Mol. Cryst. Liq. Cryst., Vol. 550: pp. 134–148, 2011
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.600610

Taylor & Francis
Taylor & Francis Group

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

MOHAMMAD KAMRUZZAMAN,[1] YUTAKA KUWAHARA,[1]
TOMONARI OGATA,[1] SEIJI UJIIE,[2] AND SEIJI KURIHARA[1,*]

[1]Department of Applied Chemistry and Biochemistry, Graduate School
of Science and Technology, Kumamoto University, Kurokami 2-39-1,
Kumamoto 860-8555, Japan
[2]Department of Applied Chemistry, Faculty of Engineering, Oita University,
Dannoharu 700, Oita 870-1192, Japan

New type of polyethylene imine having butyl ($-C_4H_9$*) substituent azobenzene side chain group through methylene spacer group (PEI64) was successfully synthesized by solution polycondensation reaction. Synthesized polymer was characterized by DSC, Polarized Optical Microscopic and X-ray diffraction analysis. The effect of reaction parameters on degree of substitution of PEI64 also studied and optimized the reaction conditions. Synthesized polymer possessed liquid crystalline (LC) properties. Photochemical, thermooptical as well as photoorientational behavior of the polymer were investigated elaborately. Spin coated PEI64 film showed out-of-plane molecular orientation on annealing. PEI64 both in solution and in solid film exhibited photoresponsive properties upon irradiation of UV and visible light. PEI64 film also exhibited reversible molecular orientation from random state to out-of-plane and from out-of-plane to random state on annealing, non-polarized UV and visible light irradiation.*

Keywords azobenzene polymer; polyethylene imines; thermal alignment behavior; liquid crystalline properties; out-of-plane ordering

Introduction

In recent years, azobenzene containing polymers have been the object of intensive investigations because of their potential applications in the field of photonics and optoelectronics. It was shown that under irradiation with an appropriate wavelength of light the azobenzene moieties change their spatial orientation [1–4], through photochemical *trans-cis-trans* isomerization (Weigert effect). In this way anisotropy—dichroism and birefringence—is generated in optically isotropic polymers with azobenzene moieties in the side chain. The mechanism for the alignment involves the photochemical *trans-cis* isomerization and photochemical and/or thermal *cis-trans* isomerization of the azobenzene groups. By repetition of these *trans-cis-trans* isomerization cycles and the resultant molecular motion, the optical axis of the azobenzene groups becomes aligned perpendicular to the electric vector of the polarized actinic light. This process was used for optical switching [5], digital and

---

[*]Corresponding author. E-mail: kurihara@gpo.kumamoto-u.ac.jp

holographic data storage [6] and optical modulators [7]. In addition the 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 strongly dependent on the substitution and the wavelength of the excitation.

"Photochemical phase transition" between a liquid crystalline phase and a random state [8–10] and photoalignment between in-plane and out-of-plane structures, which is called "command surface" [11, 12] are the two typical liquid crystalline systems in relating to the photo-cotnrol of the molecular orientation by means of photoisomerization of azobenzene compounds. 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 $\Delta(n_{\|} - n)$, where $n_{\|}$ 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 liquid crystals. 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 liquid crystals. In contrast, in photochemical phase transition system, polymeric materials could be used to improve memory stability. However, to obtain $\Delta(n_{\|} - n_{\perp})$ relating to the photochemical phase transition, alignment layer is required.

On the contrary, in literature so far very few papers are published on spontaneous out-of-plane molecular orientation of polymeric liquid crystals (PLCs) [4, 13–16]. In addition, Ujiie et al. [17, 18] 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. So by photochemically controlling the molecular orientation of PEIs between random state and out-of-plane structures, one can fabricate the optical switching system showing excellent memory stability by coating PEIs on a substrate without any alignment process.

So in this article, we synthesized polyethylene imine having butyl substituent azobenzene side chain group through methylene spacer group (PEI64) and investigated its photochemical as well as thermal alignment behavior on annealing, UV and non-polarized visible light irradiation. And, we also demonstrated the multiple reorientation of the azobenzene chromophores in PEI64.

Experimental

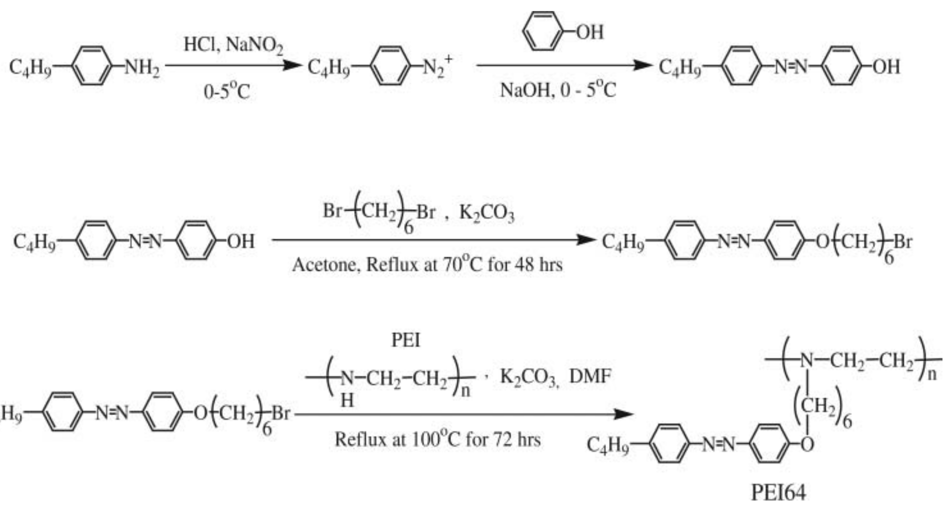
Materials

4-Butyl aniline was purchased from Wako Pure Chemical Industries Ltd and used as received. 1,6-Dibromohexane was purchased from TCI and polyethylene imine of low molecular weight (Mn = ca.1800) and high molecular weight (Mn = ca. 10,000) were purchased from Polysciences Inc. Reagents were used without further purification, unless stated. *N,N*-dimethylformamide (DMF) was purchased from Wako Pure Chemical Industries Ltd and was dried up with molecular sieves prior to use.

