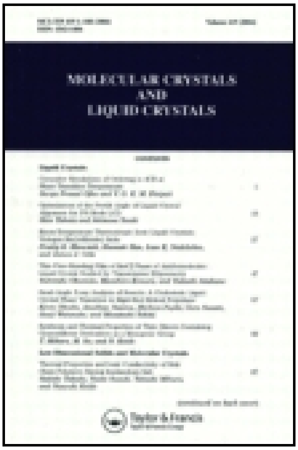

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 27 Oct 2006

To cite this article: Mina Han, Giancarlo Galli, Lachezar Komitov, Kunihiro Ichimura & Emo Chiellini (2001): Photoisomerization Behavior of Smectic Liquid Crystalline AZO Polymers, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 365:1, 459-466

To link to this article: http://dx.doi.org/10.1080/10587250108025325

Mol. Cryst. and Liq. Cryst., 2001, Vol. 365, pp. 459-466
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Gordon and Breach Science Publishers imprint,
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Photoisomerization Behavior of Smectic Liquid Crystalline AZO Polymers

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We have investigated photoisomerization and photoorientation behavior of a liquid crystalline polymethacrylate bearing *p*-methoxyazobenzene side groups (C6MeO) and copolymethacrylates with *p*-alkoxylated azobenzene side chains, (poly(AZO-1) and poly(AZO-2)). Irradiation with linearly polarized visible light generated photoinduced optical anisotropy for all polymers as a result of the reorientation of the azobenzenes toward the direction perpendicular to the electric vector of actinic light. On annealing of the photoirradiated films, the azobenzene chromophores of poly(AZO-1) and poly(AZO-2) showed out-of-plane reorientation, whereas those of C6MeO underwent a marked amplification of in-plane orientation.

Keywords: azobenzene; liquid crystalline polymer; photoisomerization; photoorientation; annealing

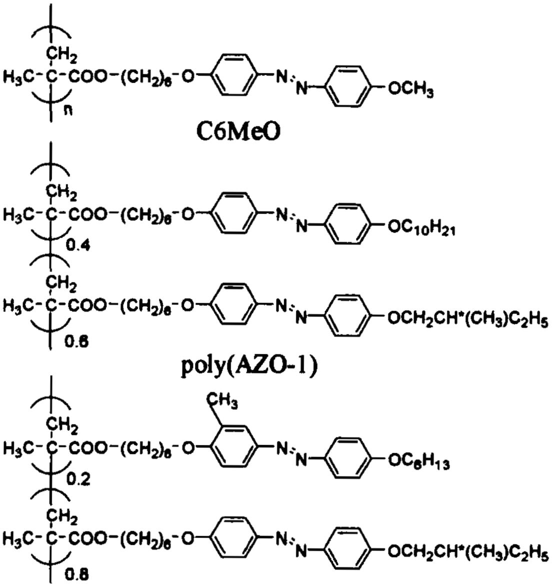
INTRODUCTION

Liquid crystalline polymers are promising materials for their practical applicabilities for optical data storage, switching devices and non-linear optics.[1,2] These systems show electro-optic response due to efficient molecular orders.[3] The introduction of photochromic azobenzene groups as mesogenic units into polymeric systems makes possible changes of the material characteristics to take place due to E/Z photoisomerization induced by alternating irradiation with UV and visible light. Linearly polarized light irradiation of azobenzenes in polymer films leads to molecular reorientation involving angular-selective isomerization, followed by angular redistribution and rotational diffusion to minimize light absorption through reversible E/Z photoisomerization cycles.[4,5] Stumpe *et al.*[6,7] presented that this kind of optical anisotropy induced by irradiation with linearly polarized light is outstandingly enhanced by thermal treatment when films of liquid crystalline polymers with azobenzene side chains are prepared by spin-coating. Orientational behavior of azobenzene groups in polymer matrices is significantly affected by polymer structures such as the length of the spacer connecting the azobenzene groups, chemical structures of the azobenzene, the nature of polymer backbones and contents of the azobenzene groups.[8-11] In this context, the major purpose of this report is to investigate molecular orientation of liquid crystalline polymers with azobenzene side chains substituted with terminal alkoxyl groups of different lengths under light irradiation followed by thermal treatment. We employ here two kinds of liquid crystalline polymers displaying smectic phase; a polymethacrylate with *p*-methoxyazobenzene side chains (C6MeO) and copolymethacrylates possessing azobenzene side chains substituted with long-chain alkoxyls at the *p*-positions (poly(AZO-1) and poly(AZO-2))[12] (Figure 1).

