Synthesis, Thermal, and Photo Alignment Behavior of Polyethylene Imines Having Nitro Substituent Azobenzene Side Chain Group

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ABSTRACT: Polyethylene imines having nitro substituent azobenzene side chain group with different methylene spacer groups (PEImN) were successfully synthesized and characterized by differential scanning calorimetry, polarized optical microscopic, and X-ray diffraction analysis. All synthesized polyethylene imines showed liquid crystalline properties and the glass transition temperature (Tg) of PEImN decreased as the number of methylene spacers increased. Melting temperatures (Tm) of synthesized PEImN showed an odd-even effect. Photochemical, thermo-optical, as well as photo alignment behavior of PEImN were investigated and out-of-plane orientational behavior of polymeric films was dependent on number of methylene spacers and polyethylene imines having higher number of methylene spacers (six or more) showed high order parameter values that revealed the well pronounced tendency for the development of out-of-plane order from random state on annealing. And the molecular orientation of PEImN between random and out-of-plane structures has been achieved by the combination of thermal and photochemical processes. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 950–959, 2011

Key words: azobenzene polymer; polyethylene imines; molecular orientation; liquid crystalline properties; out-of-plane order

INTRODUCTION

The photogeneration of anisotropy in organic photochromic materials is a promising approach for reversible optical data storage, photoalignment of liquid crystals (LC), or for fabrication of optical components. It was shown that under irradiation with an appropriate wavelength of light the azobenzene moieties change their spatial orientation.[1–4] In this way, anisotropy—dichroism and birefringence—is generated. This process was used for optical switching,[5] digital and holographic data storage[6] and optical modulators.[7] Azobenzene derivatives are known to undergo *trans/cis* photo-isomerization on irradiation. This is not a simple switching process between the two photochromic isomers, because a steady state is strongly dependent on the substitution and the wavelength of the excitation. There are two typical LC systems in relating to the photo-control of the molecular orientation by means of photo-isomerization of azobenzene compounds: one is "photochemical phase transition" between a LC phase and a random state[8–10] the other is photoalignment between in-plane and out-of-plane structures, which is called "command surface."[11,12] 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 $\Delta(n_\parallel - n)$, where $n_\parallel$ is extraordinary index and $n_\perp$ is ordinary index. The command surface system consists of azobenzene monolayer on a glass substrate and low molecular weight LC. Therefore, the system requires a cell, and its memory stability is not so high due to thermal back reaction of azobenzene, and fluidity of low molecular weight LC. In contrast, in photochemical phase transition system, polymeric materials could be used to improve memory stability. However, to obtain $\Delta(n_\parallel - n_\perp)$ relating to the photochemical phase transition, alignment layer is required.

In contrast, so far very few articles are published on spontaneous out-of-plane molecular orientation of polymeric LC.[4,13–16] Several studies on the photo-induced molecular reorientation of azobenzene-containing polymeric films with different spacer lengths have been reported,[17–20] and out-of-plane reorientation and in-plane reorientation have been observed with long alkylene spacers. Furthermore, it was reported that some polyethylene imines (PEIs) having azobenzene groups as side groups show LC
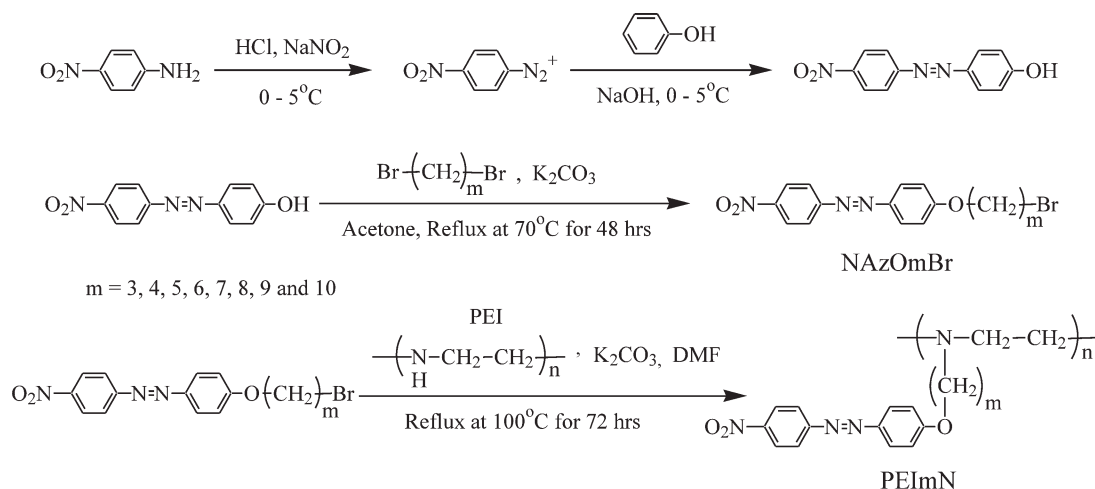
Scheme 1 Synthetic route for monomers and polymers.

phases and align perpendicular direction to the substrate spontaneously by heating into an isotropic phase and following cooling without any alignment process.[21,22] So, if we control photochemically the molecular orientation of PEIs between random state and out-of-plane structures, we can fabricate simply the optical switching system showing excellent memory stability by coating PEIs on a substrate without any alignment process.

In this work, we synthesized a series of PEI having nitro substituent azobenzene side chain groups with different methylene spacer groups and investigated their thermal and photo alignment behavior on annealing, UV, and nonpolarized visible light irradiation.

EXPERIMENTAL

Materials

p-Nitroaniline was purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) and used as received. All monomers were synthesized in good yield and purity. For azobenzene monomer synthesis, 1,3-dibromopropane, 1,4-dibromobutane, 1,5-dibromopentane, 1,6-dibromohexane, 1,7-dibromoheptane, 1,8-dibromooctane, 1,9-dibromononane, and 1,10-dibromodecane were purchased from TCI (Tokyo, Japan) and for polymer synthesis, PEI of low and high molecular weight were purchased from Polysciences, Inc. (Warrington, PA, USA). Reagents were used without further purification, unless stated. *N,N*-dimethylformamide (DMF) was purchased from Wako Pure Chemical Industries and was dried up with molecular sieves before use.