Synthesis of Azobenzene Monomers

Synthesis of 4-Butyl-4′-hydroxyazobenzene (4Az-OH)

To a solution of 4.9 g (33 mmol) of 4-butylaniline dissolved in 240 ml of water and 14 cm^3 (170 mmol) of HCl was added dropwise a solution of 3.3 g (48 mmol) of $NaNO_2$



Scheme 1. Synthetic route for monomer and polymer.

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 to adjust pH 4 to 5. The precipitated product was filtered, washed with excess amount of water and dried under vacuum.

Yield: 59% as solid. ^{1}H-NMR ($CDCl_3$, δ): 7.95 (2H, dd, aromatic), 7.86 (2H, dd, aromatic), 7.06 (2H, d, aromatic), 6.95 (2H, d, aromatic), 5.29 (1H, s, -OH), 1.03 (3H, s, -CH_3). Anal. Calcd for $C_{16}H_{18}N_2O$ (254.33): C- 75.56; H- 7.13; N- 11.01. Found: C- 74.98; H- 7.14; N- 10.88.

*Synthesis of 4-(6-Bromo-*n*-hexyloxy)-4′-butyl azobenzene [4AzO6Br]*

4-(6-bromo-*n*-hexyloxy)-4′-butyl azobenezene was synthesized by the following procedure: To a mixture of 1.12 g (4.4 mmol) of 4-butyl-4′-hydroxyazobenzene and 0.91 g (6.6 mmol) potassium carbonate dissolved in 100 ml of dried acetone, 5.39 g (22.3 mmol) of 1,6-dibromohexane was added. After refluxing for 48 h at 70°C the reaction mixture was filtered and evaporated the solvent from filtrate and the product 4AzO6Br was re-crystallized from methanol twice. The reaction scheme is shown in Scheme 1.

Yield: 76.1% as solid. Anal. Calcd for $C_{22}H_{29}BrN_2O$ (417.38): C- 63.31; H- 7.00; N- 6.71. Found: C- 63.89; H- 6.76; N- 6.91.

Synthesis of Polyethylene Imines Having Azobenzene Side Chain Group (PEI64)

Polyethylene imines having butyl substituent azobenzene side chain group with six methylene spacer groups was synthesized using different reaction conditions. The typical procedure is as follows: 4-(6-Bromo-*n*-hexyloxy)-4′-butyl azobenzene 1.75 g (4.2 mmol), polyethylene imine 0.18 g (4.0 mmol), potassium carbonate 1.8 g (6.0 mmol) and 50 ml dry 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 polymer (PEI64) was purified by precipitation from chloroform/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

To identify the structure and composition of the synthesized monomers and polymer, elemental analyses were performed with a YANAKO CHN CORDER MT-6. The structures of the compounds were also determined using ^{1}H NMR spectroscopy with $CDCl_3$ or acetone as solvent and tetramethylsilane as internal standard. The spectra were recorded at ambient temperature with a JEOL JNM-EX400, 400 MHz NMR-spectrometer.

The phase transition behavior of the polymer 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 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 θ-θ wide angle goniometer and scintillation detector was used for X-ray diffraction (XRD) measurement. Cu K alpha (λ 1.5406 Å) was used as target. XRD sample was made by casting solution (40 mg polymer in 1 ml of THF) onto a 1.5×1.5 cm^2 glass substrate. Thick film of PEI64 was heated to 100 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 follows: speed of rotation 3000 rpm and time of rotation 30 sec with 4 wt% of polymer in THF.

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 (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. 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 Characterization of PEI64

In this study, liquid crystalline polyethylene imine having butyl substituent azobenzene side chain group through methylene spacer group (PEI64) was successfully synthesized

Table 1. Reaction conditions and properties of synthesized polyethylene imine PEI64

	Reaction conditions						
Polymer	Temp. °C	Reaction time, h	Azo (mmol)	PEI (mmol)	Yield (%)	Degree of substitution (%)[a]	Phase transition temperature, °C
PEI64	100	72	4.2	4.0	78.8	66.3	G12 S 102 N 148 I

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

by solution polycondensation reaction. For good thermal and photo alignment behavior, polyethylene imines should have high degree of substitution. It was assumed that as the introduction of azobenzene group into polyethylene imine main chain increased the out-of-plane alignment behavior of the polymers also increased. So in synthesis step, to achieve higher degree of substitution in polyethylene imines, reaction conditions were optimized by changing the reaction parameters such as temperature, reaction time, molar ratio of azobenzene monomer and PEI, and reaction solvent. The degree of substitution of PEI64 has considerable effect on all of 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 (above 72 h), the degree of substitution did increase little but the solubility of PEI64 decreased probably due to the formation of gel. So finally we synthesized PEI64 by optimizing the reaction conditions as temperature 100°C, reaction time 72 h, molar ratio of azobenzene monomer to PEI = 4.2:4.0, and solvent (DMF) = 50 ml. Synthesized polymer showed good solubility in DMF, chloroform, THF and cyclohexanone. Table 1 represents the reaction conditions and properties of synthesized polyethylene imine.

Thermal characteristics of synthesized polyethylene imine were studied using DSC with a heating rate of 10 K/min and polarized optical microscopy (POM) analysis. Figure 1 shows the DSC thermogram of PEI64 for the second heating scan. PEI64 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, the polymer is stable up to 190°C.