EXPERIMENTAL

C6MeO were prepared according to our previous paper.[13] Both copolymers formed a smectic phase, with layer spacing of 49.4 Å for poly(AZO-1) and 27.7 Å for poly(AZO-2).[12] In neither case was a glass transition temperature clearly detected. 1.5 wt % of toluene solutions of the polymers were spin-coated on fused silica plates cleaned in KOH/ethanol to give films of about 50 nm thickness. The films were irradiated with 365 nm or 436 nm light from a Hg-Xe lamp

(UVF-203S produced by SAN-EI Electric MFG Co.) through the combinations of Toshiba color filters, UV-D36A + UV-35 and Y-43 + V-44, respectively. The evaluation of induced optical anisotropy was carried out by polarized UV-Visible absorption spectra taken on a Hewlett-Packard diode array spectrometer 8452A. A hot stage (Mettler FP800 thermosystem) was employed to control heating temperatures.



Polymer	M_w	M_w/M_n	Phase transition[a] (°C)
C6MeO	125,000	2.8	G 76 S 95 N 137 I
poly(AZO-1)	92,000	2.3	G −[b] S 138 I
Poly(AZO-2)	112,500	2.5	G −[b] S 107 I

[a] G, glassy; S, smectic; N, nematic; I, isotropic. [b] Glass transition temperatures were not clearly detected

FIGURE 1 Chemical structures of the polymers.

RESULTS AND DISCUSSION

Isomerization

The absorption spectra of the azobenzene-containing polymers in toluene displayed intense symmetrical bands at around 360 nm corresponding to π–π* absorption band of *E*-azobenzenes (see Figure 2). The absorption bands centered at 346 nm, 342 nm and 342 nm for C6MeO, poly(AZO-1) and poly(AZO-2), respectively, were broadened in spin-coated films owing to the formation of H-aggregates among the aromatic chromophores. UV irradiation of the films led to the decrease in absorbance at the absorption maximum (λ_{max}) and the increase in absorbance at 450 nm due to n-π* transition as a consequence of *E*-to-*Z* photoisomerization.

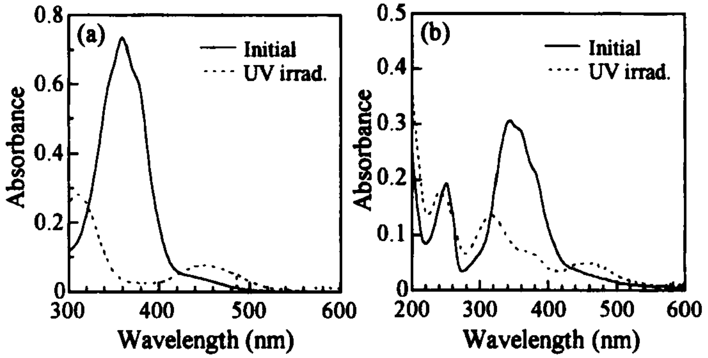


FIGURE 2 UV-Visible spectra of (a) in a toluene solution and (b) thin film of poly(AZO-1) before and after irradiation with UV light.

