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Thermal and Photochemical Properties of Polyethylene Imines Having Azobenzene Side Chain Groups

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Polyethylene imines (PEIs) having 4-butylazobenezene group through methylene spacer groups were prepared, and their thermal as well as photochemical properties was investigated. PEI104 having longer methylene spacer was found to form an out-of-plane structure by heating into an isotropic phase and following cooling. The photochemical control of the molecular orientation of PEI104 between in-plane and the out-of-plane structures could be achieved by combination of thermal and photochemical processes.

Keywords: azobenzene; homeotropic; molecular orientation; out-of-plane; polyethylene imine

1. INTRODUCTION

There have been many studies on the photo-control of the molecular orientation of polymer liquid crystals (PLCs) containing azobenzene compounds. The azobenzene compounds show a reversible

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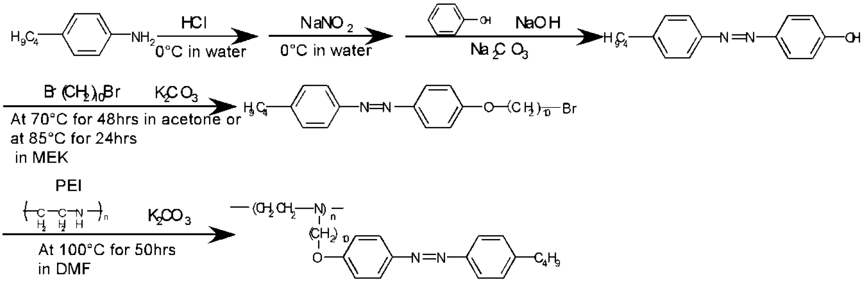
photoisomerization between trans-form and cis-form. There are two typical liquid crystalline systems in relating to the photo-cotnrol of the molecular orientation by means of photoisomerization of azobenzene compounds: one is "photochemical phase transition." between a liquid crystalline phase and a random state [1–3], the other is photo-alignment between in-plane and out-of-plane structures, which is called as a "command surface" [4] 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 $\Delta(n_{\parallel} - n_{\perp})$ is larger than $\Delta(n_{\parallel} - n)$: $\Delta(n_{\parallel} - n_{\perp})$ and $\Delta(n_{\parallel} - n)$ express differences in refractive indices between $n_{\parallel}$, $n_{\perp}$, and n, where $n_{\parallel}$, $n_{\perp}$ are extra-ordinary and ordinary refractive indices of a liquid crystal in a liquid crystalline phase, and n is a refractive index in an isotropic phase, respectively. 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.

On the other hand, 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 [5,6]. 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 study, we investigated the thermal and photochemical properties of PEIs having azobenzene side groups with respect to the change in the molecular orientation between the in-plane and the out-of-plane structures.

2. EXPERIMENTAL

2.1 Materials

The azobenzene derivatives, (4-(10-bromo-*n*-decyloxy)-4′-butylazobenezene, and 4-(6-bromo-*n*-hexyloxy)-4′-butylazobenezene), were synthesized by diazo-coupling reaction of 4-*n*-buthylaniline (4.8 g, 33 mmol) with phenol (4.5 g, 48 mmol) in water, and following etherification with 1,6-dibromohexane or 1,10-dibromodecane in acetone at 70°C for 24 h. The resulting azo-compounds were recrystallized from methanol. Two PEIs, PEI104 (m = 10) and PEI64 (m = 6), were synthesized by reacting polyethylene imine (DP = ca.20) with 4-(10-bromo-*n*-decyloxy)-4′-butylazo-benezene, and 4-(6-bromo-*n*-hexyloxy)-4′-butylazo-benzene,



Scheme Synthetic route for PEI-104

SCHEME 1 Scheme synthetic route for PEI-104.

respectively, in dimethyl formamide (DMF) at 100°C (Scheme). After evaporation of half amount of DMF, PEIs were obtained by repricipitation of the solution into methanol. Both PEIs showed LC phases: K•30°C•SmA1•39°C•N•94°C•I for PEI64, and SmF•68°C•SmA1•114°C•I for PEI104.

2.2 Control of Molecular Alignment

Uniaxially oriented PEI films were prepared by spin coating PEI toluene solutions (3 wt%, 600 rpm) on a glass substrate coated with polyimide and rubbed. In order to explore the molecular orientation of the films prepared, the order parameter was evaluated by measuring polarized absorption spectra (Shimadzu UV-1600). In addition, the transmitted light intensity (365nm) through the PEI films was measured as a function of angle between light polarization and rubbing direction (Fig. 1). Photo-irradiation was carried out using a 500 W high pressure Hg lump (Ushio SX-UI 500H) equipped with a filter (Sigma koki Co. UTVAF-35). The photoisomerization behavior was investigated by measuring absorption spectra with Ocean (USB2000 Ocean optics) under irradiation of UV light. Xenon lump was used as a monitor light source. To improve the molecular orientation, PEI films was heated into the isotropic phase and cooled rapidly to the room temperature.