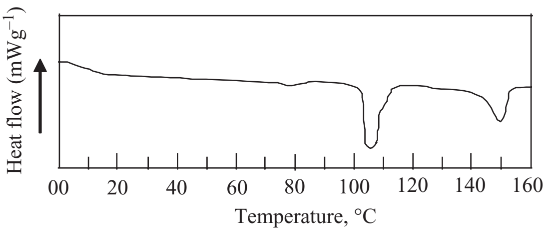


Figure 1. DSC thermograms of synthesized polyethylene imine (PEI64) obtained at 10°C min^{-1} for the second heating run.

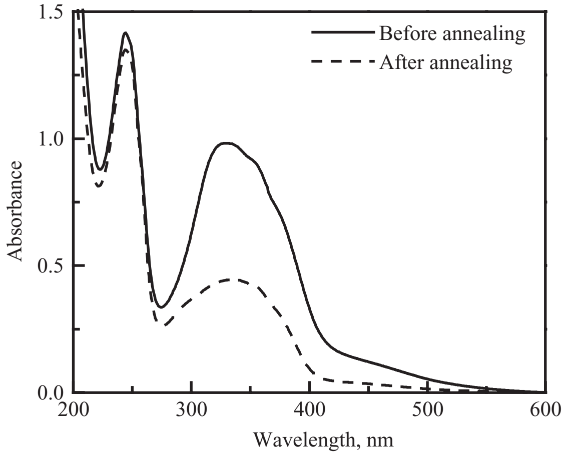


Figure 2. UV-vis absorption spectra of PEI64 single layer film before and after annealing at 100°C during 5 min. Longer time of annealing does not lead to additional changes.

Thermooptical Alignment Behavior of PEI64 in Film

To investigate the thermal induced optical anisotropy in PEI64 solid film, the changes in absorbance of spin coated polymeric films on annealing were demonstrated. In this study, all experiments were performed for polymeric films with a thickness ranging from 200 to 300 nm. The films were prepared by spin coating technique. Upon annealing the test films at room temperature, no marked changes took place. However, when the films were kept at the temperature, which is above its glass transition temperature corresponding to LC state, one may observe the significant spectral changes (Figure 2). On annealing, the absorption in the region of the π–π^* transition is related to out-of-plane ordering was decreased by about 60%. The position of the absorption maximum remained almost unchanged [Figure 2]. It should be noted that, the profiles of the corresponding spectra and absorption in the region of the φ–φ^* transitions were preserved.

On the other hand, the absorption maxima of the PEI64 solid film was blue-shifted compared to that in THF [Figure 3], indicating the formation of H-aggregate in the solid film. In addition, the relative intensity of π–π^* absorption band to absorption band around 250 nm which is assigned to the φ–φ^* transition of the aromatic ring [15, 19], was varied as shown in Figure 4. It has been reported that the φ–φ^* transition is insensitive to the molecular orientation, consequently, the change in the relative intensity of π–π^* absorption band to φ–φ^* absorption band ($A_{\pi-\pi^*}/A_{\varphi-\varphi^*}$) 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 film may be attributed to the out-of-plane molecular orientation and consequent formation of H-aggregate [15, 20]. From Figure 4, it is also clear that the out-of-plane molecular orientation proceeded in a few minutes.

Therefore, to quantify the thermal induced anisotropy in PEI64 solid film, polarized absorption spectra were measured and explored the angular dependency of absorbance before and after annealing of the film. Annealing of the PEI64 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 5. The order parameter, the

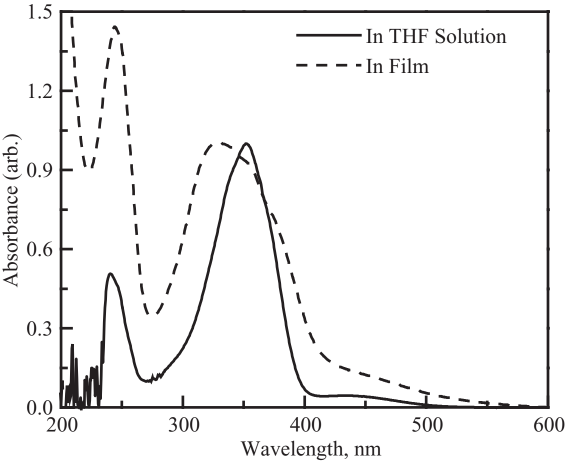


Figure 3. Normalized UV-vis absorption spectra of polyethylene imine, PEI64 in THF solution and in solid film.

degree of out-of-plane ordering, was calculated from polarized absorption spectra by using equation (1).

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 evaluate the quantity of out-of-plane molecular orientation. From polarized absorption spectra, polar plot for polymeric film was also plotted and is shown in Figure 6. After annealing at a temperature corresponding to the LC state of the polymer, the absorbance parallel to the polarization direction of actinic light was higher than that perpendicular to the polarization direction of actinic light. From polar plot, it is clear that, before annealing, little angular dependency was observed, indicating that the azobenzene chromophores were slightly orientated perpendicularly on glass substrate in solid film. But after annealing, PEI64 solid film showed

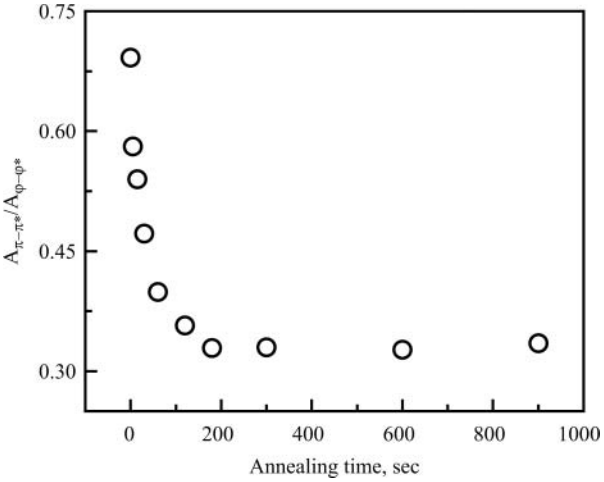


Figure 4. Changes in $A_{\pi\text{-}\pi^*}/A_{\varphi\text{-}\varphi^*}$ values of PEI64 single layer film on annealing time.

