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Factors Affecting In-Plane and Out-of-Plane Photoorientation of Azobenzene Side Chains Attached to Liquid Crystalline Polymers Induced by Irradiation with Linearly Polarized Light

Mina Han, Shin'ya Morino, and Kunihiro Ichimura*

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

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ABSTRACT: Photoinduced orientational behavior of polymethacrylates with side chains (amorphous polymers, pMAz2 and C2MeO, and liquid crystalline polymers, C6MeO and C12MeO) with different alkylene spacer lengths ($n = 2, 6, 12$) were investigated by means of polarized Fourier transform infrared (FT-IR) and UV−vis absorption spectroscopy. Being different from pMAz2, C2MeO showed high optical anisotropy due to in-plane orientation and the excellent thermostability even above T_g, which can be explained in terms of potential liquid crystallinity to be able to have a tendency to form a well-ordered domain. We observed marked dependence of photoorientation processes on film temperatures of C6MeO. While in-plane orientation was generated in glassy state as well as at 76 °C, irradiation at 90 °C slightly lower than T_{SN} (transition temperature between smectic and nematic phases) gave rise to the distinct transformation from in-plane orientation at the early stage to successive out-of-plane reorientation, which was accompanied by H-aggregation. This situation enabled ones to record optical images in a C6MeO film on the basis of the difference in birefringences between two orientational modes. The biaxial reorientation occurred also for C12MeO, though both in-plane and out-of-plane photoorientation occurred simultaneously at room temperature as well as elevated film temperatures.

1. Introduction

Photoorientation behavior of azobenzene side chains generating optical anisotropy has been extensively studied so far[1] for amorphous,[2] semicrystalline,[3] and liquid crystalline polymers[4,5] on account of their applicabilities to polarization holography,[6] optical data storage,[7] nonlinear optoelectronics,[8] and so on. The optical anisotropy is induced by photoirradiation with linearly polarized light in films of amorphous polymers and disappears above their T_g due to the enhanced molecular mobility causing orientational randomization.[9] On the other hand, photoinduced orientation of azobenzene side chains in films of liquid crystalline polymers remains unchanged even above the T_g, and the resultant high optical anisotropy can be enhanced at near T_g and is maintained up to their clearing temperatures.[10]

The rod-shaped *E*-isomer of azobenzenes absorbs photons of linearly polarized light proportionally to $\cos^2 \varphi$ of the energy whereas φ is the angle between the molecular axis and the electric vector of the light. According to Sekkat et al.,[11] the molecules are subjected to angular-selective isomerization, followed by angular redistribution and rotational diffusion to minimize light absorption through the reversible *E*/*Z* photoisomerization cycles. Two kinds of orientation modes are possible as extreme cases when linearly polarized light with the electric vector parallel to the *xz*-plane comes along with the *z*-direction, as illustrated in Figure 1; the uniaxial in-plane orientation of the azobenzene with a electric transition dipole moment parallel to the *x*-axis from the *x*- to *y*-direction and the out-of-plane (homeotropic) one toward the *z*-direction. When compared with intensive studies on the former in-plane reorientation in polymer films, to our knowledge, no systematic investigation has yet been carried out on the latter (out-of-plane orientation), although the following reports have been made in connection with the photoinduced out-of-plane reorientation of azobenzenes.

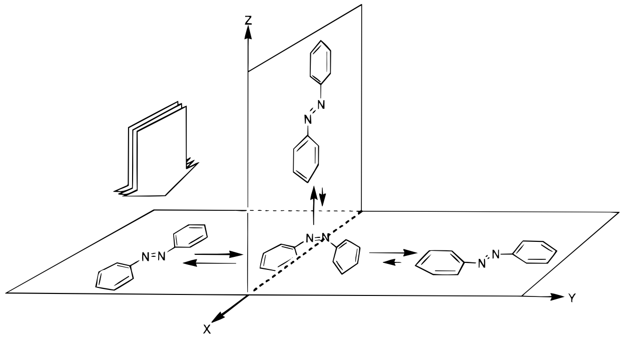

Figure 1. Illustrative presentation of in-plane and out-of-plane photoorientation of azobenzene induced by linearly polarized light irradiation.