3. RESULTS AND DISCUSSION

Figure 2(A) shows changes in absorbance at absorption maximum (345nm) of PEI104 film by varying temperature. The absorbance of the film was about 0.35 at 25°C immediately after spin coating. The

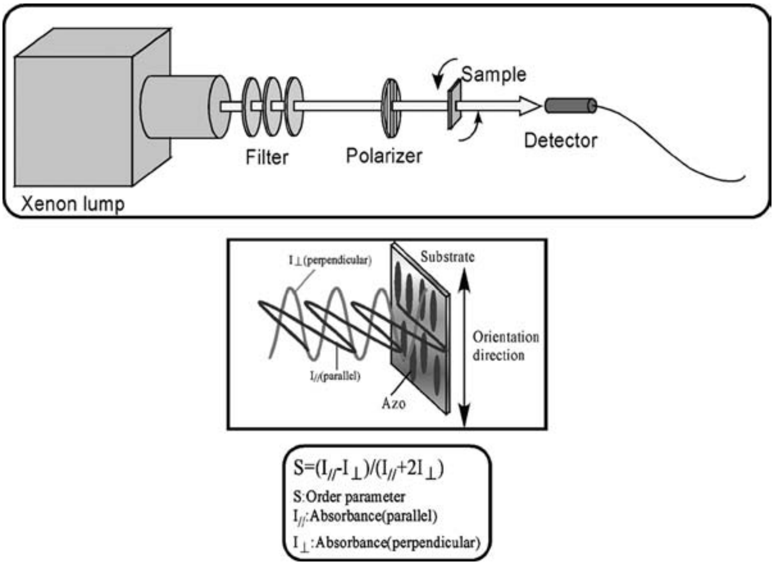


FIGURE 1

absorbance was increased by heating, and decreased in a temperature range from 50 to 70°C. The absorbance was increased again by heating higher than 70°C up to 120°C. On the other hand, the absorbance decreased linearly with decreasing temperature, and the absorbance became 0.2 at 25°C. After heating to an isotropic phase once, the

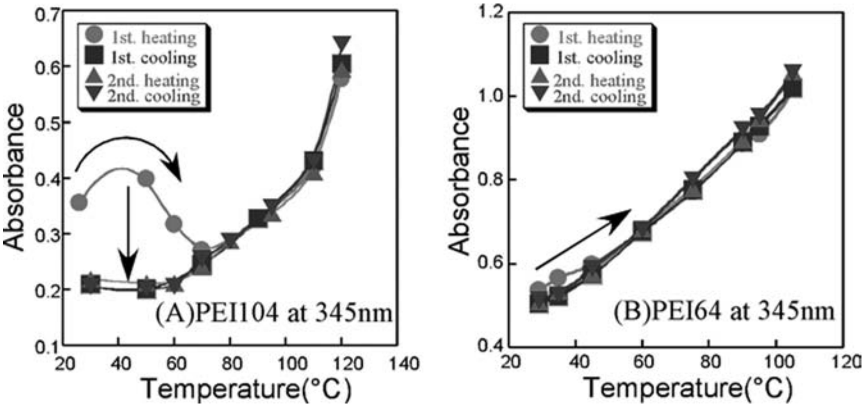


FIGURE 2 Changes in absorption spectra of EI LC films by heating and cooling.

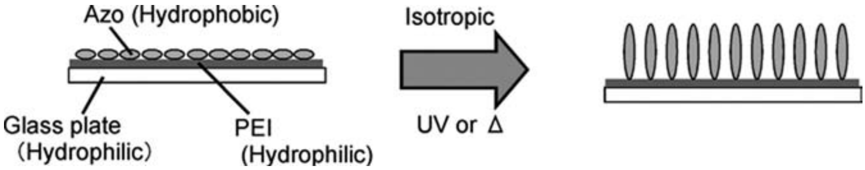


FIGURE 3 Reorientation of PEI liquid crystals after isotropic state.

PEI film was found not to recover the initial absorbance (0.4) by further heating and cooling cycle. This result means that the mesogenic azobenzene groups transform from in-plane structure to out-of-plane structure by the heating and cooling cycle (Fig. 3). Contrary to PEI104, PEI64 didn't show such hysteresis of the change in the absorbance by the heating-cooling cycle as shown in Figure 2(B). These results can be explained in terms of the hydrophobicity of the side chains of the PEIs. In the membrane consisting of amphiphilic compounds on the cleaned glass substrate, the polar groups are in contact with the surface of the glass substrate, contrary the hydrophobic groups are spatially directed to air. Namely, the azo-side groups in PEI104 is more hydrophobic, and consequently tend to align perpendicular to the glass substrate.