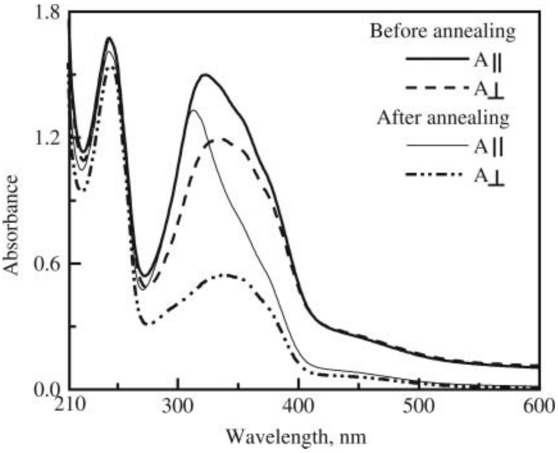


Figure 5. Polarized UV-vis. absorption spectra of PEI64 single layer film before and after annealing at 100°C during 5 min. $A_{\parallel}$ and $A_{\perp}$ donate absorption parallel and perpendicular to the polarization direction of actinic light respectively. Spectral measurements were made at 45° to film normal.

big angular dependency and the shape of the corresponding polar plot is purely concave, allowing to assess the level of order parameter [4]. The out-of-plane order parameter value before and after annealing were 0.107 and 0.381 respectively.

Influence of Annealing Temperature on Out-of-Plane Molecular Orientation

PEI64 solid film showed different spectral changes at different annealing temperatures. To investigate the effect of annealing temperature on molecular orientation, absorption spectra

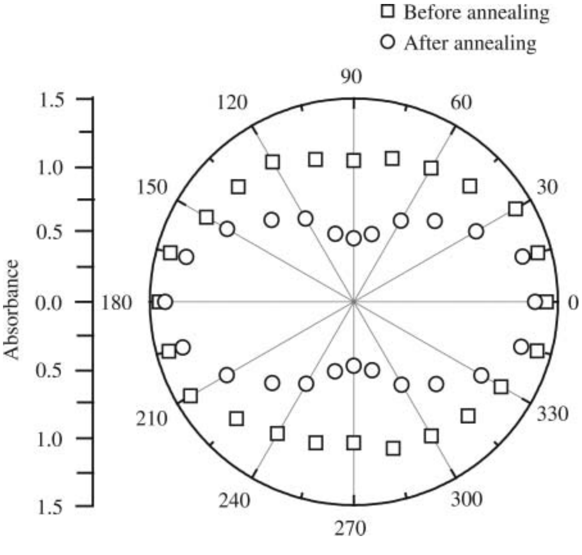


Figure 6. Polar plot for PEI64 ($\lambda = 313$ nm) single layer film before and after annealing. Spectral measurements were made at 45° to film normal.

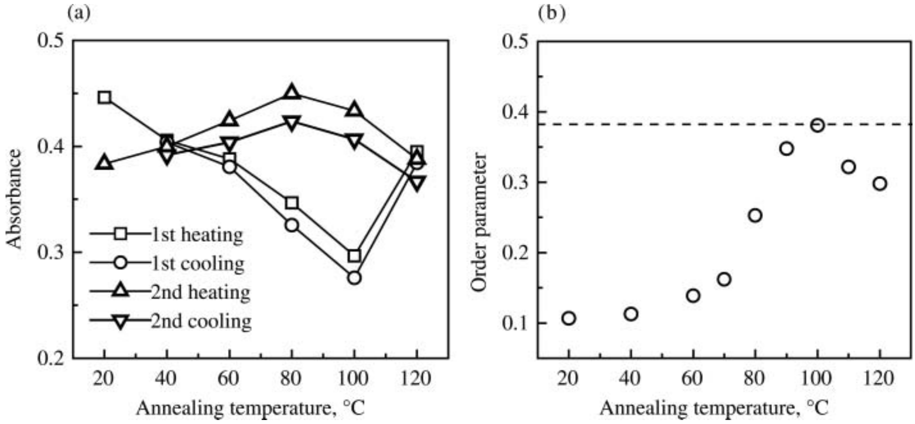


Figure 7. (a) Changes in absorbance of PEI64 single layer film at absorption maxima ($\lambda_{max.} = 330$ nm) on annealing temperature and (b) Changes in out-of-plane order parameter of PEI64 single layer film on annealing temperature. Annealing time = 5 min.

of PEI64 solid film was measured after annealing for 3 min at different temperatures ranging from 40 to 120°C. As shown in Figure 7(a), absorbance of PEI64 film at 330 nm was decreased by heating up to 100°C and again increased as the temperatures increased. Figure 7(b) plots the thermally enhanced order parameters of the polyethylene imine film as functions of the annealing temperatures. As the temperature increased the values of order parameter increased showing big optical anisotropy at elevated temperatures. But at high temperature (above their LC state) again the optical anisotropy decreased and that seems to be related to the change in the mesophase from smectic to nematic phases [21–23].

The orientation of the azobenzene side chain groups was furthermore investigated by XRD measurements. Figure 8 shows the X-ray diffraction patterns for synthesized polyethylene imine film on glass substrate cast from THF, and confirms that the polymer is smectic layer structures [24–26]. PEI64 exhibited strong few diffraction peaks in small angle region. On the basis of X-ray diffraction patterns, the smectic layer spacings were calculated from the XRD peaks using Bragg's law and the results are listed in Table 2.