Thermal treatment

In order to investigate the molecular orientation by thermal treatment, spin-coated films were heated at 75 °C for C6MeO and at 80 °C for poly(AZO-1) and poly(AZO-2). As shown in Figure 3, π–π* absorbance of C6MeO was increased by about 10 % with respect to the initial one after annealing at 75 °C, whereas the π–π* absorption bands of poly(AZO-1) and poly(AZO-2) films showed pronounced reduction and sharp blue-shift to around 340 nm. These spectral changes by the thermal treatment are likely to be not only due to the increase in Haggregation as a result of intermolecular interaction of azobenzene side groups, but also due to molecular reorientation.

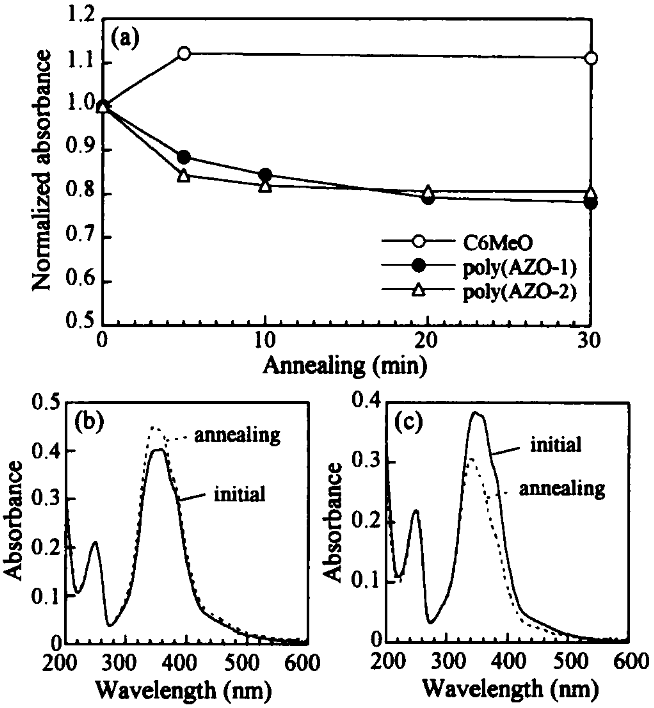


FIGURE 3 (a) Normalized absorbances of films of C6MeO, poly(AZO-1) and poly(AZO-2) at λ_{max} after annealing at 75 °C, 80 °C and 80 °C, respectively. Measurements of UV-Visible spectra of annealed films were carried out at room temperature. Absorption spectral changes of (b) C6MeO and (c) poly(AZO-2).

Photoinduced orientation

Irradiation with linearly polarized visible light was performed to generate photoinduced reorientation of azobenzene groups. Levels of photoinduced dichroism were characterized by using dichroic ratios (DR = $[A_{\perp} - A_{\parallel}]/[A_{\perp} + A_{\parallel}]$), whereas $A_{\perp}$ and $A_{\parallel}$ denote absorbances at λ_{max} obtained by using polarized probe light with the electric vector perpendicular and parallel, respectively, to that of the actinic polarized light.

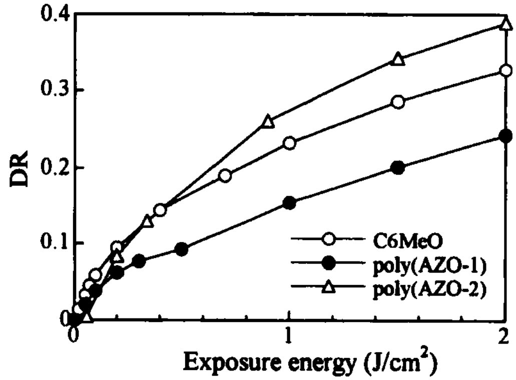


FIGURE 4 Changes in DR during linearly polarized visible light irradiation.