Spiess et al.[12] have observed by means of polarized IR spectroscopy that the biaxial reorientation is induced upon irradiation with polarized light of uniformly homogeneous samples of liquid crystalline copolymers with *p*-cyanoazobenzene and cyanophenyl benzoate side chains to give rise to the preferential reorientation of the azobenzene mesogens toward the direction perpendicular to a film surface. Natansohn et al.[13] have suggested that the photobleaching of a film of a copolymer with azobenzene side chains caused by irradiation with circularly polarized light is attributed to the reorientation of the azobenzene chromophores in line with the propagation direction of the light. Schönhoff et al.[14] and Stumpe et al.[15] have described recently that polarized light irradiation of Langmuir−Blodgett films of a hydrophobically substituted aminoazobenzene and thin films of liquid crystalline polymers with azobenzene

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* Corresponding author. Tel +81-45-924-5266, Fax +81-45-924-5276, E-mail kichimur@res.titech.ac.jp.

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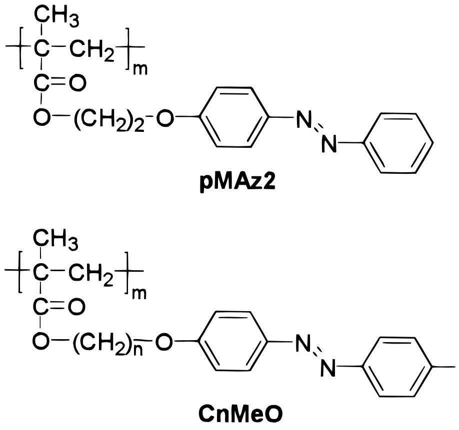

Figure 2. Chemical structures of the polymers used in this study.

side chains, respectively, results in disagreements between the increase of absorbances perpendicular to and the decrease of those parallel to the electric vector of the polarized light, suggesting the occurrence of out-of-plane reorientation. Holme et al.[16] demonstrated 10 000 cycles of optical rewrittability of a thin film of a liquid crystalline polyester with azobenzene side chains, which was exposed alternately to linearly polarized 488 and 351 nm laser beams. They reported a decay of the photogenerated anisotropy in an exponential manner in such a way that the prominent decrease in the photobirefringence occurs in the early stage of the alternate irradiation of 200 cycles. The overall decrease in the anisotropy may be associated with the fact that the azobenzenes align perpendicularly to the film surface, being in parallel with the direction of incident light. Furthermore, Buffeteau et al.[17] have showed that photoinduced biaxiality is quantified for a semicrystalline polymer and for amorphous copolymers containing azobenzene side chains. When a semicrystalline polymer film was irradiated with a polarized laser beam, cooperative motions of azobenzene and phenylene groups occur to induce the biaxial reorientation of the chromophores.

We have reported recently the spectroscopic evidence supporting that azobenzene side chains tethered to amorphous[18] as well as liquid crystalline[19] polymer backbones reorient in their films toward the propagation direction of nonpolarized light. Our further observation has revealed that the exposure of a film of a liquid crystalline polymer with azobenzene side chains to linearly polarized 436 nm light results in the successive occurrence of uniaxial in-plane orientation, followed by out-of-plane orientation of the azobenzenes.[20] The purpose of this paper is to review the effect of alkylene spacer length and film temperature on photoreorientation of azobenzenes, in particular, focusing on the biaxial reorientation behavior of azobenzene side chains during irradiation with linearly polarized light.

2. Experimental Section

2.1. Materials. Chemical structures of the polymers used in this study are shown in Figure 2. The monomers for the polymers were synthesized according to literature.[21] A 10 wt % solution of a monomer and 1 wt % of AIBN as an initiator in toluene was degassed under vacuum using the freeze−pump−thaw method and heated in a water bath at 65 °C. The polymerization was terminated after 10 h by precipitation of a polymer in ethanol. The polymer was collected by filtration and washed with ethyl acetate and ethanol several times.

Table 1. Phase Transition Temperatures, Refractive Indices, and Notation of the Studied Azobenzene-Containing Polymers

polymer	n	M_w[a]	M_w/M_n[b]	phase transition[c] (°C)	refractive index (n)[d]
pMAz2	2	150 000	2.5	G88	1.64
C2MeO	2	226 000	3.3	G 120, 171 M	1.63
C6MeO	6	125 000	2.8	G 76 S 95 N 137 I	1.64
C12MeO	12	59 000	2.8	G 68 S 131 I	1.64

[a] M_w, weight-average molecular weight. [b] M_w/M_n, molecular weight distribution. [c] G, glassy; S, smectic; N, nematic; I, isotropic; M, melting temperature (To discriminate amorphous and liquid crystalline polymer, we here use M and I describing the clearing temperature in bulk state.) [d] Refractive indices (n_{film}) of casted polymers were taken from an Abbe refractometer at 23.5 °C in the dark room.