Moreover, molecular length of azobenzene side chain group (Scheme 2) in PEI64 was calculated by MOPAC (PM3 level) method and compared the value with smectic layer spacings. The value of smectic layer spacings is slightly higher than the calculated value. We also calculated the value of L/L′ (where L is the smectic layer spacing and L′ is the

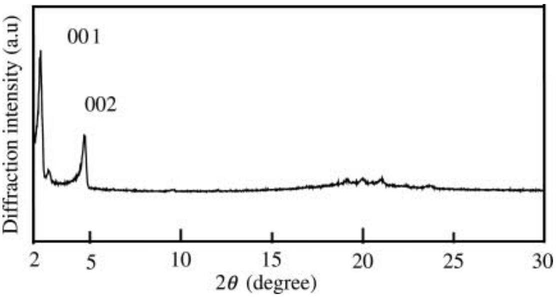
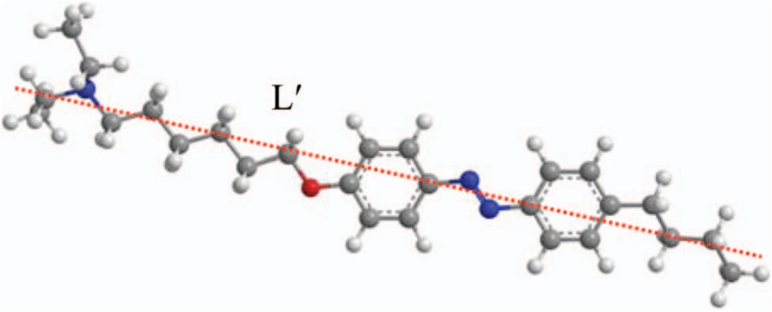


Figure 8. X-ray diffraction pattern of synthesized polymer PEI64 in it's LC state.



Scheme 2. Molecular model of polyethylene imine PEI64. Black color for carbon atom, gray for hydrogen atom, red for oxygen atom and blue for nitrogen atom.

calculated molecular length of azobenzene side chain group) and listed in Table 2. For PEI64, the value of L/L′ is comparatively large, indicating loose packing of molecules in PEI64.

Photoinduced Optical Anisotropy in PEImM Solid Films

To investigate the photo alignment behavior of PEI64, the photochemical behavior of PEI64 in solution and solid state was examined. The changes in the UV-vis. absorption spectra of PEI64 in THF by irradiation of UV and visible light is shown in Figure 9. Before irradiation, PEI64 in THF showed a strong absorption at 352 nm and a weak absorption around 460 nm, corresponding to π–π^* transition and n–π^* transition of the azo-chromophores, respectively. UV irradiation caused decrease and increase in absorption at 352 and 460 nm, respectively, indicating photoisomerization from *trans*-form to *cis*-form. It became photostationary in 10 sec in case of *trans-cis* photoisomerization by UV light irradiation and 30 sec in case of *cis-trans* isomerization by visible light irradiation. Photoisomerization of the polymer in solution shows isosbestic points, indicating uniform photoreactions. The subsequent *cis-trans* isomerization by visible light irradiation rebuilt the initial state completely, which demonstrates the reversibility of the reaction. In addition, it is obvious that both *trans*-form and *cis*-form of PEI64 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 PEI64 will be brought about by irradiation of the light in this region [19, 26, 27].

In order to understand photochemical and photoinduced optical anisotropy in polymeric films, the spectral changes were investigated in polymeric film under irradiation with

Table 2. Smectic layer spacings and molecular length of PEI64

Polymer	$2\theta(1)$	$2\theta(2)$	dist. 1 (Å), L	dist. 2 (Å)	Molecular length (Å)[a], L′	L L/L′
PEI64	2.32	4.75	37.70	8.70	27.6	1.37

[a] Calculated by MOPAC (PM3) method.

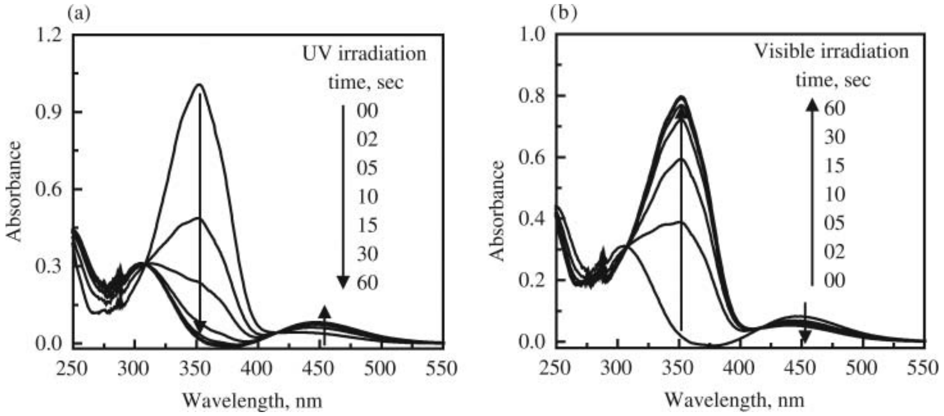


Figure 9. Changes in UV-vis. absorption spectra of PEI64 in THF by irradiation of (a) UV (365 nm) and (b) visible light (435 nm). The intensity of UV and visible light was 7.0 mWcm^{-2} and 80 mWcm^{-2} respectively.

UV and non-polarized visible light of different wavelengths. Depending on the irradiation wavelength, different steady states of *cis-trans* photo-isomerization were established allowing or preventing the photo-orientation of azobenzene chromophores in PEI64.

