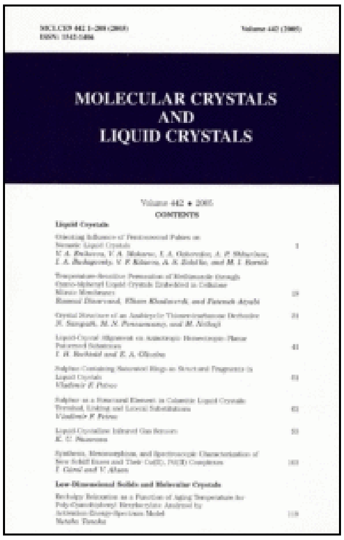

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Thermal and Photo Alignment Behavior of Polymers in Multiply-Layered Films Composed of Polyethylene Imines Having Azobenzene Side Chain Groups and Polyvinyl Alcohol

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Thermal and Photo Alignment Behavior of Polymers in Multiply-Layered Films Composed of Polyethylene Imines Having Azobenzene Side Chain Groups and Polyvinyl Alcohol

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Polyethylene imines having 4-methoxyazobenezene group through methylene spacer groups (PEI6 M) were synthesized and their photochemical, thermooptical as well as photoorientational behavior were investigated. PEI6 M films showed high dichroism and order parameter values after annealing and developed out-of-plane order. Multiply-layered films exhibited reflection band and reflection band was almost disappeared by annealing the films at 80°C. In addition reflection band was again observed by UV light irradiation because of reorientation of azobenzene groups from out-of-plane order to random state. The photochemical control of molecular orientation of PEI6 M between random state and out-of-plane structures were achieved by combination of thermal and photochemical processes.

Keywords Azobenzene polymer; molecular orientation; out-of-plane order; photochemical properties; polyethylene imines

Introduction

Azobenzene containing polymers have been the object of intensive investigations because of their potential applications in the field of photonics and optoelectronics. Azobenzene derivatives are known to undergo *trans/cis* photo-isomerization upon irradiation. This is not a simple switching process between the two photochromic isomers, because a steady state is established which strongly depends on the substitution and the wavelength of the excitation. The interaction of linearly polarized light with photochromic moieties offers the opportunity to orient these groups in polymeric films and thereby to generate optical anisotropy [1–6]. Some mechanisms

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to orient the azobenzene moieties are already known [7–9]. One of these processes can be characterized as photoorientation in the steady state of the photoisomerization [10–12]. This photochemically induced orientation process takes place via the repetition of angular-selective excitation, a number of photoisomerization cycles and rotational diffusion within the steady state. In this way the photochromic groups become oriented perpendicular to the electric field vector **E** of the incident light [10–12]. This approach is very promising for reversible optical data storage, the orientation of photochromic polymers [2], the photoalignment of liquid crystals [6] and all-optical processing. There are two typical liquid crystalline systems in relating to the photo-cotnrol of the molecular orientation by means of photoisomerization of azobenzene compounds: one is "photochemical phase transition" between a liquid crystalline phase and a random state [13–15], the other is photoalignment between in-plane and out-of-plane structures, which is called as a "command surface" [16]. It is expected that larger change in the refractive index can be induced in the command surface system compared to the photochemical phase transition, because $\Delta(n_{\|} - n_{\perp})$ is larger than $\Delta(n_{\|} - n)$. The command surface system consists of the command surface and low molecular weight liquid crystals. Therefore, the system requires a cell, and its memory stability is not so high. So far we know there are few papers on spontaneous out-of-plane molecular orientation of polymeric liquid crystals (PLCs) [17–19]. Bobrovsky et al. reported that polyacrylate copolymer containing 4-ethoxy-4′-hexoxyazobenzene and cholesterol groups as side chains showed spontaneous out-of-plane molecular orientation on a glass substrate by annealing at 75°C, whereas only partial out-of-plane molecular orientation was observed for polyacrylate homopolymer [19]. On the other hand, polymeric multi-layered mirrors can be fabricated by use of various techniques. The self-assembly [20], the co-extrusion [21] and the spin coating [22,23] have ever been used for fabrication of the periodic structures of the high and low refractive-indices. Among them, spin coating is the simplest and lowest-cost method of obtaining polymeric thin-films. Due to photonic band gap (PBG), multi-layered mirrors obtained by spin coating, reflect light of specific wavelength λ, according to Bragg diffraction equation as follows:

$$m\lambda = 2a\sqrt{n_1^2\frac{d_1}{a} + n_2^2\frac{d_2}{a}} \tag{1}$$

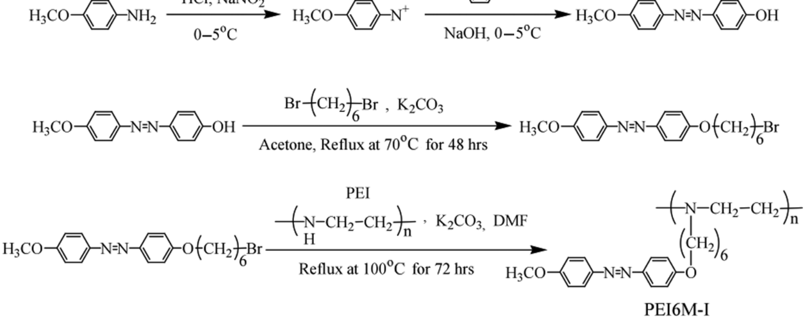
where a is the film thickness of each bilayer, n_1, n_2, and d_1, d_2 are the refractive indices and the thicknesses of stacked materials 1 and 2 in each bilayer respectively, and m is the diffraction order integer [22]. So the wavelength of multiply-layered mirrors can be controlled by the thickness of each layer and/or changing the refractive index. In addition, peak reflectance, R of multiply-layered mirror is given by following equation for normal incidence of light [24]:

$$R = \left[\frac{1 - (n_H/n_L)^{2q}(n_H^2/n_S)}{1 - (n_H/n_L)^{2q}(n_H^2/n_S)}\right]^2 \tag{2}$$

where n_H and n_L are high and low refractive-index of the stacked materials in each bilayer, respectively, n_S is the refractive index of a substrate and q is the number of periods of the stacked layers. According to this equation, it is clear that a larger number of q and a higher ratio of n_H to n_L will provide higher reflection and broader bandwidth of high reflection. So if one can control the difference in refractive indices of the stacked materials between equal state ($n_H = n_L$) and different state ($n_H \neq n_L$), one can realize on-off switching of the reflection. However, there has been no report on the on-off switching of the reflection so far. Moreover, it was reported that some polyethylene imines (PEIs) having azobenzene groups as side groups show liquid crystalline phases and align perpendicular direction to the substrate spontaneously by heating into an isotropic phase and following cooling without any alignment process [25,26]. If we control photochemically the molecular orientation of the PEIs between the in-plane and the out-of-plane structures, we can fabricate simply the optical switching system showing excellent memory stability as well as larger change in the refractive index by coating PEIs on a substrate without any alignment process. In this paper, we investigated photochemical, thermooptical as well as photoorientational behavior of polyethylene imines having azobenzene side chain groups (PEI6 M) under the action of heat and UV light. PEI6 M showed out-of-plane molecular orientation in multiply-layered PEI6 M/PVA film and one can achieve on-off switching of reflection by the combination of spontaneous molecular orientation and photoisomerization of azobenzene groups in PEI6 M.

Experimental

The azobenzene derivative, 4-(6-bromo-*n*-hexyloxy)- 4′-methoxyazobenezene), was synthesized by diazo-coupling reaction of *p*-anisidine (6.16 g, 0.05 mol) with phenol (4.7 g, 0.05 mol) in water and following etherification with 1,6-dibromohexane in acetone at 70°C for 48 h. The resulting azo-compound was recrystallized from methanol two times. PEIAzos (PEI6 M-I, PEI6 M-II) were synthesized by two different ways, one long time reaction conditions, reported by Ujiie group [18] and other short time reaction conditions by reacting polyethylene imine (high molecular weight) with 4-(6-bromo-*n*-hexyloxy)-4′-methoxyazobenezene in dimethyl formamide (DMF) at 100°C for 72 h (Sch. 1). After evaporating of half amount of DMF, PEIAzos were obtained by repricipitation of the solution into methanol. The phase transition behavior of the polymers were studied by differential scanning calorimetry (DSC; Seiko SSC-5020) with a heating rate of 10 K/min and polarizing optical microscopy



Scheme 1. Synthetic route for PEI6 M-I.