2.2. Characterization. Gel permeation chromatography was carried out on a JASCO system consisting of an 860-CO column oven equipped with an 875 UV detector at a flow rate of 1.0 mL/min with THF as an eluent. Molecular weights of the polymers were determined according to a polystyrene calibration curve. Differential scanning calorimetry (DSC) was conducted on a DSC200 of Seiko Electrics Co., Ltd. Transition temperatures including T_g, T_{SN}, and T_{NI} of polymers were recorded on the second heating from 10 to 180 °C at a rate of 5 °C/min. No definite liquid crystalline phase was observed for pMAz2 and C2MeO (Table 1). T_g of the polymers gradually decreased with the increase in the alkylene spacer length,[22] and longer spacer lengths favor the generation of a smectic phase at a lower transition temperature while only a smectic phase appears in C12MeO with dodecamethylene spacer.[23]

2.3. Measurements. 1.5 wt % of solutions of C2MeO in cyclohexanone and of pMAz2, C6MeO, and C12MeO in toluene were spin-coated on quartz plates cleaned in KOH/ethanol for UV−vis absorption measurements or on CaF_2 plates for UV−vis or IR transmission measurements, respectively. Transparent films were 60 ± 10 nm in thickness for spectroscopic measurements and about 500 nm for conoscopic measurements (Olympus BX50F), as measured by a DEKTAK 3ST. The films were irradiated with 365 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−vis absorption spectra taken on a Hewlett-Packard diode array spectrometer 8452A. FT-IR spectra were recorded on a Bio-Rad FTS 6000 spectrometer equipped with a DTGS detector. All the data were gained at a spectral resolution of 4 cm^{-1}. A hot stage (Mettler FP800 thermosystem) was employed to control heating temperatures. Birefringence of a thin film was measured by a JASCO BFA-150 transmission ellipsometer.

2.4. Evaluation of Photoorientation with p- and s-Polarized Probe Light. To monitor the photoinduced in-plane planar (uniaxial) and out-of-plane orientation of the azobenzene groups, absorption spectra of photoirradiated films were taken at various incident angles (θ_m) of probe light of the spectrometer, which is defined as an angle contained by the propagation direction of light and surface normal (Figure 3). Reference spectra at various incident angles were subtracted from sample spectra taken at different θ_m of p- and s-polarized probe light to discard the effect of additional multiple reflection on polymer films. p-Polarized light with the electric vector parallel to the plane of incidence (yz-plane) is sensitive to the out-of-plane orientation, while s-polarized light with the electric vector perpendicular to the plane of incidence is relatively inert to that. Accordingly, it is possible to evaluate the spatial orientation of azobenzene chromophores by using p- and s-polarized probe light.[24] The dependence of θ_m on the following two parameters was evaluated to obtain information concerning three-dimensional orientation of azobenzenes. The first is $A_{p\lambda_{max}}/A_{s\lambda_{max}}$, whereas $A_{p\lambda_{max}}$ and $A_{s\lambda_{max}}$ are $\pi-\pi^*$ absorbances at the λ_{max} (= 344, 346, 346, and 342 nm for pMAz2,

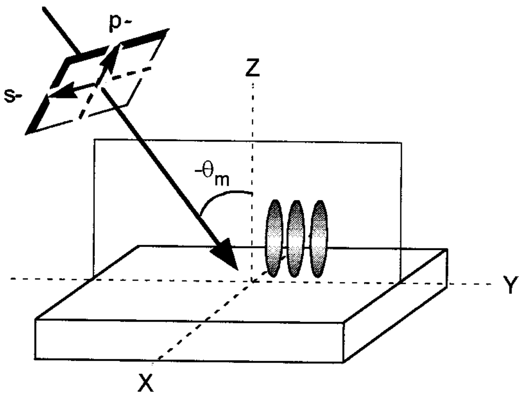

Figure 3. Geometry for measurements of absorption spectra of a film taken by p- and s-polarized probe light at an incident angle (θ_m).