Upon irradiation of non polarized UV light on spin coated solid films of PEIs, significant spectral changes were observed in polymers which are typical for *trans-cis* photoisomerization [1, 27, 28]. In PEI64 film, photostationary state with a little high content of the *cis* isomeric form was achieved within 2 or 3 min as shown in Figure 10(a). In film, due to molecular aggregation, *trans-cis* photoisomerization rate is not as high as in solution. On the subsequent irradiation with visible light of 435 nm, the reverse changes occurred establishing a steady state with a high concentration of *trans* isomers [Figures 10(b)]. The recovery of the initial spectrum was complete, even the value of absorption maxima corresponding to π–π^* transition exceeded the initial value. This phenomenon was related to the partial out-of-plane molecular ordering of azobenzene moieties on glass substrate.

Upon a prolonged irradiation ($>$5 s), one may observe a decrease in the absorption in both regions corresponding to the π–π^* and n–π^* transitions as shown in Figures 10(c). Within the first 5 seconds of irradiation with visible light, the back *cis–trans* photoisomerization occurred, while upon continued irradiation, the azobenzene groups were oriented along the normal of film due to photo-orientation [4]. In this case, the transition moment of these groups become oriented perpendicular to the plane of films; as a result, the probability of light absorption and, thus, optical density markedly decreased [4]. So irradiation with non-polarized visible light (435 nm) caused the induction of anisotropy in the films by photoorientation of azobenzene side groups. It was established that the photoorientation process took place in the steady state of the photoisomerization via numerous angular-selective photo-isomerization cycles leading to a preferred orientation of the azobenzene groups perpendicularly to the electric field vector of the excitation light.

Multiple Thermal and Photo Reorientation of PEImM Films

Since the synthesized polyethylene imine showed thermal alignment behavior and *cis- trans* photo isomerization on UV and visible light irradiation as described in the above section, it is essential to investigate the multiple reorientation behavior of azobenzene chromophores

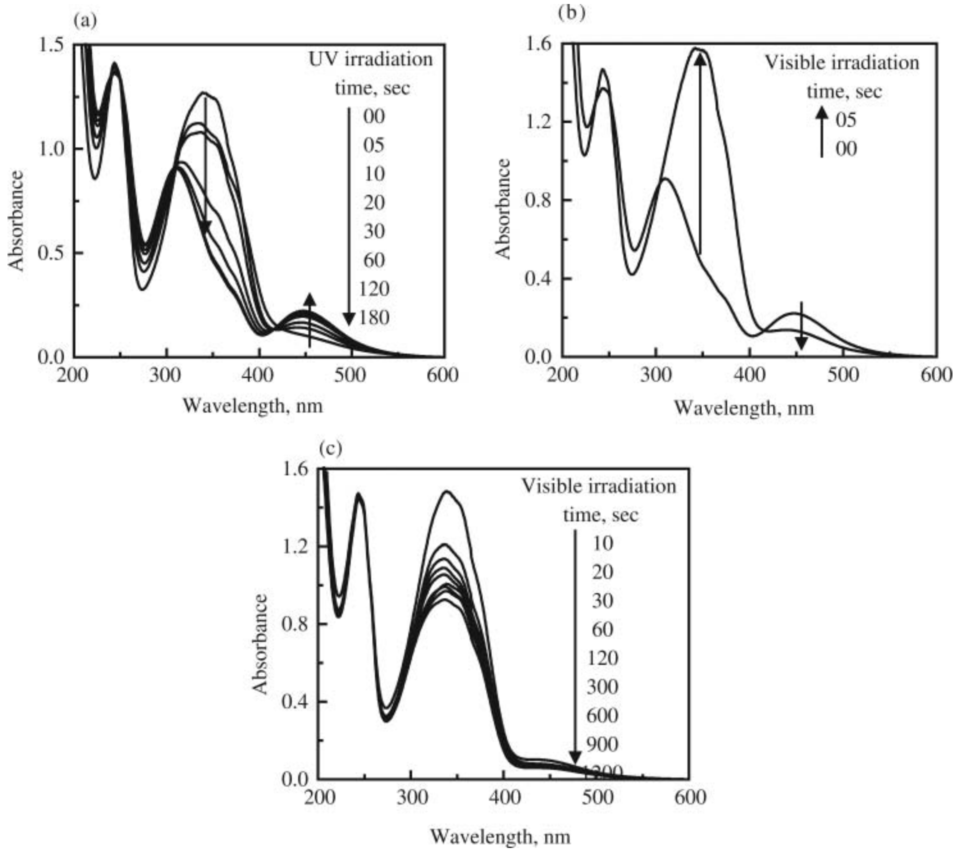


Figure 10. Changes of absorption spectra of PEI64 polymeric film during (a) UV irradiation (365 nm), (b) first 05 sec visible light irradiation and (c) further visible light irradiation (435 nm). The intensity of UV and visible light was 7.0 mWcm^{-2} and 80 mWcm^{-2} respectively.

in PEI64. In order to show the possibility of reversible reorientation of azobenzene chromophores in PEI64, molecular ordering behaviors were observed at different conditions. And synthesized polymer showed reversible molecular alignment behavior from random state to out-of-plane order and from out-of-plane order to random state. In all cases we observed the angular dependency on absorbance at different conditions and plotted the polar plots. Figure 11 illustrates the polar plots for PEI64, showing the changes in absorbance on annealing, UV and non polarized visible light irradiation. The shape of the corresponding polar plots at various conditions has demonstrated the nature of the alignment behaviors.