Synthesis of 4-nitro-4′-hydroxyazobenzene (NAz-OH)

To a solution of 5.3 g (33 mmol) of *p*-nitroaniline dissolved in 150 mL of water and 14 cm³ (170 mmol) of HCl was added dropwise a solution of 3.3 g (48

mmol) of NaNO$_2$ dissolved in 140 mL water at such a rate that the temperature did not exceed 5°C. At the same temperature, a solution of 1.8 g (44 mmol) sodium hydroxide, 15.9 g (150 mmol) of sodium carbonate, and 4.5 g (48 mmol) of phenol in 130 mL water was added slowly to the resulting diazonium salt solution. After stirring at room temperature for 1 h, the resulting mixture was acidified with concentrated HCl. The precipitated product was filtered, washed with copious amount of water, and dried under vacuum. Yield: 68% as solid. ^{1}H-NMR (CDCl$_3$, δ): 8.38 (2H, dd, aromatic), 8.30 (2H, dd, aromatic), 7.95 (2H, d, aromatic), 6.98 (2H, d, aromatic), 5.39 (1H, s, -O*H*). Anal. Calcd for C$_{12}$H$_9$N$_3$O$_3$ (243.06): C- 59.26; H- 3.73; N- 17.28. Found: C- 58.56; H- 3.96; N- 17.82.

Synthesis of 4-(m-bromo-n-alkyloxy)-4′-nitro azobenzene [NAzOmBr; m = 3−10]

A series of 4-(*m*-bromo-*n*-alkyloxy)-4′-nitro azobenzene with different methylene spacers were synthesized by the following procedure: to a mixture of 1.1 g (4.4 mmol) of 4-nitro-4′-hydroxyazobenzene (NAz-OH) and 0.91 g (6.6 mmol) potassium carbonate dissolved in 100 mL of dried acetone, 20.8-22.3 mmol of dibromoalkane was added. After refluxing for 48 h at 70°C, the reaction mixture was filtered and evaporated the solvent from filtrate and the product NAzOmBr was recrystallized from methanol twice. The general reaction scheme is shown in Scheme 1. Table I also represents the synthesis and the characterization of NAzOmBr.

Synthesis of PEI having azobenzene side chain group (PEImN)

A series of PEI having nitro substituent azobenzene side chain group with different methylene spacer groups were synthesized using different reaction conditions. The typical procedure is as follows: Azobenzene containing monomers, NAzOmBr (4.2

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TABLE I
Synthesis and Characterization of 4-(m-bromo-n-alkyloxy)-4'-Nitro Azobenzene [NAzOmBr; m = 3−10]

</div>

| Monomer | Spacer | Yield (%) | Elemental analysis | | | | | |
| | | | Calculated | | | Found | | |
			C (%)	H (%)	N (%)	C (%)	H (%)	N (%)
NAzO3Br	C_3H_6	67.4	49.47	3.87	11.54	50.29	3.98	11.04
NAzO4Br	C_4H_8	73.8	50.81	4.26	11.11	51.29	4.36	11.54
NAzO5Br	C_5H_{10}	77.4	52.05	4.63	10.71	52.86	4.52	11.28
NAzO6Br	C_6H_{12}	72.6	53.21	4.96	10.34	53.24	4.95	10.63
NAzO7Br	C_7H_{14}	80.4	54.30	5.28	10.00	55.29	5.13	10.87
NAzO8Br	C_8H_{16}	78.5	55.31	5.57	9.67	56.27	5.38	10.72
NAzO9Br	C_9H_{18}	76.8	56.26	5.85	9.37	56.61	5.66	9.90
NAzO10Br	$C_{10}H_{20}$	83.8	57.15	6.10	9.09	57.15	6.06	9.15

mmol), PEI (4.0 mmol), potassium carbonate (6.0 mmol), and 50 mL DMF were added into a round bottom flask equipped with a condenser. With continuous stirring the reaction mixture was refluxed at 100°C for 72 h. After the reaction, the mixture was filtered and evaporated the half amount of DMF from filtrate and then poured into methanol. The resulting polymers (PEImN) were purified by precipitation from chloroform/tetrahydrofuran (THF) into methanol two to three times. The removal of the monomer was monitored using thin-layer chromatography. Finally, the product was dried in vacuum for 24 h (Scheme 1).

Characterization

The phase transition behavior of the polymers was studied by differential scanning calorimetry (DSC; Seiko SSC-5020) with a heating rate of 10 K/min and polarizing optical microscopy (Olympus BHSP polarizing microscope; Mettler FP-80 and FP 82 hot stage and controller).

X-ray diffraction (XRD) was used to confirm the nature of the LC phases and to determine the spacing of the smectic layers. Rigaku, RINT 2100/PC XRD machine (X-Ray, 40 kV/200 mA) equipped with a - wide angle goniometer and scintillation detector was used for all XRD measurements. Cu K alpha (λ 1.5406 Å) was used as target. XRD samples were made by casting solutions (40 mg polymer in 1 mL of THF) onto a 1.5 × 1.5 cm^2 glass substrate. Thick films of PEI3N, PEI4N, PEI5N, PEI6N, PEI7N, PEI8N, PEI9N, and PEI10N were heated to 100, 120, 80, 110, 100, 110, 100, and 100°C, respectively, for 10 min, cooled to room temperature and measured the XRD.

Thin films for thermo-optical experiments were obtained by spin-coating technique using solutions in THF on quartz glass substrates. For drying, the spin-coated films were kept at room temperature during 1 h. Typical coating was performed as fol-

lows: speed of rotation 3000 rpm and time of rotation 30 sec with 4 wt% of polymer in THF.

Photoirradiation was performed by using a 500W high-pressure Hg lamp with adequate cut filter for UV and visible light at room temperature. The orientational order was studied using polarized UV-Vis spectroscopy (Perkin–Elmer Lambda 650 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 order parameter determined by spectroscopic method were calculated by eq. (1)[4]

$$S = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}} \tag{1}$$

where $A_{\parallel}$ is the absorbance at the preferred direction; $A_{\perp}$ is the absorbance perpendicular to this direction. Order parameter is used to describe the orientational order of the LC polymer. To study the out-of-plane thermal/photoorientation phenomena, we measured the angular distribution of the polarized absorption spectra at an angle of 45° to film normal and calculated the order parameter using eq. (1).

RESULTS AND DISCUSSION

Synthesis and thermal characterization of PEImN

We successfully synthesized PEI having nitro substituent azobenzene side chain group with different methylene spacer groups (PEImN). To optimize the reaction conditions, we changed the different reaction parameters such as temperature, reaction time, molar ratio of azobenzene monomer and PEI, and reaction solvent. The experimental results for the synthesis of PEI having nitro substituent azobenzene side chain group with six methylene spacer (PEI6N) are shown in Table II.