(Olympus BHSP polarizing microscope; Mettler FP-80 and FP 82 hot stage and controller). Multiply-layered films were fabricated by alternative spin coating of solutions containing PEI6 M and PVA on a glass substrate (25 × 20 mm). Typical coating was performed as follows: speed of rotation 3000 rpm and time of rotation 30 sec with 5 wt% of PEI6 M in cyclohexanone and 4 wt% of PVA in water. After spin coating each layer was dried for 5 min at room temperature and cyclohexanone and water were evaporated. Multiply-layered films showed reflection band at around 700 nm. The reflection spectra of the multiply-layered films were measured with a spectrometer (Ocean optics USB2000). Photoirradiation was performed by using a 500 W high-pressure Hg lamp with adequate cut filter for UV and Vis light at room temperature. The orientational order was studied using polarized UV-Vis spectroscopy, because the transition moment of the *trans* isomer of azobenzene moiety is directed along the long axis of this group. For this purpose the angular dependence of the absorbance was measured. The values of dichroism were calculated from the spectra using Eq. (3):

$$D = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + A_{\perp}} \tag{3}$$

where $A_{\parallel}$ is the absorbance at the preferred direction; $A_{\perp}$ is the absorbance perpendicular to this direction. The values of order parameter determined by spectroscopic method were calculated by Eq. (4)

$$S = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}} \tag{4}$$

To study the out-of-plane photoorientation phenomena we measured the angular distribution of the polarized absorption spectra at an angle equal of about 45° to film normal and calculated dichroism and order parameter using Eqs. (3) and (4) respectively.

Results and Discussion

In this work, polyethylene imines having azobenzene side chain groups, PEI6 M were synthesized by two different processes, one using short reaction time, PEI6 M-I and other long reaction time, PEI6 M-II. In case of long time reaction we obtained the polymer having high degree of substitution compared to polymer obtained by short time reaction. For PEI6 M-I the degree of substitution is 56% and for PEI6 M-II, the degree of substitution is 68%. Both of these two polymers showed very good solubility in DMF, chloroform, THF and cyclohexanone.

Photochemical Behavior of PEI6 M in Solution

The photochemical behavior of PEI6 M in solution and solid state was examined. Figure 1 shows the changes in the absorption spectra of PEI6 M-II in chloroform by irradiation of UV and visible light. Before irradiation, PEI6 M-II in chloroform showed a strong absorption at 361 nm and a weak absorption around 450 nm, corresponding to π–π^* transition and n–π^* transition of the azo-chromophores,