Figure 12 also demonstrates the reversibility of the alignment behavior of PEI64 at different conditions in terms of order parameter, estimated by measuring polarized absorption spectra. Polymeric film showed very little out-of-plane ordering before annealing. Upon annealing, polymeric film showed high order parameter value showing out-of-plane molecular alignment. Irradiation with the 365 nm light brings the film always into the isotropic state and erases any previously induced anisotropy. So after the irradiation of UV light on annealed films, the value of order parameter for the polymeric film decreased via *cis-trans* photoisomerization and reached to almost initial level. Namely the azobenzene molecules aligned randomly on the glass substrate. Following non polarized visible

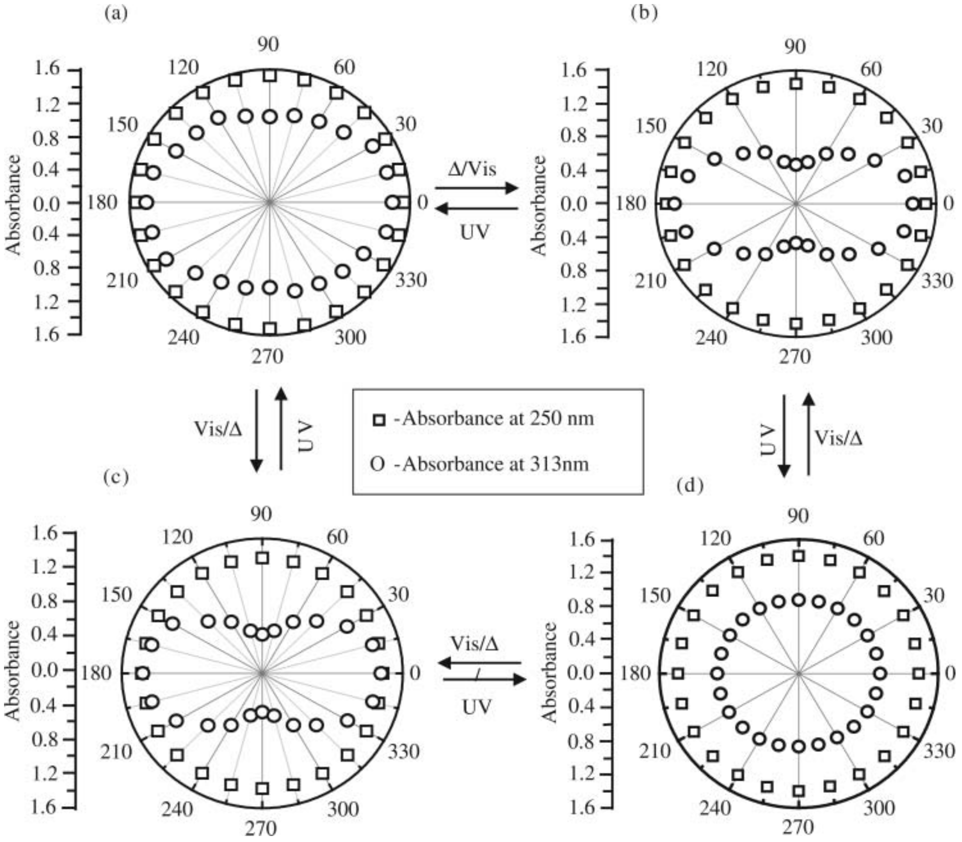


Figure 11. Polar plots for PEI64 ($\lambda = 250$ nm and $\lambda = 313$ nm) single layer film (a) before annealing, (b) after annealing, (c) after non-polarized UV irradiation and (d) after non-polarized visible light irradiation. Spectral measurements were made at 45° to film normal.

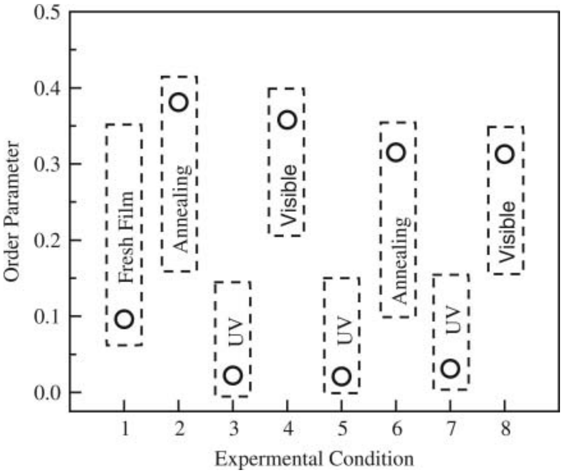
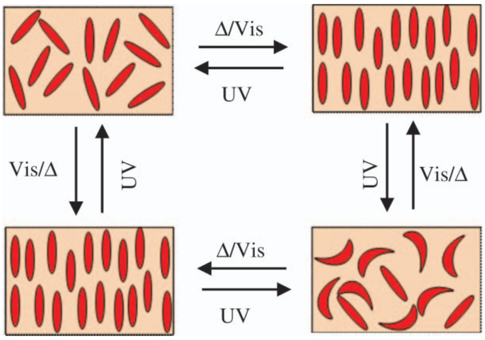


Figure 12. Reversibility of alignment behavior of polyethylene imine, PEI64 on different experimental conditions (1-fresh film, 2-annealing, 3-UV irradiation, 4-visible irradiation, 5-UV irradiation, 6-annealing, 7-UV irradiation and 8-visible irradiation).



Scheme 3. Schematic representation of the alignment behavior of azobenzene chromophores in PEI64 on glass substrate at different conditions.

light irradiation again increased the order parameter value, indicating the transformation of molecular orientation of azobenzene molecules from random state to out-of-plane order due to photo-orientation. The efficiency of the induction of anisotropy in the polymeric film was higher for the 435 nm non-polarized visible light compared with that of annealing because the pre-irradiation with the 365 nm light strongly increased the effectiveness of photoorientation process [29]. Again upon UV irradiation, the azobenzene group aligned randomly on the glass substrate. It should be noted that after each step of irradiation with the 365 nm UV light the angular-dependent spectra were exactly the same. This indicates a complete erasure of the previously written orientation was achieved. In this way, the reversibility of the alignment behavior of azobenzene groups in polyethylene imine could be achieved by changing the conditions such as annealing, UV and non polarized visible light irradiation (Scheme 3). All these results indicated that the optical information in the polymer can be rewritten in the system without any memory effects of previous irradiation or annealing. Several steps of annealing (writing) and the irradiation by light of 365 nm (erasing) and 435 nm non polarized visible light (writing) showed that optical anisotropy in the polymeric film could be completely erased and rewritten again without any losses; the orientation direction is always perpendicular to the electric field vector.