From Table II, it is clear that the degree of substitution of PEI6N has considerable effect on all of

TABLE II
**Experimental Conditions for the Synthesis of Polyethylene Imines Having Nitro Substituent
Azobenzene Side Chain Groups**

Polymer	Reaction conditions						Degree of substitution (%)[a]
	Temp °C	Reaction time, h	Azo (mmol)	PEI (mmol)	Solvent (ml)	PEI, Mn	
PEI6N-H1	80	72	4.0	4.0	a (50)	10,000	46.8
PEI6N-H2	100	96	4.0	4.0	a (50)	10,000	50.7
PEI6N-H3	100	72	4.2	4.0	a (50)	10,000	57.4
PEI6N-H4	100	96	4.2	4.0	a (50)	10,000	58.6
PEI6N-H5	100	120	4.2	4.0	a (50)	10,000	59.3
PEI6N-H6	100	72	4.2	4.0	a (40)	10,000	56.8
PEI6N-H7	100	300	4.2	4.0	a (50)	1800	60.3
PEI6N-L3	100	72	4.2	4.0	a (50)	1800	68.2
PEI6N-L4	120	72	4.2	4.0	a (50)	1800	63.2
PEI6N-L5	100	120	4.2	4.0	a (40)	1800	67.8
PEI6N-L6	100	300	4.2	4.0	a (50)	1800	67.4
PEI6N-L7	70	72	4.2	4.0	b (50)	1800	51.7
PEI6N-L8	70	300	4.2	4.0	b (50)	1800	54.4
PEI4N-L9	70	72	4.2	4.0	b+c (30+30)	1800	56.6
PEI6N-L10	70	300	4.2	4.0	b+c (30+30)	1800	59.2

a, DMF; b, THF; c, acetonitrile.
[a] Determined from UV absorption spectra.

these parameters. With the increase in reaction temperature and reaction time, the degree of substitution increased, and best results were obtained at a temperature of 100°C and reaction time of 72 h. At high temperature more than 100°C and longer reaction time (>72 h), the degree of substitution did increase little but the solubility of PEI6N decreased probably due to the formation of gel. So finally we synthesized PEI6N-L3 by optimizing the reaction conditions as temperature 100°C, reaction time 72 h, molar ratio of azobenzene monomer to PEI = 4.2 : 4.0, molecular weight of PEI = 1800, and solvent (DMF) = 50 mL. Using earlier reaction conditions, we also synthesized a series of PEImN with different methylene spacer groups and almost similar degrees of substitution were obtained for different polymers

and all synthesized polymers showed good solubility in DMF, chloroform, THF, and cyclohexanone. Table III represents the reaction conditions and properties of synthesized PEImN.

Thermal characteristics of synthesized PEI were studied using DSC with a heating rate of 10 K/min and polarized optical microscopy (POM) analysis. Figure 1 shows the DSC thermograms of PEI3N, PEI4N, PEI5N, PEI6N, PEI7N, PEI8N, PEI9N, and PEI10N for the second heating scan. All polymers showed two endothermic peaks with low glass transition temperatures. On the basis of the DSC and POM measurements, these two peaks were assigned to smectic-nematic and nematic-isotropic thermal phase transitions and all polymers are stable up to 200°C. DSC studies revealed that the glass transition temperatures (T_g) decreased as the

TABLE III
Reaction Conditions and Properties of Polyethylene Imines, PEImN

Polymer	Spacer	Reaction conditions			Degree of substitution (%)[a]	Phase transition temperature, °C
		Temp °C	Azo (mmol)	PEI (mmol)		
PEI3N	C_3H_6	100	4.2	4.0	61.8	G 59 S 129 N 169 I
PEI4N	C_4H_8	100	4.2	4.0	65.3	G 54 S 141 N 172 I
PEI5N	C_5H_{10}	100	4.2	4.0	68.1	G 37 S 123 N 167 I
PEI6N	C_6H_{12}	100	4.2	4.0	68.2	G 33 S 112 N 144 I
PEI7N	C_7H_{14}	100	4.2	4.0	70.2	G 31 S 110 N 123 I
PEI8N	C_8H_{16}	100	4.2	4.0	63.4	G 30 S 115 N 137 I
PEI9N	C_9H_{18}	100	4.2	4.0	69.8	G 28 S 98 N 121 I
PEI10N	$C_{10}H_{20}$	100	4.2	4.0	66.5	G 27 S 106 N 127 I

Molecular weight of PEI = ca 1800, reaction time = 72 h, reaction solvent = DMF (50 ml).
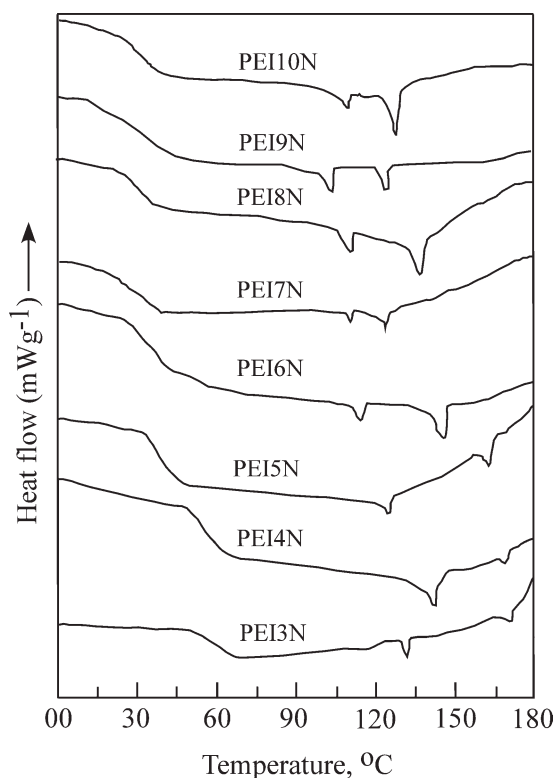[a] Determined from UV absorption spectra.