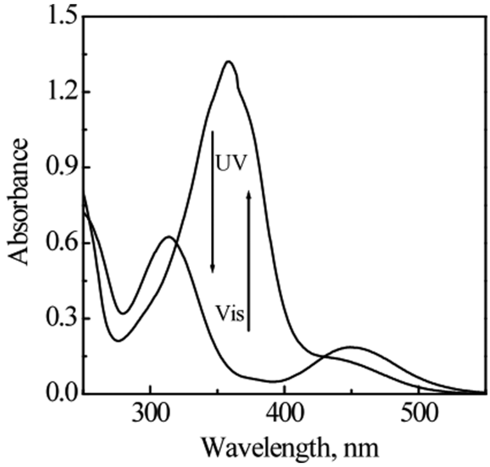


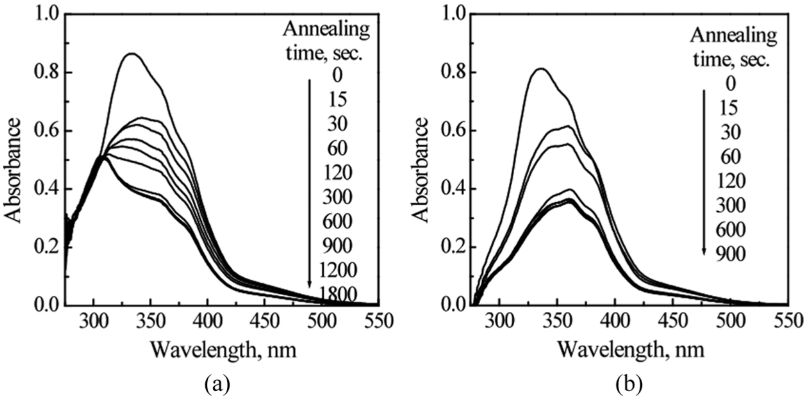
Figure 1. Changes in absorption spectra of PEI6 M-II in chloroform by irradiation of UV and visible light.

respectively. UV irradiation caused decrease and increase in absorbances at 360 and 450 nm, respectively, indicating photoisomerization from *trans*-form to *cis*-form. In addition, it is obvious that both *trans*-form and *cis*-form of PEI6 M have weak absorption around 488 nm. Therefore, the irradiation of light in this wavelength region should cause the photoisomerization from the *trans*-form to the *cis*-form for the *trans*-form, and vice verse for the *cis*-form. Consequently, *trans–cis–trans* photoisomerization cycle of PEI6 M will be brought about by irradiation of the light in this region [27–29].

Thermooptical Properties of Spin-Coated PEI6 M Films

To explore the molecular orientation behavior of multiply layered PEI6 M and PVA film we measured the change in absorbance of bi-layered film before and after annealing and also measured the polar plot of the PEI6 M film.

Figure 2 presents the change in absorption spectra of the PVA/PEI6 M film by annealing at 80°C. Upon annealing the test films at room temperature, no marked changes take place; however, when the films are kept at the temperature, which is above their glass transition temperature say 80°C corresponding to the LC phase, one may observe the dramatic spectral changes (Figs. 2a and 2b). By annealing, the absorbance at 330–360 nm was significantly decreased in both polymers (PEI6 M-I and PEI6 M-II). However, for PEI6 M-I and PEI6 M-II, the character of the changes appears to be different. In the case of PEI6 M-I, to attain the thermal stationary state it took long time say 10 min but in case of PEI6 M-II the polymeric film attained thermal stationary state within short time (2 min) (Fig. 3). In both cases the absorbance in the region of the π–π^* transition decreased by about 50%. When the absorption spectra are recorded at an angle of 45° to the film normal using polarized light, one may observe a significant anisotropy indicating the development of an out-of-plane order. The corresponding plots (Figs. 4a and 4b) allow us to assess the level of dichroism. In the case of PEI6 M-I, the dichroism before annealing is equal -0.096 and after annealing is 0.198 and order parameter before annealing is



(a) (b)

Figure 2. Changes in absorption spectra of PEI6 M/PVA 1-bilayer solid films on annealing; (a) for PEI6 M-I and (b) for PEI6 M-II. Longer time of annealing does not lead to additional changes.

−0.061 and after annealing is 0.141; at the same time, for PEI6 M-II, the dichroism before annealing is equal −0.059 and after annealing is 0.314 and order parameter before annealing is −0.039 and after annealing is 0.234.

Therefore, the analysis of the absorption spectra and thermotropic properties of PEI6 M-I and PEI6 M-II makes it possible to reveal a well-pronounced tendency for the development of the out-of-plane order. In the case of PEI6 M-II, the value of order parameter and dichroism are higher than that of PEI6 M-I and the annealing time is lower than in case of PEI6 M-II film. This is because in case of PEI6 M-II, the ratio of azo in polymer is higher than that of in PEI6 M-I. These results also support that the annealing at 80°C cause not only the transformation of molecular orientation from random state to out-of-plane molecular orientation but also the formation of H-aggregate [19].