Conclusion

Liquid crystalline polyethylene imine (PEI64) having butyl ($-C_4H_9$) substituent azobenzene side chain group through methylene spacer group was successfully synthesized by solution polycondensation reaction and characterized by DSC, Polarized Optical Microscopic and XRD analysis. The effect of reaction parameters on degree of substitution of PEI64 also studied and optimized the reaction conditions. The synthesized polymer exhibited nematic and smectic phases with low glass transition temperature. Photochemical, thermooptical as well as photoorientational behavior of the polymer were investigated elaborately. Spin coated PEI64 film showed out-of-plane molecular ordering on annealing. PEI64, both in solution and in solid film exhibited photoresponsive properties upon irradiation of UV and visible light. PEI64 film also exhibited reversible molecular orientation from random state to out-of-plane and from out-of-plane to random state on annealing, non-polarized UV and visible light irradiation. This reversibility of molecular ordering has been achieved by the combination of thermal and photochemical processes. The reversible molecular ordering of azobenzene chromophores showed that optical anisotropy in the film can be completely erased and rewritten again without any memory effect of the previous irradiation or annealing.

References

[1] Natansohn, A. and Rochon, P. *Chem. Rev.*, **102**, 4139, (2002).

[2] Yaroshchuk, O. V., Kiselev, A. D., Zakrevskyy, Yu., Bidna, T., Kelly, J., Chien, L-C., and Lindau J. *Phys. Rev. E* **68**, DOI 011803, (2003).

[3] Schab-Balcerak, E., Sapich, B., and Stumpe, J. *Polymer*, **46**, 49, (2005).

[4] Bobrovsky, A., Boiko, N., Shibaev, V., and Stumpe, J. *J. Photochem. and Photobio A: Chem.*, **163**, 347, (2004).

[5] Tang, T., Zeng, F., Wu, S., Tong, Z., Luo, D., and She, W. *Optical Materials*, **27**, 585, (2004).

[6] Han, Y-K. and Ko, B-S. *Optical Materials*, **21**, 621, (2002).

[7] Djurado, D., Delabouglise, D., Caix-Cecillon, C., Cecchetto, L., Decker, I., and Petit, J. P. *Solid State Ionics*, 154–155, **29**, (2002).

[8] Ikeda, T., Horiuchi, D. B., Karanjit, D. B., Kurihara, S., and Tazuke, S. *Macromolecules*, **23**, 36, (1990).

[9] Ikeda, T. and Tsutsumi, O. *Science*, **268**, **1873**, (1995).

[10] Kurihara, S., Yoneyama, D., and Nonaka, T. *Chem. Mater.*, **13**, 2807, (2001).

[11] Ichimura, K. *Chem. Rev.*, 100, **1847**, (2000).

[12] Ichimura, K., Suzuki, Y., Seki, and T. Lungmuir, **4**, 1214, (1988).

[13] Ujiie, S. and Iimura, K. *Macromolecules*, **25**, 3174, (1992).

[14] Ujiie, S. and Iimura, K. *Poly. J.*, **25**, 347, (1993).

[15] Sapich, B., Vix, A. B. E., Rabe, J. P., Stumpe, J., Wilbert, G., and Zentel, R. *Thin Solid Films*, **514**, 165, (2006).

[16] Uekusa, T., Nagano, S., and Seki, T. *Macromolecules*, **42**, 312, (2009).

[17] Ujiie, S. and Iimura, K. *Chem. Lett.*, **19**, 995, (1990).

[18] Ujiie, S. and Yano, Y. *Chem. Commun.*, **1**, 79, (2000).

[19] Fabian, J. and Hartmann, H. *Light Absorption of Organic Colarants*; Springer-Verlag: Berlin, pp. 32–79, (1980).

[20] Kasha, M., Rawls, H. R., and Bayoumi, M. A. *El. Pure Appl. Chem.*, **11**, 371, (1965).

[21] Wu, Y., Demachi, Y., Tsutsumi, O., Kanazawa, A., Shiono, T., and Ikeda, T. *Macromolecules*, **31**, 1104, (1998).

[22] Hvilsted, S., Andruzzi, F., Kulinna, C., Siesler, H. W., and Ramanujam, P. S. *Macromolecules*, **28**, 2172, (1995).

[23] Ivanov, S., Yakovlev, I., Kostromin, S., Shibaev, V., Läsker, L., Stumpe, J., and Kreysig, D. *Makromol. Chem., Rapid Commun.*, **12**, 709, (1991).

[24] Liu, J. H., Yang, P. C., Chiu, Y. H., and Suda, Y. *J Polym Sci Part A: Polym Chem.*, **45**, 2026, (2007).

[25] Uekusa, T., Nagano, S., and Seki, T. *Langmuir*, **23**, 4642, (2007).

[26] Freiberg, S., Labarthet, F. L., Rochon, P., and Natansohn, A. *Macromolecules*, **36**, 2680, (2003).

[27] Alam, M. Z., Ohmachi, T., Ogata, T., Nonaka, T., and Kurihara, S. *Optical Materials*, **29**, 365, (2006).

[28] Ishiguro, M., Sato, D., Shishido, A., and Ikeda T. *Langmuir*, **23**, 332, (2007).

[29] Rais, D., Zakrevskyy, Y., Stumpe, J., Nešpůrek, S., and Sedláková, Z. *Optical Materials*, **30**, 1335 (2008).