

Photo Alignment Behaviour of Polyethene Imine Having Cyano Azobenzene Side Chain

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Abstract

New type of polyethene imine having cyano (-CN) side chain through six methylene spacer group (PEI6C) was successfully synthesised and characterised. The effect of reaction parameters on degree of substitution of PEI6C was also studied and the reaction conditions were optimised. Photochemical as well as photoorientational behaviour of the polymer were investigated. PEI6C in solid film exhibited photoresponsive properties upon irradiation with UV and visible light. PEI6C film also exhibited reversible molecular orientation from random state to out-of-plane and from out-of-plane to random state upon non-polarised visible and UV light irradiation.

Keywords: Azobenzene polymer, Polyethene imines, Photo alignment behaviour, Out-of-plane orientation.

I. Introduction

Azobenzene containing polymers have attracted considerable attention for the possibility of changing the molecular orientation by irradiation with an appropriate wavelength of light, and the potential applications in reversible optical storage, holographic grating and optical switching^{1,2}. Azobenzene derivatives are known to undergo *cis/trans* photo-isomerisation upon irradiation. There are two typical liquid crystalline systems in relating to the photo-control of the molecular orientation by means of photoisomerisation of azobenzene compounds: one is "photochemical phase transition" between a liquid crystalline phase and a random state^{3,5}, the other is photoalignment between in-plane and out-of-plane structures, which is called *command surface*^{1,6}. Very few papers have been published on spontaneous out-of-plane molecular orientation of polymeric liquid crystals (PLCs)⁷⁻¹¹. Bobrovsky group⁷ 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. We also reported that PEI having nitro substituent azobenzene side chain group showed out-of-plane molecular orientation on a glass substrate by annealing but not upon non-polarized visible light irradiation¹². In addition, Ujiie group^{13,14} reported that some polyethene imines (PEIs) having azobenzene as side groups show liquid crystalline phases and align perpendicular to the substrate spontaneously by heating and followed by 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.

In this article, we synthesised polyethene imine having cyano azobenzene side chain group through six methylene spacer group (PEI6C) and investigated its photochemical as well as photo alignment behaviour on non-polarised visible and UV light irradiation.

II. Materials and Methods

Materials

4-Cyano phenylamine, 1,6-Dibromohexane and polyethene imine of low ($M_n \approx 1800$) and high ($M_n \approx 10,000$) molecular weight were used without further purification. *N,N*-dimethylformamide (DMF) was dried with molecular sieves prior to use.

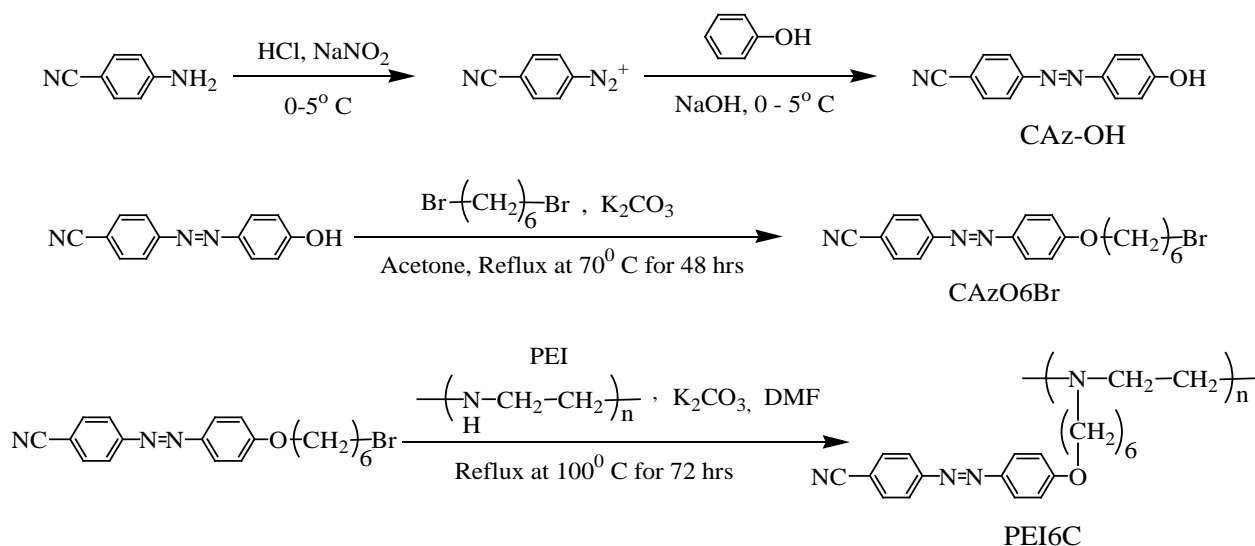
Synthesis of azobenzene monomer and polymer