Figure 1 DSC thermograms of synthesized polyethylene imines (PEImN) obtained at 10°C min^{-1} for the second heating run.

number of methylene spacers increased, due to the increase of the flexibility of the side chain groups. Melting temperatures (Tm) showed an odd-even effect.[23] Polymers with an even number of methylene spacers showed higher Tm than neighboring polymers with an odd number of spacers (except for PEIs having short spacer length) as shown in Figure 2.
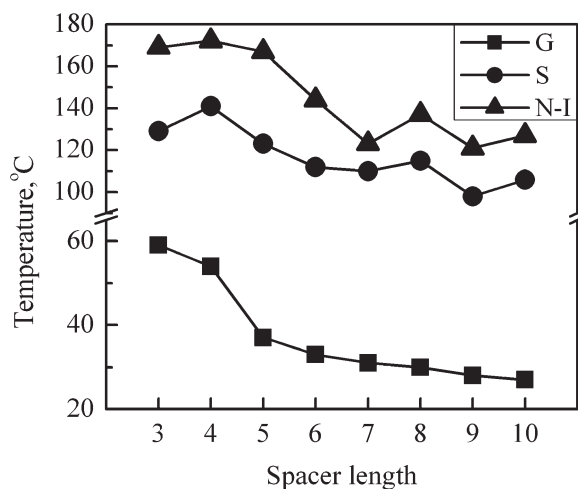

Figure 2 Phase transition behavior of synthesized polyethylene imines (PEImN). G, glass transition; S, smectic; and N-I, nematic-isotropic.
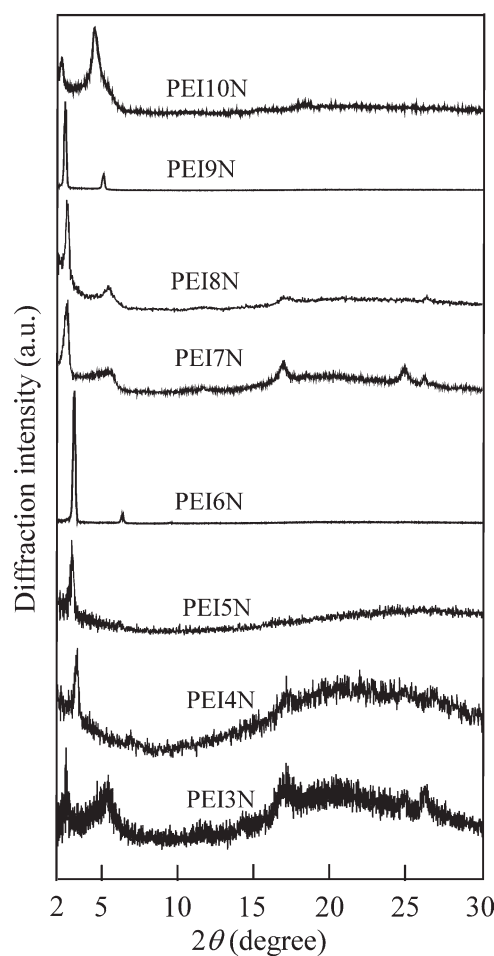
Figure 3 XRD patterns of all synthesized polyethylene imines (PEImN) in their LC state.

XRD of PEImN films

XRD was used to confirm the nature of the LC phases of PEImN and to determine the spacing of the smectic layers. Figure 3 shows the XRD patterns for all synthesized PEI films on glass substrate cast from THF and confirms that all of the polymers are smectic layer structures.[24–26] As expected, the smectic layer spacings increased with the spacer length.[26] All synthesized PEImN exhibited strong few

TABLE IV
X-ray Diffraction Patterns of all Synthesized Polymers in their LC State

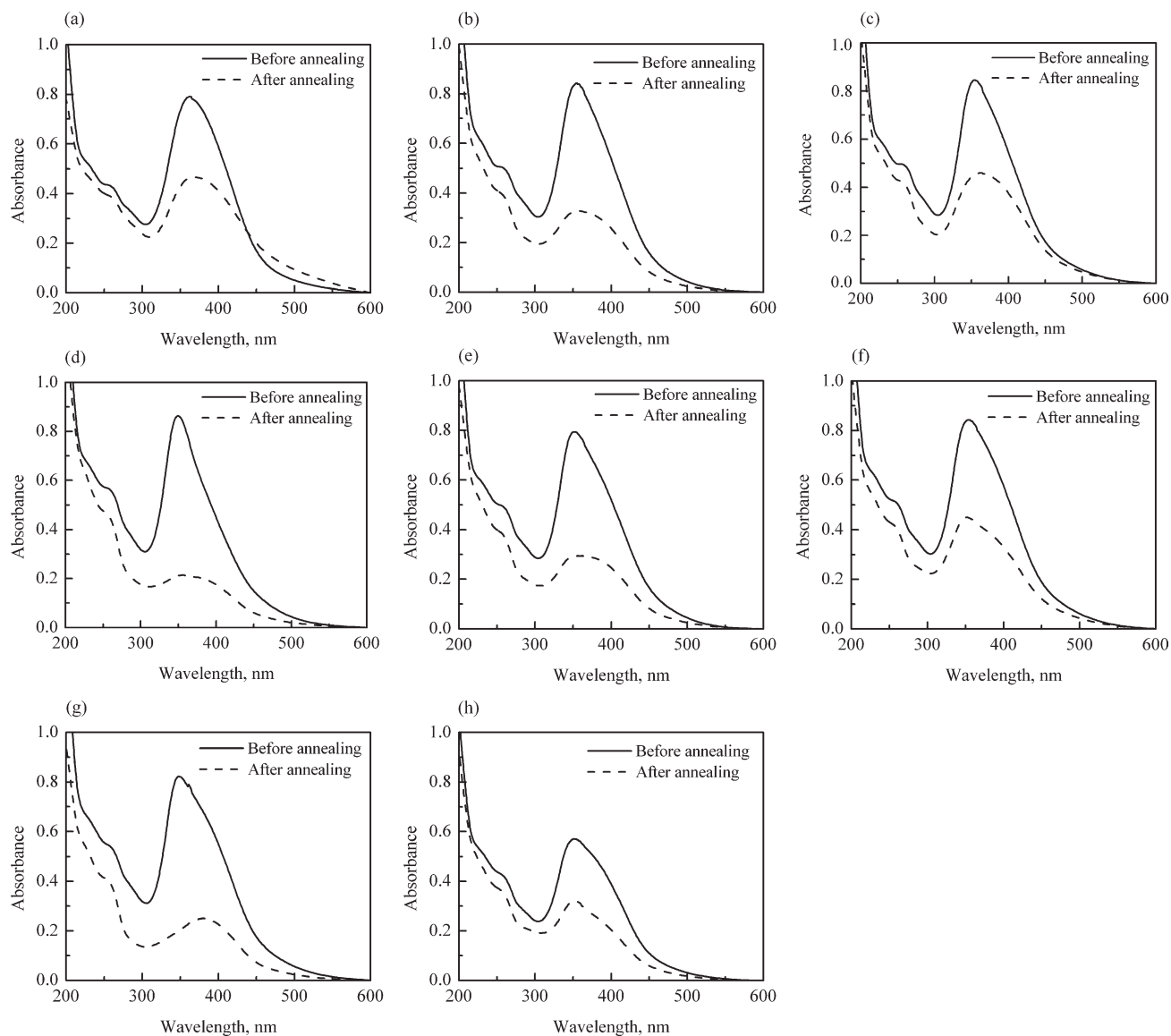| Polymer	2θ (1)	2θ (2)	dist.1 (Å)	dist.2 (Å)
PEI3N	2.54	5.26	34.75	16.79
PEI4N	3.26	6.85	27.14	12.88
PEI5N	3.03		29.1	
PEI6N	3.12	6.23	28.26	14.16
PEI7N	2.64	5.38	33.44	16.41
PEI8N	2.70	5.47	32.59	16.14
PEI9N	2.42	4.95	36.41	17.82
PEI10N	2.23	4.39	39.44	20.09

