer experiment was performed on a computer-controlled KSV-5000 instrument with a Whilhelmy plate system. The film was spread from DMF/CHCl$_3$ (2:8, volume ratio) mixed solution in the concentration of 0.75mg/ml on pure Mill-Q water (15MΩ). Compression rate was 20mm/min.

Z-type LB films were deposited on a thoroughly cleaned quartz plate for photo-induced dichroism and birefringence experiment. The deposition pressure is maintained at 20 mN/m.

Optical storage

The photo-induced dichroism and birefringence were induced with a linearly polarized continuous argon laser beam at 514.5 nm. The dichroism was measured on a Shimadazu UV-3100 spectrometer. The birefringence was measured by placing the sample between two crossed linear polaroids. A low-power He-Ne laser at 632.8 nm was used to measure the power which was transmitted through this optical setup. The transmission was measured using a fast photomultiplier and was recorded by computer and the transmission signal will be transferred as birefringence signal. The photo induced birefringence was erased by circularity polarized Argon laser beam at 514.5nm. All measurements were performed at room temperature.

Results and Discussion

Fig. 2 is the π-A isotherm of amphiphilic polymer PazoNE, from which we can see that PazoNE can form stable liquid-condensed monolayer. The average molecular area is about 500Å^2. Considering the average grafting degree is about 10.6, the average area occupied by every azo group is about 47Å^2. Compared with the cross section area 30 Å^2 of an azo moiety, we can see that azo groups of PazoNE pack loosely in the monolayer and there are much free volume in the vicinity of azo groups. It is generally recognized that the trans-cis isomerization requires a minimum, critical size of local free volume (about 0.12nm^3) in the vicinity of the azo chromphore(7) , otherwise, the trans-cis isomerization may be hindered. Hence, the azo groups' loose packing in the monolayer of PazoNE provide enough space of azo groups to undergo trans-cis isomerization.

This monolayer can be readily transferred as Z-type LB multilayer with transfer ratio close to unity. Compared to the film formed by small azo dyes, this multilayer film shows very good optical homogeneous. Polarized UV-Vis spectra shows that the 5 layer LB films of PazoNE don't show any anisotropy, and indicates that the azo groups dispersed isotropically in the monolayer. Hence, inherent dichroism and birefringence of LB films are avoid, this fact will benefit to increase the noise-signal ratio of the optical storage.

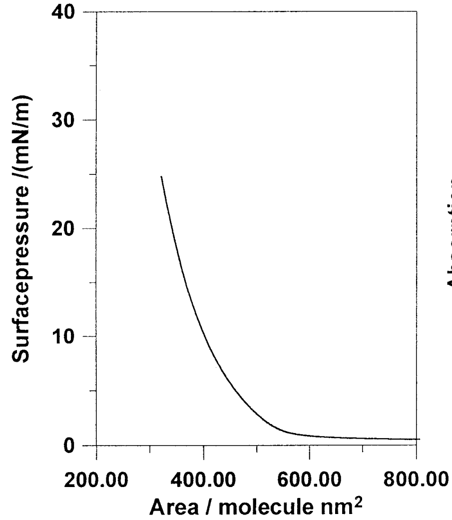

Fig. 2 π-A isotherm of amphiphilic polymer PazoNE

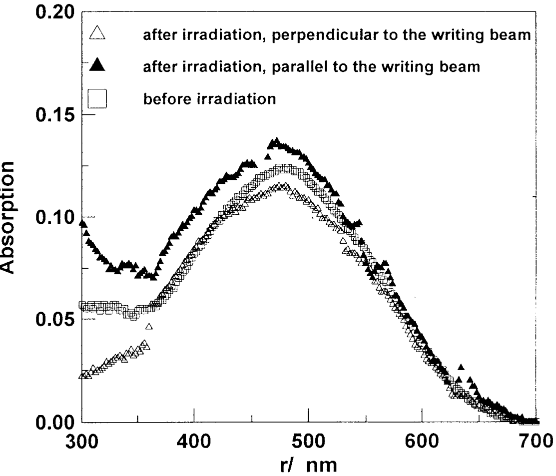

Fig. 3 Polarized UV-Vis spectra of 5 layers LB film of PazoNE *(when the polarized direction of writing beam is parallel to the film dipping direction, it is termed as 0°)