C2MeO, C6MeO, and C12MeO, respectively) of the azobenzene taken by p- and s-polarized probe light. Note that changes in optical path lengths for the measurements are canceled by this treatment. On the other hand, A_{p320}/A_{p360} was employed as the second parameter to reveal the out-of-plane photoreorientation of H-aggregated azobenzene, while A_{p360} and A_{p320} denote p-polarized absorbances centered at around 360 nm corresponding to monomeric species and at around 320 nm due to H-aggregates. The spectral blue-shift is considered to result from the H-aggregation, which consists of a cofacial card-packed orientation of azobenzene chromophores.[25] The difference in optical path length at each incident angle of the probe light was corrected by taking eq 1 into account. Generally the following relation is obtained:[26] $n_e > n_{\rm film} > n_o$; here n_e and n_o correspond to the extraordinary refractive index parallel to the long axis of a molecule and the ordinary refractive index parallel to the short axis of the molecule, respectively. Nevertheless, for simplicity, we used the refractive indices of the polymers ($n_{\rm film}$) taken by an Abbe refractometer at 23.5 °C in a dark room. From the Snell's law, $n_{\rm air} \sin\theta_m = n_{\rm film} \sin\theta_r$, where $n_{\rm air}$ (=1.00) and $n_{\rm film}$ (Table 1) are the refractive indices of air and the polymers, respectively, and θ_m and θ_r are incident and refractive angles of the light. Therefore, we obtain

$$A = A_{\rm corr} = A_{\rm obs} \cos\left\{\sin^{-1}\left(\frac{\sin\theta_m}{n_{\rm film}}\right)\right\} \qquad (1)$$

whereas $A_{\rm corr}$ and $A_{\rm obs}$ denote corrected and observed absorbances, respectively.

3. Results

3.1. Photoisomerization. Four polymethacrylates with azobenzene side chains were used here (Figure 2), focusing on the influence of level of molecular orders of the polymers on photoreorientation behavior. No characteristic liquid crystalline phase was detected for pMAz2 and C2MeO by DSC measurement and polarized microscope observation, whereas C6MeO possesses both of smectic and nematic phases and C12MeO shows only a smectic phase.[23] The absorption maximum of pMAz2 at 344 nm in film due to the $\pi-\pi^*$ transition of *E*-azobenzene was the same as that in solution, exhibiting that no pronounced aggregation occurred in solid film. The absorption maxima of the three *p*-methoxyazobenzene-containing polymers with different alkylene spacers in toluene solutions centered at around 360 nm, whereas spin-coated films showed broader $\pi-\pi^*$ absorption bands at $\lambda_{\max}$ of 346, 346, and 342 nm for