Figure 4   UV-vis. absorption spectra of PEImN films before and after annealing at (a) PEI3N, 100°C; (b) PEI4N, 120°C; (c) PEI5N, 80°C; (d) PEI6N, 110°C; (e) PEI7N, 100°C; (f) PEI8N, 110°C; (g) PEI9N, 100°C; and (h) PEI10N, 100°C during 5 min. Longer time of annealing does not lead to additional changes.

diffraction peaks in small angle region corresponding to layer structure and the intensity of the peaks were increased with the increase of spacer length. On the basis of XRD patterns, the smectic layer spacings were calculated from the XRD peaks using Bragg's law, and the results are listed in Table IV.

Thermal alignment behavior of PEImN in solid films

In this work, all experiments were performed for polymeric films with a thickness ranging from 200 to 300 nm. The films were prepared by spin-coating method from THF solutions. To explore the molecular orientation behavior of PEI having nitro substitu-

ent azobenzene side chain group, we demonstrated the changes in absorbance of spin coated polymeric films on annealing and also measured polarized absorption spectra and polar plot of the polymeric films before and after annealing. On annealing the test films of all synthesized polymers at room temperature, no marked changes took place; however, when the films were kept at elevated temperatures, one may observe the dramatic spectral changes (Fig. 4). In addition, the relative intensity of π-π* absorption band to absorption band ∼ 250 nm, which is assigned to the φ-φ* transition of the aromatic ring,[15,27] was varied as shown in Figure 5. It has been reported that the φ-φ* transition is insensitive to the orientation, consequently, the change in
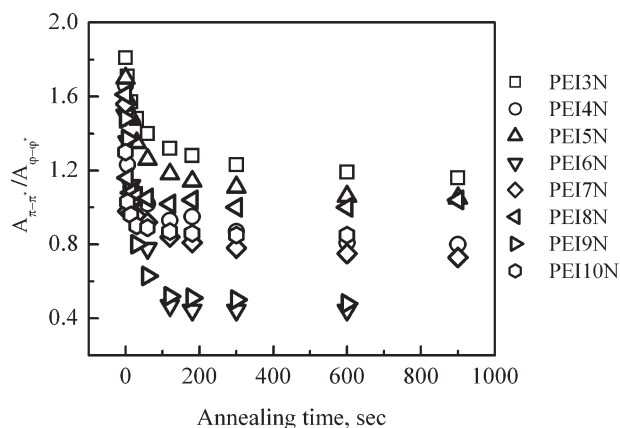
Figure 5 Changes in $A_{\pi\text{-}\pi^*}/A_{\varphi\text{-}\varphi^*}$ values of PEImN single layer films on annealing time.

the relative intensity of π-π* absorption band to φ-φ* absorption band ($A_{\pi\text{-}\pi^*}/A_{\varphi\text{-}\varphi^*}$) is related to the out-of-plane molecular orientation.[15,16] Therefore, the change in π-π* absorption intensity and blue shift of the solid films may be attributed to the out-of-plane molecular orientation and consequent formation of H-aggregate.[15,28]

Figure 5 represents the change in $A_{\pi\text{-}\pi^*}/A_{\varphi\text{-}\varphi^*}$ of all polymeric films as a function of annealing time. It is clear that the out-of-plane molecular orientation proceeded in a few minutes for all solid films, and final value of $A_{\pi\text{-}\pi^*}/A_{\varphi\text{-}\varphi^*}$ for PEI3*N* and PEI5*N* films is larger than those of others, showing less out-of-plane molecular orientation of PEI3*N* and PEI5*N*. Namely, ordering of out-of-plane molecular
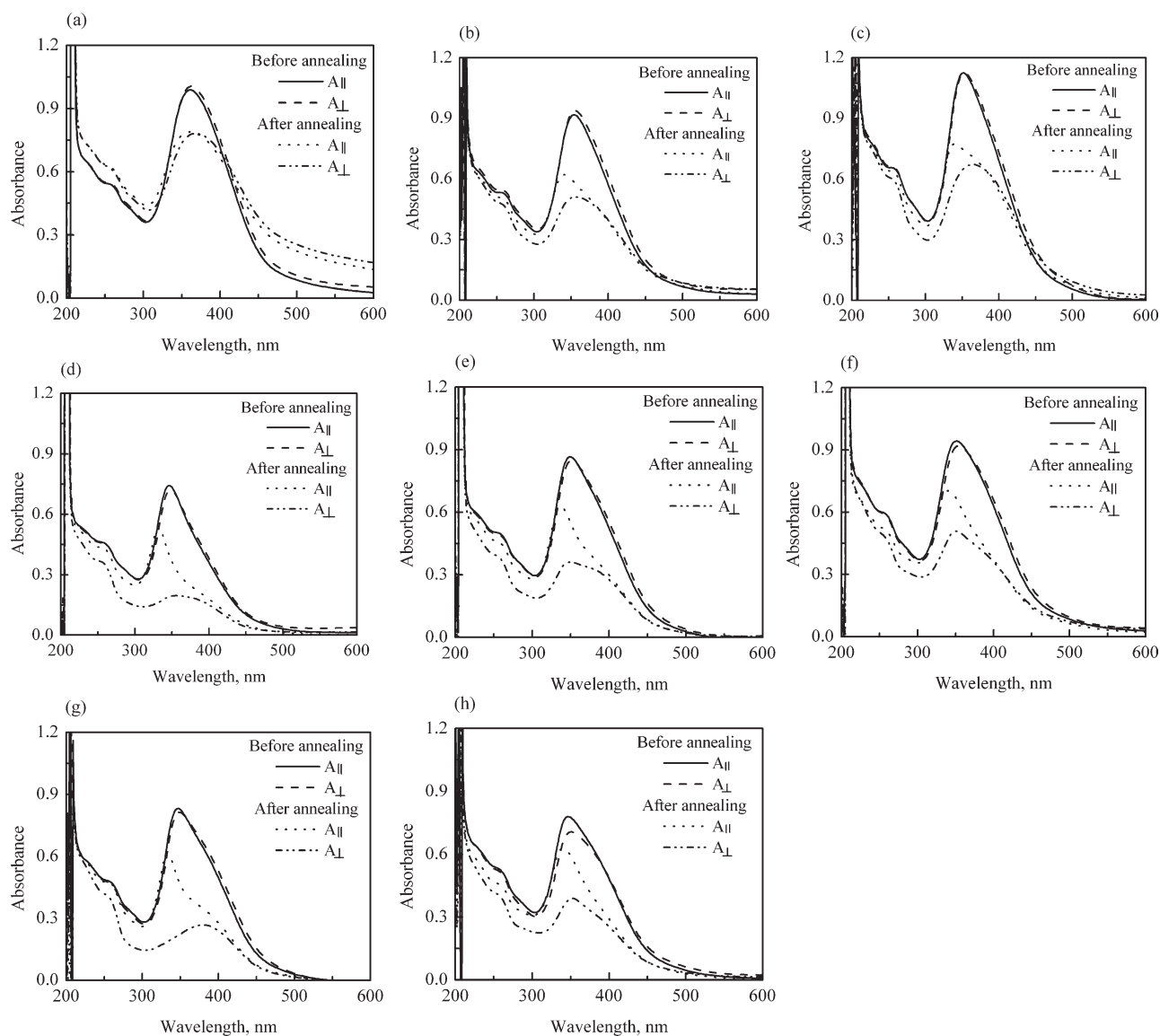