4-Cyano-4'-hydroxyazobenzene (CAz-OH): An aqueous solution (30 cm³) of NaNO₂ (3.1 g, 45 mmol) was added dropwise to another solution containing 4-cyano phenylamine (5.3 g, 45 mmol) and concentrated HCl (14 mL) at 5°C. A solution of phenol (4.7 g, 50 mmol) in aqueous NaOH (2M, 75 mL) was then added at the same temperature. The mixture was then stirred for a further period of 2 h. The precipitate formed was filtered and washed to neutral with water. The separated precipitate was then suspended in ethanol (50% aq.) and acidified (HCl) when precipitate of CAz-OH was formed. The precipitated orange colour product was filtered, recrystallised from ethanol twice and dried under vacuum.

Yield: 61.5% as solid. Melting point: 202-203° C. ¹H-NMR (CDCl₃, δ): 7.83 (2H, dd, aromatic), 8.21 (2H, dd, aromatic), 7.92 (2H, d, aromatic), 6.88 (2H, d, aromatic), 5.28 (1H, s, -OH). Anal. Calcd for C₁₃H₉N₃O (223.23): C- 69.95; H- 4.06; N- 18.82. Found: C- 70.10; H- 4.22; N- 18.81.

4-(6-Bromo-n-hexyloxy)-4'-cyano Azobenzene [CAzO6Br]: 4-(6-Bromo-*n*-hexyloxy)-4'-cyano azobenzene was synthesised by the following procedure: To a mixture of 0.98 g (4.4 mmol) of 4-cyano-4'-hydroxyazobenzene (CAz-OH) and 0.91 g (6.6 mmol) potassium carbonate dissolved in 150 mL of dried acetone, 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 orange colour product CAzO6Br was re-crystallised twice from methanol. The reaction scheme is shown in Scheme 1.

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Scheme 1. Synthetic route for monomer and polymer.

Yield: 67.4% as solid. Melting point: 132-134° C. Anal. calcd for C₁₉H₂₀BrN₃O (386.29): C- 59.08; H- 5.22; N- 10.88. Found: C- 59.94; H- 4.83; N- 10.54.

Azobenzene containing polyethene imine (PEI6C): Polyethene imines having cyano substituent azobenzene side chain group with six methylene spacer groups was synthesised using different reaction conditions. The typical procedure is as follows: 4-(6-Bromo-*n*-hexyloxy)-4'-cyano azobenzene 1.62 g (4.2 mmol), polyethene 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 ~50% of DMF was evaporated from the filtrate and then poured into methanol. The resulting polymer (PEI6C) 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.

Characterisation

To confirm the structure and composition of the synthesised monomers and polymer, elemental analyses were performed with a YANAKO CHN CORDER MT-6. The nmr spectra were recorded in CDCl₃ or acetone using TMS as an internal standard on a JEOL JNM-EX400, 400MHz NMR-spectrometer.

The phase transition behaviour of the polymer was studied by differential scanning calorimetry (DSC; Seiko SSC-5020) with a heating rate of 10 Kmin⁻¹ and polarising optical microscopy (Olympus BHSP polarising microscope; Mettler FP-80 and FP 82 hot stage and controller).

X-ray diffraction was used to determine the LC phases and determine the lattice spacing of the smectic layers. Rigaku, RINT 2100/PC XRD machine (X-Ray, 40kV/200mA) equipped with a θ - θ wide angle goniometer and scintillation

detector was used for X-ray diffraction (XRD) measurement.

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 polarised UV-Vis spectroscopy (Perkin Elmer Lambda 650 UV/Vis Spectroscopy) and the angular dependence of the absorbance was measured. The values of order parameter determined by spectroscopic method were calculated by Eq. (1)⁷

$$S = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}} \dots\dots\dots (1)$$

where A_{\parallel} is the absorbance at the preferred direction; A_{\perp} is the absorbance perpendicular to this direction.