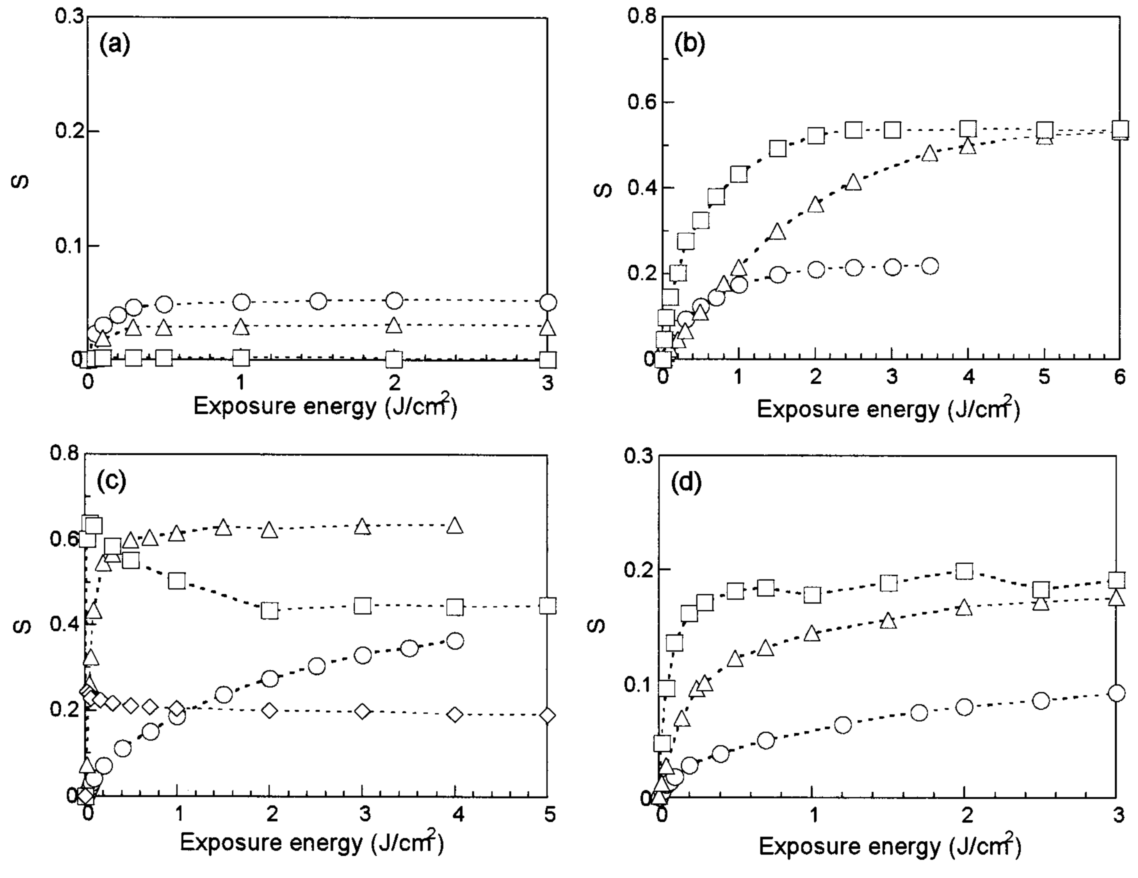

Figure 4. Changes in order parameters (*S*) of films of the polymers during irradiation with linearly polarized 436 nm light at various heating temperatures: (a) pMAz2: room temperature, ○; 70 °C, △; 105 °C, □; (b) C2MeO: room temperature, ○; 115 °C, △; 135 °C, □; (c) C6MeO: room temperature, ○; 76 °C, △; 90 °C, □; 120 °C, ◇; (d) C12MeO: room temperature, ○; 63 °C, △; 85 °C, □.