Figure 6 Polarized UV-vis. absorption spectra of PEImN films before and after annealing at (a) PEI3N, 100°C; (b) PEI4N, 120°C; (c) PEI5N, 80°C; (d) PEI6N, 110°C; (e) PEI7N, 100°C; (f) PEI8N, 110°C; (g) PEI9N, 100°C; and (h) PEI10N, 100°C during 5 min. $A_{\parallel}$ and $A_{\perp}$ donate absorption parallel and perpendicular to the polarization direction of actinic light respectively. Spectral measurements were made at 45° to film normal.
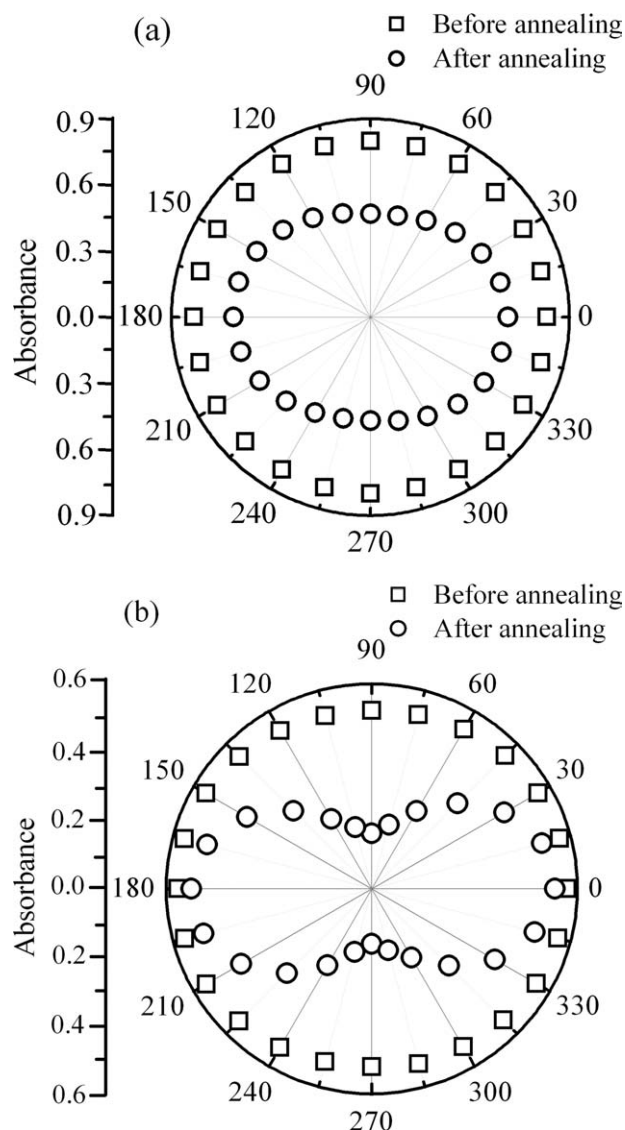
Figure 7 Polar plots for (a) PEI4*N* (= 340 nm) and (b) PEI6*N* (= 313 nm) single layer films before and after annealing at PEI4*N*, 120°C and PEI6*N*, 110°C during 5 min. Spectral measurements were made at 45° to film normal.

orientation significantly depends on the number of methylene spacer attached to the azobenzene side chain group.

So, to quantify the thermo-optical anisotropy of PEImN solid films we measured the polarized absorption spectra, and explored angular dependency of absorbance before and after annealing of the films. Annealing of the PEImN films brought about not only decrease in absorbance corresponding to the π-π* transition without polarizer, but also change in the polarized absorption spectra as shown in Figure 6.

The polarized absorption spectra were recorded at an angle of 45° to the normal of the films, and by following rotation of the film for polar plot to evalu-

ate the quantity of out-of-plane molecular orientation. Figure 7 shows the polar plots for PEI4*N* and PEI6*N* before and after annealing. In the case of PEI4*N* solid film, no angular dependency was observed before and after annealing [Fig. 7(a)], indicating no significant change in molecular orientation of azobenzene molecules on glass substrate by annealing. The presence of some spacer was needed between the rigid polymer main chain and the azo groups, since the spacer would allow the flexibility necessary for the required movement.[29] In contrast, PEI6*N* and PEI9*N* solid films after annealing showed big angular dependency and the shape of their corresponding polar plots is purely concave [Fig. 7(b) for PEI6*N*], allowing to assess the level of order parameter.[4] The order parameter of the annealed solid films is in the order of PEI6*N* (0.433), PEI9*N* (0.429), PEI10*M* (0213), PEI8*N* (0.138), PEI5*N* (0.101), PEI4*N* (0.089), and PEI3*N* (0.033) as given in Table V. Therefore, the out-of-plane molecular ordering is perhaps in this order.