III. Results and Discussion

Synthesis and characterisation of PEI6C

Liquid crystalline polyethene imine having methoxy substituent azobenzene side chain (PEI6C) was successfully synthesised. For a good photo alignment behaviour, polyethene imines should have high degree of substitution. It is assumed that the introduction of azobenzene group into polyethene imine main chain increase the out-of-plane alignment behaviour of the polymers. So in synthetic step, to achieve higher degree of substitution in PEI, reaction conditions were optimised by changing the reaction parameters such as temperature, reaction time, molar ratio of azobenzene monomer and PEI, molecular weight of PEI and reaction media. The degree of substitution of PEI6C 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 temperature more than 100° C and longer reaction time (above 72 h), the degree of substitution increased slightly but the solubility of PEI6C decreased probably due to the formation of a gel. Finally we synthesised PEI6C having degree of substitution 63.7 by optimising the reaction conditions such as temperature 100° C, reaction time 72 h, molar ratio of azobenzene monomer to PEI (Mn~1800) = 4.2:4.0, and solvent (DMF) = 50 cm³. Synthesised polymer showed good solubility in DMF, CHCl₃, THF and cyclohexanone.

Thermal characteristics of synthesised PEI6C was studied using differential scanning calorimetry (DSC) with a heating rate of 10 Kmin⁻¹ and polarised optical microscopy (POM) analyses. On DSC thermogram, PEI6C showed two endothermic peaks with low glass transition temperature (G 38 S 115 N 147 I). On the basis of the DSC and POM measurements, these two peaks were assigned to smectic-nematic, and nematic-isotropic thermal phase transitions. The polymer is stable up to 215° C.

The synthesised polymer was also characterised by X-ray diffraction measurement. The X-ray diffraction patterns for synthesised polyethene imine film confirmed that the polymer is smectic layer structures and exhibited few strong 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

Photoinduced alignment behavior of PEI6C in solid film

The photo alignment behaviour and photochemical behaviours of PEI6C in solution and in solid state were examined. The changes in the UV-vis. absorption spectra of PEI6C in THF are shown in Figure 1. Before irradiation, PEI6C in THF showed a strong absorption at 352 nm and a weak absorption around 460 nm, corresponding to $\pi \rightarrow \pi^*$ transition and $n \rightarrow \pi^*$ transition of the azo-chromophores, respectively. UV irradiation caused decrease and increase in absorption at 352 and 460 nm, respectively, indicating photoisomerisation from *trans*→*cis* form. It became photostationary in 10 sec in case of *trans*-*cis* photoisomerisation by UV light irradiation and 30 sec in case of *cis*-*trans* isomerisation by visible light irradiation. Photoisomerisation of the polymer in solution shows isosbestic points, indicating uniform photoreactions. The subsequent *cis*-*trans* isomerisation by visible light irradiation rebuilt the initial state completely, which demonstrates the reversibility of the reaction. Therefore, the irradiation of light in this wavelength region should cause the photoisomerisation from the *trans*-form to the *cis*-form and vice-verse for the *cis*-form. Consequently, *trans*-*cis*-*trans* photoisomerisation cycle of PEI6C will be brought about by irradiation of the light in this region¹⁵⁻¹⁷.

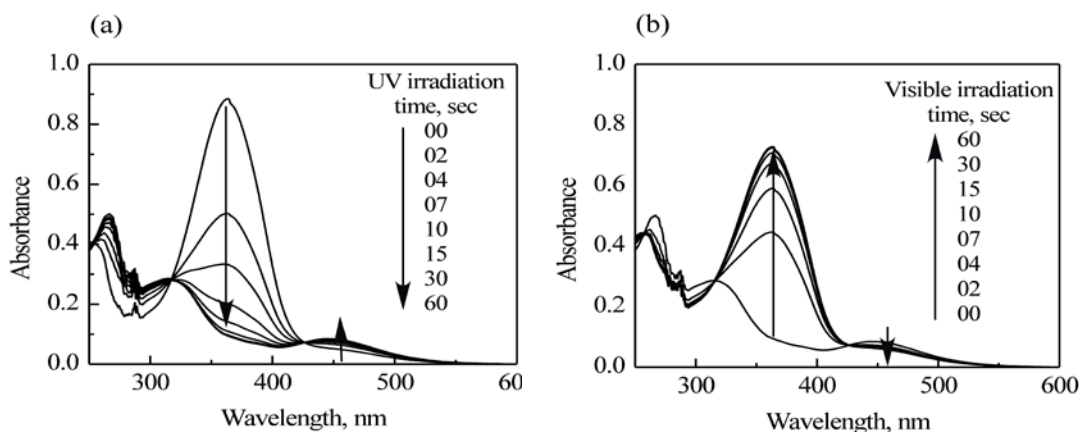


Fig. 1. Changes in UV-Vis. absorption spectra of PEI6C in THF by irradiation of (a) UV (365 nm) and (b) Visible light (435 nm). The intensity of UV and visible light was 7.0 mWcm⁻² and 80 mWcm⁻² respectively.

results are $2\theta(1) = 2.28$; $2\theta(2) = 5.68$; $\text{dist.1}(\text{\AA}) = 31.30$ and $\text{dist.2}(\text{\AA}) = 15.54$.