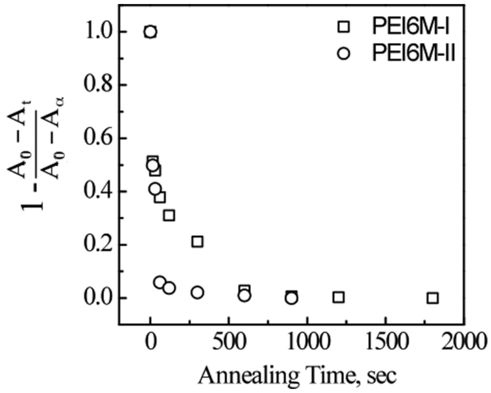
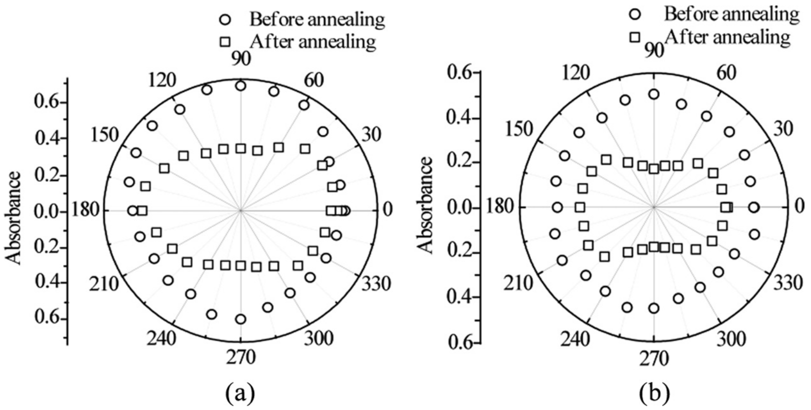


Figure 3. Comparison of annealing time of PEI6 M-I and PEI6 M-II 1-bilayer film to attain the steady state.



(a) (b)

Figure 4. Polar plots for (a) PEI6 M-I and (b) PEI6 M-II single layer film, respectively before and after annealing (for $\lambda = 324$ nm). For polar plots spectral measurement were made at 45° to film normal.

Studies on Reflectance of PEI6 M Multiply-Layered Films

Multiply-layered films were fabricated on a glass substrate by spin coating of PEI6 M/cyclohexanone solution and PVA/water solution alternatively in order to explore their color reflectance property. According to Eq. (2), the reflection depends on the bilayer number and difference in refractive indices of the components constituting the multiply-layered films. As shown in Figure 5, the reflectance of the fabricated multiply-layered film increased with an increase of the bilayer number and consequently color of reflection was visually observed. In both cases (PEI6 M-I and PEI6 M-II), the reflectance of the fabricated multiply-layered films increased with an increase of the bilayer number. Moreover, the reflection band almost disappeared by annealing at 80°C as can seen in Figure 6. In case of PEI6 M-I multiply-layered film, the time required to disappear the reflection band was higher than that

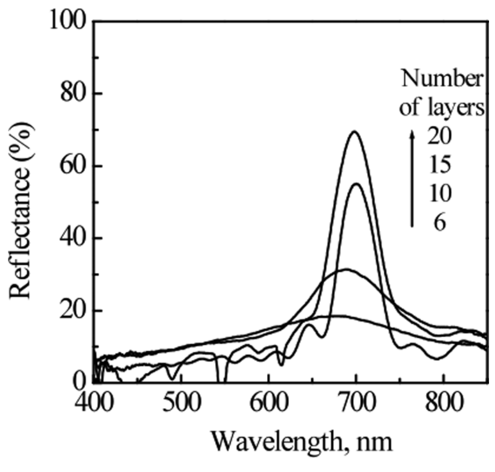


Figure 5. Changes in reflection spectra of PEI6 M-I/PVA multiply-layered films on number of bilayers.