Temperature dependency of out-of-plane molecular orientation

To clarify the effect of annealing temperature on molecular orientation, absorption spectra of PEImN solid films were measured after annealing for 5 min at different temperatures ranging from 40 to 140°C. As shown in Figure 8(a), absorbance of PEImN films at 352 or 354 nm was decreased by heating up to 120 or 140°C. Figure 8(b) represents the changes in order parameter with annealing temperature. As the temperature increased the values of order parameter increased showing big optical anisotropy at elevated temperatures. But at high temperature (100°C or more) again the optical anisotropy decreased and that seems to be related to the change in the mesophase from smectic to nematic phases.[17,30,31]

TABLE V
Out-of-Plane Order Parameter of Different Polymers

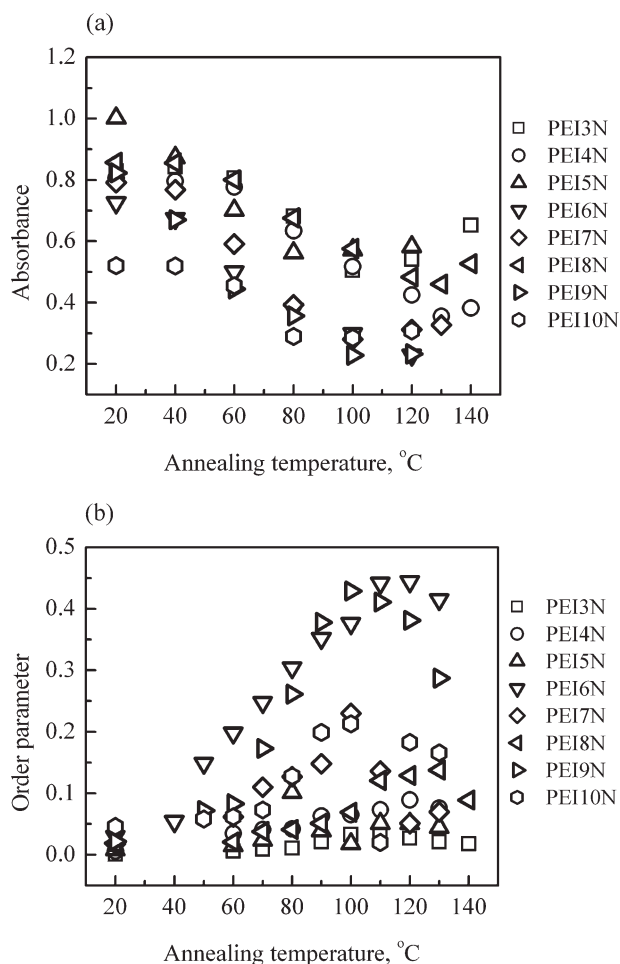| Polymer	Abs. π-π*/φ-φ*		Order parameter	
	After SC	After annealing	Before annealing	After annealing
PEI3N	1.81	1.16	0.001	0.033
PEI4N	1.66	0.80	0.006	0.089
PEI5N	1.70	1.05	0.008	0.101
PEI6N	1.50	0.44	0.03	0.433
PEI7N	1.56	0.73	0.018	0.230
PEI8N	1.61	1.04	0.019	0.138
PEI9N	1.48	0.48	0.022	0.429
PEI10N	1.30	0.85	0.046	0.213

SC, spin coating.

Figure 8 Dependency of (a) absorbance at = 352 or 354 nm and (b) order parameter of PEImN single layer films on annealing temperature.

Photoalignment behavior of PEImN in solid films

On irradiation of non polarized UV light on spin coated solid films of PEImN, spectral changes were observed in polymers which are typical for *trans-cis* photoisomerization.[1,32,33] For all polymeric films, photostationary state was achieved by prolonged irradiation of UV light as shown in Figure 9(a) for PEI6N polymeric film. This may be explained in terms of rapid reverse reaction from *cis* form to *trans* form of the azobenzenes having both electron-donating and electron-withdrawing substituents at both ends of azobenzene group.[1,34]

As a result of the subsequent irradiation with visible light of 435nm, the reverse changes occurred establishing a steady state with a little high concentration of *trans* isomers [Fig. 9(b)]. As with UV irradiation, PEImN also showed fairly less response upon visible light irradiation. The recovery of the initial spectra was not complete in all cases, but the value of absorption maxima corresponding to π-π^* transition little increased. This phenomenon was

related to little out-of-plane molecular ordering of azobenzene moieties on glass substrate. Upon irradiation longer than 60 s a decrease in the absorption in both regions corresponding to π-π^* and n-π^*
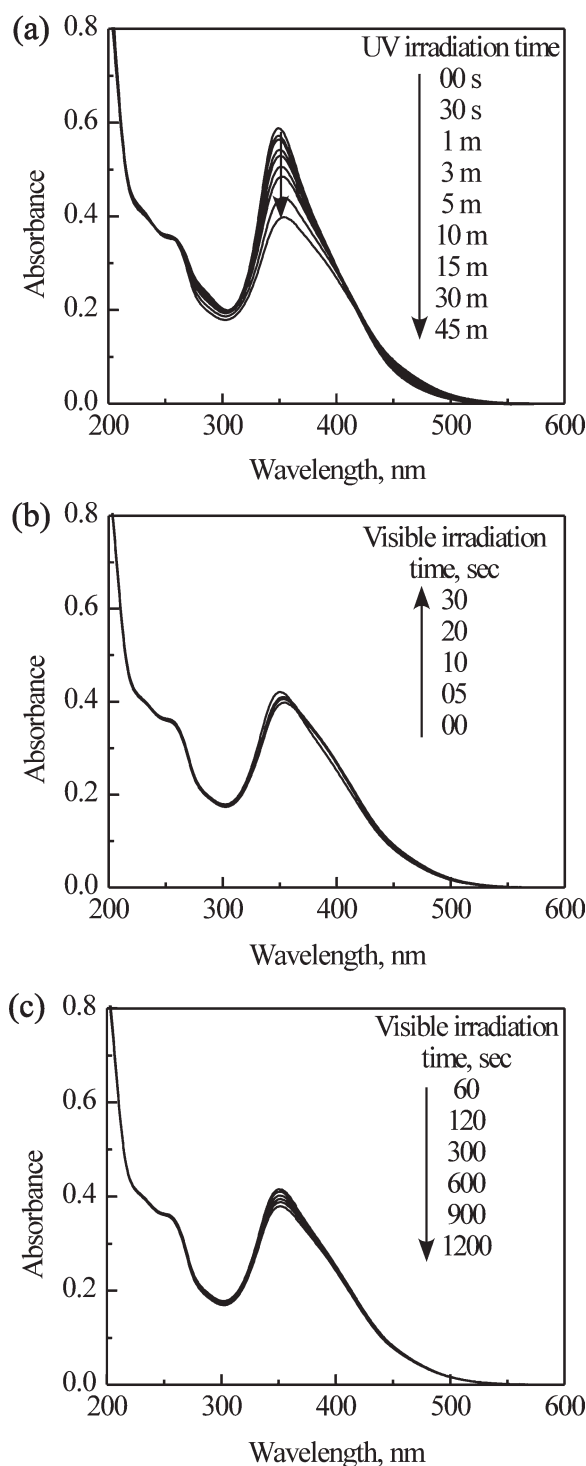