Figure 4 shows changes in DR during the irradiation of polymer films. As exposure doses increased, DR values increased gradually without giving a saturated value.[13] This result arises from the aspect of changes in $A_\parallel$ and $A_\perp$ as a function of exposure dose of light. As shown in Figure 5, the reduction of $A_\parallel$ contributes significantly to the generation of optical anisotropy during linearly polarized light irradiation, while $A_\perp$ exhibit relatively small increment. Accordingly, the normalized average absorbances ($A_{av} = [2A_\perp + A_\parallel]/3A_0$, 0.90, 0.87 and 0.87 for C6MeO, poly(AZO-1) and poly(AZO-2), respectively, at exposure dose of 2 J/cm²) during linearly polarized visible light irradiation become smaller than that of the initial state. This observation seems to be a result of the formation of *Z*-isomer as a minor component.[14] However, the annealing of photoirradiated films leads to the marked changes in $A_\parallel$ and $A_\perp$. The annealing of a C6MeO film at 76 °C results in an increase in $A_\perp$ and a decrease in $A_\parallel$ so that DR is enhanced up to 0.72, indicating that the thermal treatment amplifies the in-plane photoreorientation of azobenzene groups in this case (Figure 5(a)). The highly ordered state of the annealed films was retained up to the clearing temperature. On the other hand, the annealing of poly(AZO-1) having relatively long terminal alkoxyl group displayed the reduction of $A_\parallel$ as well as $A_\perp$, even though the dichroism was not much changed (Figure 5(b)). A similar result was also observed for a poly(AZO-2) film. This suggests that polymers bearing the long hydrophobic terminal groups favors homeotropic reorientation by light irradiation and successive thermal treatment,[15] different from the enhanced in-plane reorientation of C6MeO with methoxy substituent.

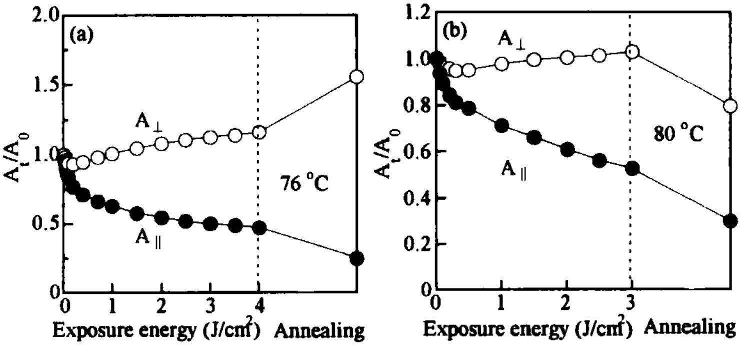


FIGURE 5 Changes in absorbances (A_t/A_0) at λ_{max} by linearly polarized visible light irradiation and the subsequent annealing at 76 °C for (a) C6MeO and at 80 °C for (b) poly(AZO-1).

CONCLUSION

Comparative studies on photoorientational behavior of azobenzene side groups was achieved by using liquid crystalline polymers, C6MeO, poly(AZO-1) and poly(AZO-2); the former has methoxy group, whereas the azobenzenes of the latter two are substituted with long *p*-alkoxyls. Thermal treatment of a spin-coated film of C6MeO at 75 °C exhibited an increase in π–π* absorbance by about 10 % of that of the initial state, while poly(AZO-1) and poly(AZO-2) displayed a decrease in π–π* absorption bands by about 20 % as well as blue-shift of λ_{max}. Irradiation with linearly polarized visible light induced molecular reorientation toward the direction perpendicular to the electric vector of incident light. Successive annealing of the

photoirradiated film of C6MeO at 76 °C led to drastic enhancement of in-plane orientation. On the other hand, poly(AZO-1) and poly(AZO-2) show a tendency to orient homeotropically by annealing, implying that the hydrophobicity of the long alkoxyl groups plays a critical role in the reorientational behavior.

Acknowledgments

L. Komitov is grateful for the financial support of his visit in Japan given by JSPS (Japan Society for the Promotion of Science).

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