On the other hand, it is known that the trans-cis photoisomerization disorganizes the molecular orientation of the liquid crystals. Therefore, it is expected that the transformation from the in-plane structure to out-of-plane will be induced by photoisomerization of azo-dyes attached in the PEIs, because the photochemical perturbation on the molecular ordering can be considered to be compatible with thermal effect. Actually the decrease in the absorbance was observed for the PEI104 film, while no change was observed for the PEI64 film.

In order to improve the photo-switching properties, uniaxially oriented films were prepared by spin coating PEI solutions on a glass substrate which is coated with polyimide and rubbed. After the spin coating, the films were heated into the isotropic phase and cooled rapidly to the room temperature. Figure 4 shows angular dependence of absorbance of linerly polarized light (365 nm) between rubbing direction and light polarization, where 0° is corresponding to perpendicular to the rubbing direction, and 90° is parallel to the rubbing direction, respectively. As can be seen in Figure 4, the absorbances at 0 and 270° are larger than others, indicating the uniaxially molecular orientation of azo groups in the films before UV irradiation. The UV irradiation on both films caused change in the angular dependence

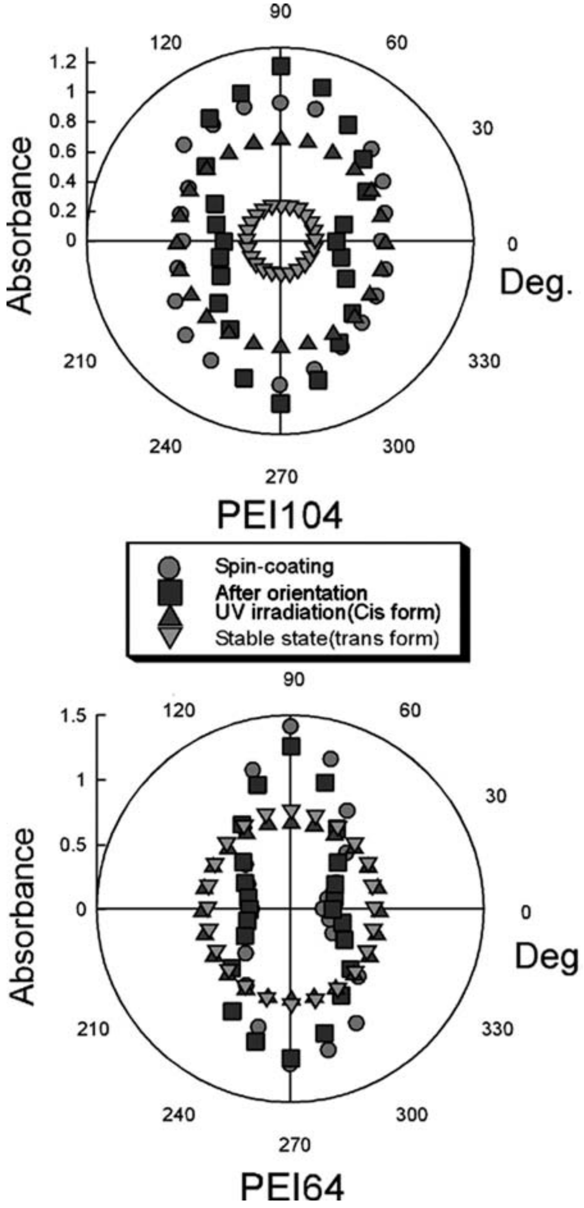


FIGURE 4 Angler dependence of orientation of PEI LCs on the incidence angle of xenon light.

of the absorbance. No angular dependence of the absorbance was observed for both films immediately after the UV irradiation. This is due to the photochemical phase transition from LC phase to the isotropic phase. By keeping the PEI64 film in the dark, no further change in the angular dependence of the absorbance was observed. On the other hand, the absorbance of the PEI104 film was decreased extremely with time, indicating the formation of the out-of-plane structure.

CONCLUSIONS

Transformation of PEI104 film from the in-plane structure to the out-of-plane structure was achieved by thermally and trans-cis photoisomerization of the azo-side groups. On the other hand, PEI6 did not show such transformation thermally as well as photochemically. The transformaton was attributed to more hydrophobicity of the azo-side groups having long spacer. However, the time more than 24 h was required for the photochemical transformation, because the slow thermal back reaction limited the photo-response properties.

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