Optical dichroism and birefringence are induced by irradiation with a linearly polarized argon laser beam at 514.5 nm. The polarized direction of the laser beam is parallel to the film dipping direction. From the polarized UV-Vis spectra of 5 layer PazoNE LB film (shown in Fig. 3) we can see that after irradiation of the laser beam, the absorbance of the film is higher for light polarized in the direction perpendicular to the writing beam, yet lower for light polarized in the direction parallel to the writing beam. These indicate that the azo groups of PazoNE have been reoriented and aligned preferably in this direction by the writing laser beam. The angular dependence of the absorbance of PazoNE at 480nm clearly shows this reorientation (as shown in Fig. 4). This dichroism can be transferred as the order parameter S=(Abs(90°) - Abs(0°))/(Abs(90°) + 2Abs(0°))= 0.3. A typical writing sequence is presented in Fig. 5. Due to the isotropy of LB film before irradiation, inherent birefringence is avoided and no birefringence is observed. When the writing beam is turned on, the birefringence is induced and birefringence signal increase rapidly and come to reach its saturation. The birefringence signal is seen to reach 60% of saturation in about 0.8s and 90% in about 4s. The saturation

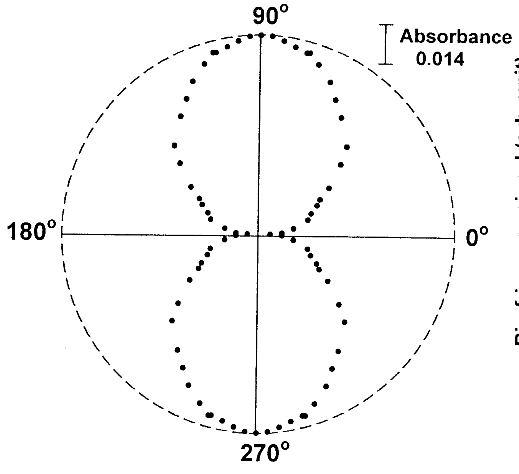

Fig. 4 Angular dependence of absorption of PazoNE LB film after irradiation with linear polarized 514.5nm beam

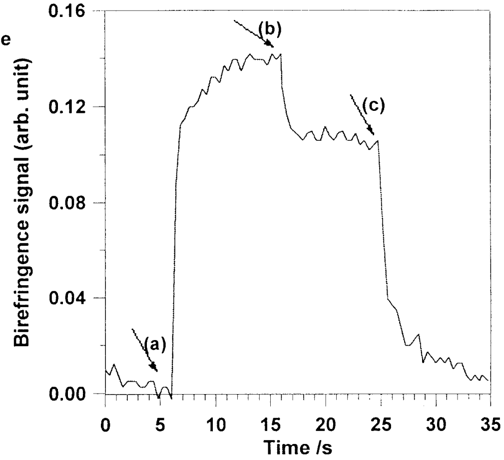

Fig. 5 A typical writing-erasing sequence of 5 layers LB film of PazoNE (a) The writing beam is turned on (b) the writing beam is turned off (c) the erasing beam is turned on

birefringence is about $\Delta n=0.07$. When the writing beam is turned off, the birefringence is observed to decrease to about 70% of the saturation value, and this value will keep constant for a long time. In our system, this induced birefringence has been stable for more than four months from the first test to present preparing this paper. When the erasing beam is turned on, the birefringence is optically erased by the circular polarized laser beam because the circular polarized light randomizes the azo groups and thus removes the macroscopic orientation of the dipole moments in the LB film.

The writing and erasing can be cycled many times, we have observed almost no appearance of any fatigue after cycled the writing and erasing 100 times, and the response time keep almost the same as the first cycle.

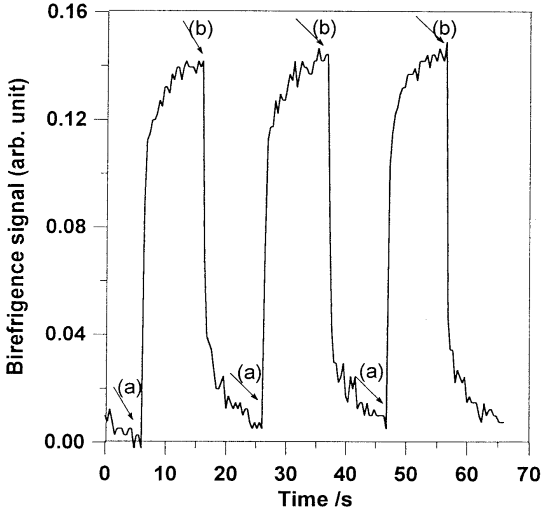

Fig. 6 Writing and erasing sequence of 5 layers LB film (a) writing beam is on (b) erasing beam is on

In summary, we have successfully realized the optically induced and erasing dichroism and birefringence based on a kind of Reversed Duckweed azo polymeric LB film. Further work is in process.

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