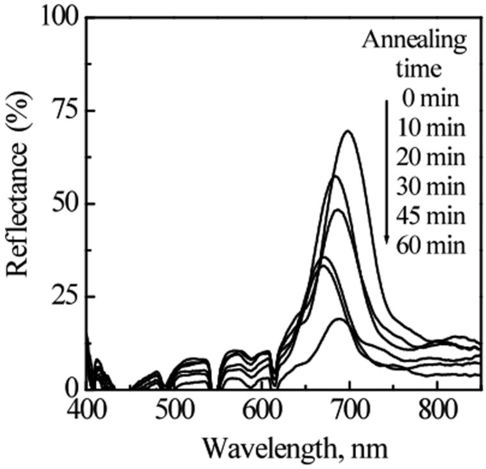
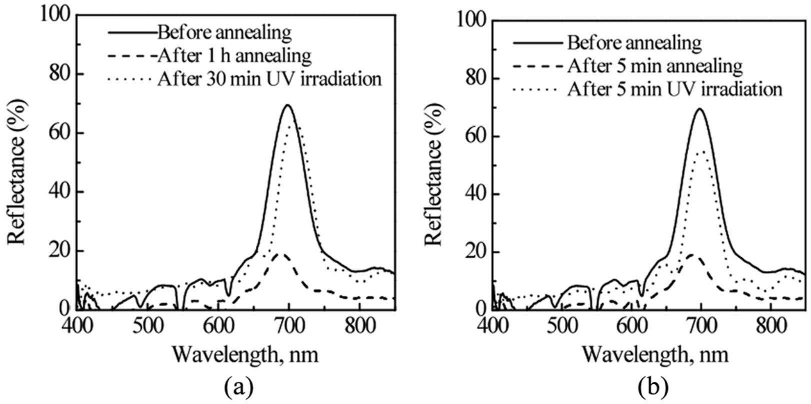


Figure 6. Changes in reflection spectra of PEI6 M-I/PVA 20–bilayered film on annealing at 80°C.

required in PEI6 M-II multiply-layered films. Based on the results of PEI6 M/PVA film, the disappearance of the reflection band can be explained as a result of change in the molecular orientation of azobenzene groups from random state to out-of-plane order even in the multiply-layered film by annealing. The small difference in the refractive indices between PEI6 M and PVA layers contributes to the disappearance of the reflection band. So, it is expected that the reflection band appears again by changing molecular orientation, leading to change in the refractive index of PEI6 M. Figure 7 represents the change in reflection band of the annealed multiply-layered film by irradiation of UV light. The reflection band again appeared by UV irradiation to cause the increase in the refractive index of PEI6 M due to transformation of out-of-plane order to photo-induced isotropic phase. The disordering of out-of-plane occurred through the *trans-cis* photoisomerization with UV light, resulting in the appearance of the reflection band. Therefore, it can be



(a) (b)

Figure 7. Changes in reflection spectra of (a) PEI6 M-I/PVA and (b) PEI6 M-II/PVA 20-bilayered films on annealing and following UV light irradiation.

demonstrated that the on-off switching of the reflection could be achieved by combination of spontaneous out-of-plane molecular orientation and photoisomerization of azobenzene group.

Conclusion

Polyethylene imines having azobenzene side chain groups were synthesized successfully and fabricated photo-tunable multiply-layered film consisting of PEI6 M and PVA by alternative spin coating. PEI6 M films showed high dichroism and order parameter values after annealing and that revealed a well-pronounced tendency for the development of the out-of-plane order. Also the multiply layered films exhibited reflection of color and the wavelength and intensity of reflection peak could be tuned by film thickness and the bilayer number respectively. The multiply-layered film showed a low reflectance after annealing at 85°C because of small difference in refrective index (n_0) of PEI6 M and PVA. But again the reflection of such multiply-layered film was increased by UV light irradiation because of reorientation of azobenzene groups from out-of-plane order to random state. In all cases PEI6 M-II single layer as well as multiply-layered films showed quicker response than PEI6 M-I because of high azo content in PEI6 M-II. So the photochemical control of the molecular orientation of PEI6 M between random state and the out-of-plane structures could be achieved by combination of thermal and photochemical processes. These results were caused due to the transformation of molecular orientation and *trans-cis* photoisomerization of azobenzene groups. Therefore, these results may provide promising ways to fabricate novel types of optical elements and devices for photonic applications.

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