In order to understand photochemical and photoinduced optical anisotropy in polymeric films, the spectral changes were investigated in polymeric film under irradiation with UV and non-polarised visible light of different wavelengths. Depending on the irradiation wavelength, different steady states of *cis*-*trans* photo-isomerisation were established

allowing or preventing the photo-orientation of azobenzene chromophores in PEI6C.

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 irradiation of non polarised UV light on spin coated solid films of PEIs, significant spectral changes were observed in

polymers which are typical for *trans-cis* photoisomerization¹⁷⁻¹⁹. In PEI6C film, photostationary state with a little high content of the *cis* isomeric form was achieved within 2-3 min as shown in Figure 2(a). Due to molecular aggregation, the rate of *trans-cis* photoisomerisation in film is not as high as that in solution. On the subsequent irradiation with visible light of 435nm, the reverse changes occurred establishing a steady state with a high concentration of *trans* isomers [Figures 2(b)]. The recovery of the initial spectrum was complete, even the value of absorption maxima corresponding to $\pi \rightarrow \pi^*$ transition exceeded the initial value. This phenomenon was related to the partial out-of-plane molecular ordering of azobenzene moieties on glass substrate.

Therefore, to quantify the photo induced anisotropy in PEI6C solid film, polarised absorption spectra were recorded and explored the angular dependency of

Upon prolonged irradiation (>10s), one may observe a decrease in the absorption in both regions corresponding to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions as shown in Figures 2(c). Within the first 10 sec of irradiation with visible light, the back *cis-trans* photoisomerisation occurred, while upon continued irradiation, the azobenzene groups were oriented along the normal of film due to photo-orientation⁷. 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 decreased⁷. So irradiation with non-polarised visible light (435nm) caused the induction of anisotropy in the films by photoorientation of azobenzene side groups.

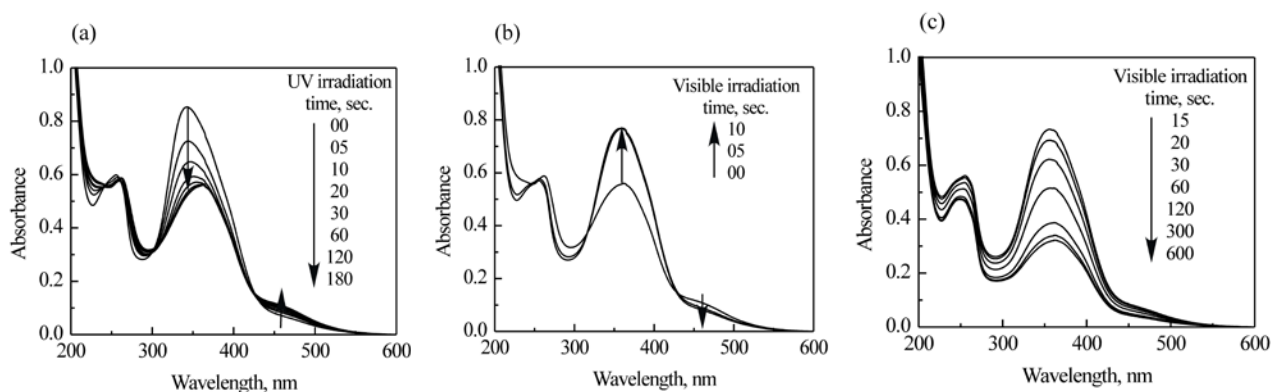


Fig. 2. Changes of absorption spectra of PEI6C polymeric film during (a) UV irradiation (365 nm), (b) first 10 sec visible light irradiation and (c) further visible light irradiation (435 nm). The intensity of UV and visible light was 7.0 mWcm^{-2} and 80 mWcm^{-2} respectively.

absorbance before and after irradiation. Irradiation of visible light on PEI6C film brought about not only by decrease in absorbance corresponding to the $\pi \rightarrow \pi^*$ transition without polariser, but also by change in the polarised absorption spectra as shown in Figure 3. The order parameter, the degree of out-of-plane ordering, was calculated from polarised absorption spectra by using equation (1).