Figure 9 Changes of absorption spectra of PEI6N polymeric film during (a) UV irradiation (365 nm), (b) first 30 sec visible light irradiation, and (c) further visible light irradiation (435 nm). The intensity of UV and visible light was 7.0 mWcm^{-2} and 80 mWcm^{-2}, respectively.

transitions was caused as shown in Figure 9(c). The rate of decrease in the absorption upon the irradiation with visible light is lower than that upon UV irradiation. In the first 30 s of irradiation with visible light, little back *cis-trans* photoisomerization occurred, whereas on continued irradiation, the azobenzene groups were slightly oriented along the normal of film due to photo-orientation. In this case, the transition moment of these groups became oriented in out-of-plane ordering in the films[4]: as a result, the probability of light absorption and, thus, optical density little decreased.

CONCLUSIONS

A series of PEI having nitro substituent azobenzene side chain group with different methylene spacer groups (PEImN) were successfully synthesized and characterized by DSC, POM, and XRD analysis. All synthesized PEI showed LC properties and the glass transition temperatures (*Tg*'s) of PEImN decreased as the number of methylene spacers increased. Out-of-plane orientational behavior of azobenzene groups in the polymeric films as induced by thermal treatment was dependent on number of methylene spacers and PEI having higher number of methylene spacers (six or more) showed high order parameter values that revealed the well pronounced tendency for the development of out-of-plane order from random state on annealing. On the other hand, because of the presence of both electron-donating and electron-withdrawing substituents at both ends of azobenzene group, PEImN showed little photo alignment ordering. And the molecular orientation of PEImN between random and out-of-plane structures has been achieved by combination of thermal and photochemical processes.

References

1. Natansohn, A.; Rochon, P. Chem Rev 2002, 102, 4139.
2. Yaroshchuk, O. V.; Kiselev, A. D.; Zakrevskyy, Yu.; Bidna, T.; Kelly, J.; Chien, L-. C.; Lindau, J. Phys Rev E 2003, 68, 011803.
3. Schab-Balcerak, E.; Sapich, B.; Stumpe, J. Polymer 2005, 46, 49.
4. Bobrovsky, A.; Boiko, N.; Shibaev, V.; Stumpe, J. J Photochem Photobio A Chem 2004, 163, 347.
5. Tang, T.; Zeng, F.; Wu, S.; Tong, Z.; Luo, D.; She, W. Opt Mater 2004, 27, 585.
6. Han, Y-. K.; Ko, B-. S. Opt Mater 2002, 21, 621.
7. Djurado, D.; Delabouglise, D.; Caix-Cecillon, C.; Cecchetto, L.; Decker, I.; Petit, J. P. Solid State Ionics 2002, 154-155, 29.
8. Ikeda, T.; Horiuchi, D. B.; Karanjit, D. B.; Kurihara, S.; Tazuke, S. Macromolecules 1990, 23, 36.
9. Ikeda, T.; Tsutsumi, O. Science 1995, 268, 1873.
10. Kurihara, S.; Yoneyama, D.; Nonaka, T. Chem Mater 2001, 13, 2807.
11. Ichimura, K. Chem Rev 2000, 100, 1847.
12. Ichimura, K.; Suzuki, Y.; Seki, T. Lungmuir 1988, 4, 1214.
13. Ujiie, S; Iimura, K. Macromolecules 1992, 25, 3174.
14. Ujiie, S; Iimura, K. Poly J 25:347, 1993.
15. Sapich, B.; Vix, A. B. E.; Rabe, J. P.; Stumpe, J; Wilbert, G; Zentel, R. Thin Solid Films 2006, 514, 165.
16. Uekusa, T.; Nagano, S.; Seki, T. Macromolecules 2009, 42, 312.
17. Wu, Y.; Demachi, Y.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T. Macromolecules 1998, 31, 1104.
18. Han, M.; Ichimura, K. Macromolecles 2001, 34, 82.
19. Han, M.; Morino, S.; Ichimura, K. Macromolecles 2000, 33, 6360.
20. Uchida, E.; Shiraku, T.; Ono, H.; Kawatsuki, N. Macromolecules 2004, 37, 5282.
21. Ujiie, S.; Iimura, K. Chem Lett 1990, 19, 995.
22. Ujiie, S.; Yano, Y. Chem Commun 2000, 1, 79.
23. Mary, L.; J F.; Kannan, P. J Polym Sci A Polym Chem 1999, 37, 1755.
24. Liu, J. H.; Yang, P. C.; Chiu, Y. H.; Suda, Y. J Polym Sci A Polym Chem 2007, 2026, 45.
25. Uekusa, T.; Nagano, S.; Seki, T. Langmuir 2007, 23, 4642.
26. Freiberg, S.; Labarthet, F. L.; Rochon, P.; Natansohn, A. Macromolecules 2003, 36, 2680.
27. Fabian, J.; Hartmann, H. Light Absorption of Organic Colarants, Springer-Verlag: Berlin 1980, 32.
28. Kasha, M.; Rawls, H. R.; Bayoumi, M. A. El Pure Appl Chem 1965, 11, 371.
29. Alderle, K.; Birenheide, R.; Eich, M.; Wendorff, J. Makromol Chem Rapid Commun 1989, 10, 477.
30. Hvilsted, S.; Andruzzi, F.; Kulinna, C.; Siesler, H. W.; Ramanujam, P. S. Macromolecules 1995, 28, 2172.
31. Ivanov, S.; Yakovlev, I.; Kostromin, S.; Shibaev, V.; Läsker, L.; Stumpe, J.; Kreysig, D. Makromol Chem, Rapid Commun 1991, 12, 709.
32. Alam, M. Z.; Ohmachi, T.; Ogata, T.; Nonaka, T.; Kurihara, S. Opt Mater 2006, 29, 365.
33. Ishiguro, M.; Sato, D.; Shishido, A.; Ikeda, T. Langmuir 2007, 23, 332.
34. Tsutsumi, O.; Kitsunai, T.; Kanazawa, A.; Shiono, T.; Ikeda, T. Macromolecules 1998, 31, 355.