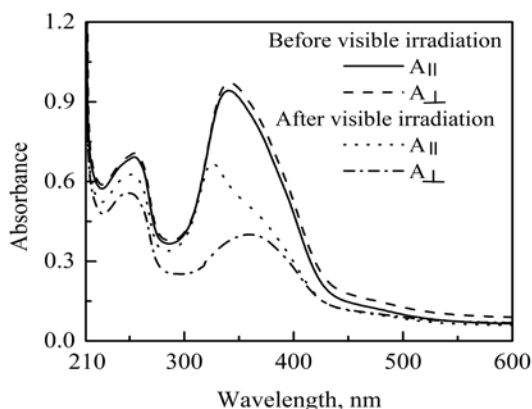


Fig. 3. Polarized UV-vis. absorption spectra of PEI6C single layer film before and after irradiation of non-polarized visible light (435 nm) during 5 min. A_{\parallel} and A_{\perp} denote absorption parallel and perpendicular to the polarization direction of actinic light respectively. Spectral measurements were made at 45° to film normal.

The polarised absorption spectra were recorded at an angle of 45° to the normal of the film, and by following rotation of the film for polar plot to evaluate the quantity of out-of-plane molecular orientation. From polarised absorption spectra, polar plot for polymeric film was also plotted and is shown in Figure 4. After irradiation of non-polarised visible light, the absorbance parallel to the polarisation direction of actinic light was higher than that perpendicular to the polarisation direction of actinic light. From polar plot, it is clear that, before irradiation, no angular dependency was observed, indicating that the azobenzene chromophores were randomly orientated on glass substrate in solid film. But after irradiation, PEI6C solid film showed big angular dependency and the shape of the corresponding polar plot is concave, allowing to assess the level of order parameter⁷. The out-of-plane order parameter values before and after irradiation were 0.006 and 0.243 respectively.

It was established that the photoorientation took place in the steady state of the photoisomerisation *via* numerous angular-selective photo-isomerisation cycles leading to a preferred orientation of the azobenzene groups perpendicular to the electric field vector of the excitation light.

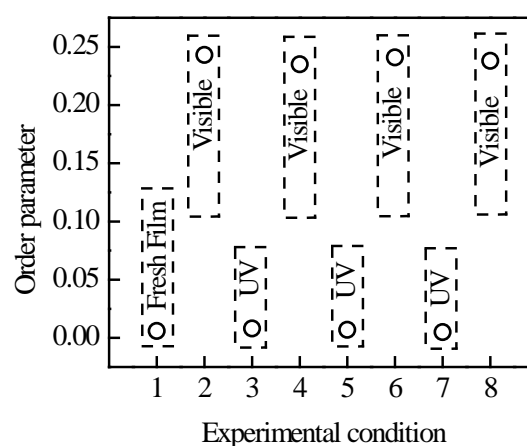
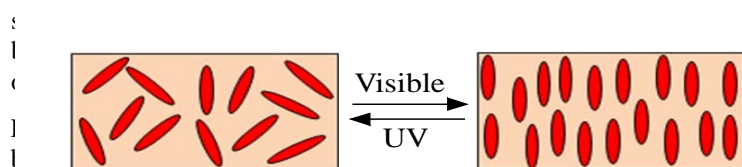


Fig. 5. Reversibility of alignment behavior of PEI6C at different experimental conditions.

Reversibility of alignment behavior of PEI6C in solid film

In order to show the possibility of reversible reorientation of azobenzene chromophores in PEI6C, molecular ordering behaviours were observed at different conditions. And



Scheme 2. Schematic representation of the alignment behavior of azobenzene chromophores under different conditions.

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 non-polarised visible light irradiated films, the value of order parameter decreased via *cis-trans* photoisomerisation and reached to almost initial level. Namely the azobenzene molecules aligned randomly on the glass substrate. Following non-polarised visible 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. Again upon UV irradiation, the azobenzene group aligned randomly on the glass substrate (Scheme 2). 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.

IV. Conclusion

Liquid crystalline polyethene imine (PEI6C) having cyano (-CN) azobenzene side chain through methylene spacer group was successfully synthesised and characterised by DSC, Polarised Optical Microscopic and XRD analysis. The effect of reaction parameters on degree of substitution of PEI6C were also studied and optimised the reaction conditions. PEI6C, both in solution and in solid film exhibited photoresponsive properties upon irradiation of UV and visible light. PEI6C film also exhibited reversible molecular orientation from random state to out-of-plane and from out-of-plane to random state on non-polarised visible and UV light irradiation. The reversible molecular ordering of azobenzene chromophores showed that optical anisotropy in the film can be completely erased and rewritten without any memory effect of the previous irradiation.

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