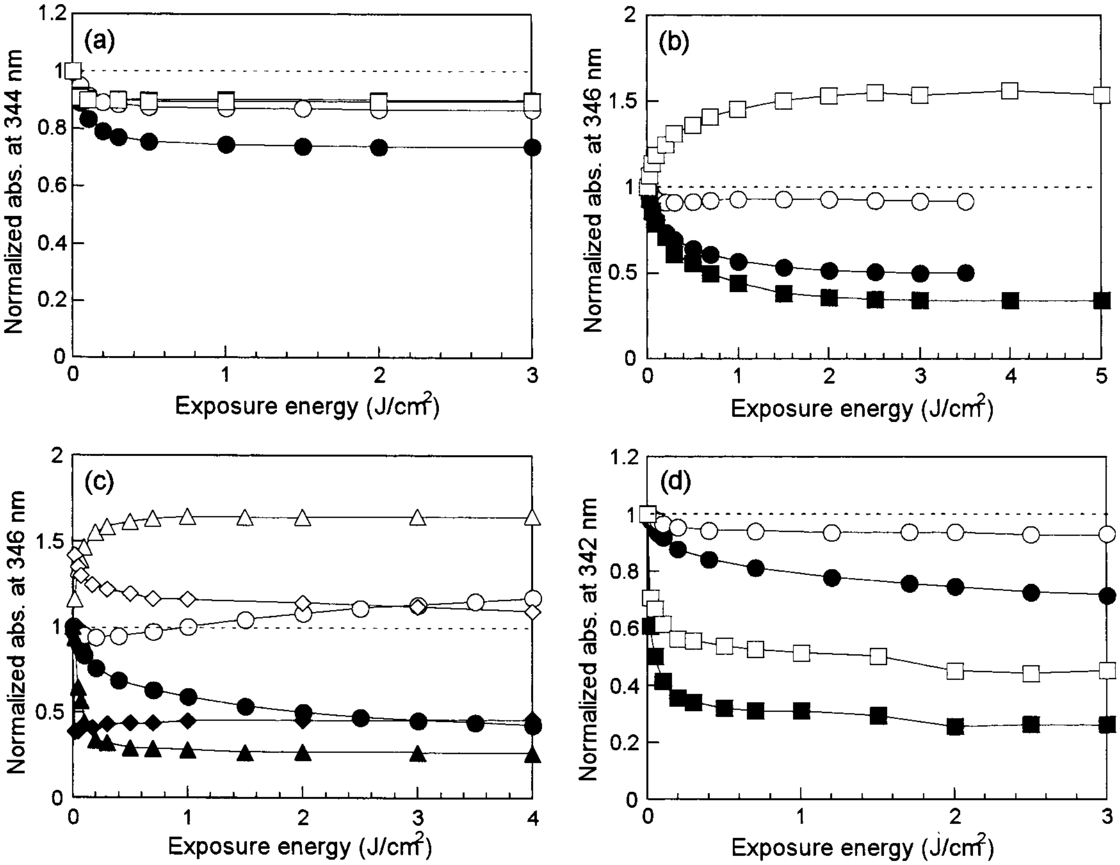

Figure 5. Changes in normalized absorbances of films of the polymers as a function of exposure energy of linearly polarized 436 nm light at various heating temperatures: (a) pMAz2 at room temperature (○, $A_\perp$; ●, $A_\parallel$) and 105 °C (□, $A_\perp$; ■, $A_\parallel$); (b) C2MeO at room temperature (○, $A_\perp$; ●, $A_\parallel$) and 135 °C (□, $A_\perp$; ■, $A_\parallel$); (c) C6MeO at room temperature (○, $A_\perp$; ●, $A_\parallel$), 76 °C (△, $A_\perp$; ▲, $A_\parallel$) and 120 °C (◇, $A_\perp$; ◆, $A_\parallel$); (d) C12MeO at room temperature (○, $A_\perp$; ▲, $A_\parallel$) and 85 °C (□, $A_\perp$; ■, $A_\parallel$).

C2MeO, C6MeO, and C12MeO, respectively, due to partial H-aggregation of the aromatic chromophores. Accordingly, no isosbestic point appeared upon UV irradiation of the films of the polymers. Subsequent irradiation of UV-irradiated films of C2MeO and C6MeO with 436 nm light caused a red-shift of the $\lambda_{\max}$ to 360 nm, implying that the H-aggregation is destroyed to give a monomeric state as a result of reversible *E*/*Z* photoisomerization cycles. On the other hand, a UV-irradiated film of C12MeO resulted in the thorough recovery of the blue-shifted $\lambda_{\max}$ at 344 nm, indicating the reconstruction of H-aggregation after the subsequent visible light irradiation.

3.2. Irradiation at Room Temperature. Films of the polymers were exposed to linearly polarized 436 nm light at room temperature and elevated temperatures near or above the T_g of each polymer to explore the effect of the spacer length and heating temperature on photoinduced orientational behavior of the azobenzene side chains. The level of photoinduced optical anisotropy of the film is estimated by order parameters (*S*) of the azobenzenes as a parameter for the in-plane orientation on the basis of their polarized UV–vis absorption spectra, whereas *S* is defined as follows:

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

whereas $A_\perp$ and $A_\parallel$ denote absorbances at $\lambda_{\max}$ (= 344, 346, 346, and 342 nm for pMAz2, C2MeO, C6MeO, and C12MeO, respectively) obtained by using polarized probe light with the electric vectors perpendicular and parallel to that of the actinic polarized light.

When the irradiation of films of the polymers is performed at room temperature, *S* values increase gradually, irrespective of whether the polymers are amorphous or liquid crystalline, though the rate and level of photoorientation are somewhat different from each other. Figure 4 shows the generation of photodichroism at various film temperatures; open circles correspond to the results for the room temperature irradiation. While *S* values for the amorphous polymers of pMAz2 and C2MeO level off at exposure doses of about 0.5 and 2 J/cm^2, respectively, the liquid crystalline polymers, C6MeO and C12MeO, display gradual increases of *S* values without the saturation even after irradiation of a few J/cm^2 doses. These results are related to the aspect of changes in $A_\perp$ and $A_\parallel$ as a function of exposure doses of linearly polarized light. As shown in Figure 5, both $A_\perp$ and $A_\parallel$ for pMAz2 and C2MeO (open and closed circles in Figure 5a,b) decrease to give saturated values, while the reduction of $A_\parallel$ occurs faster to cause the dichroism. Normalized average absorbances ($A_{av} = [2A_\perp + A_\parallel]/3A_0$, 0.82 and 0.79 for pMAz2 and C2MeO) decreases slightly when compared with the corresponding initial absorbances (A_0) because of the formation of *Z*-isomer.[27] Although liquid crystalline C6MeO and C12MeO display also slight decreases in A_{av} values, the reduction of A_{av} continues for C12MeO with the increase of exposure energy. As suggested by Schönhoff et al.[14] and Stumpe et al.,[15] the continuous reduction of A_{av} in C12MeO (A_{av} = 0.83 at exposure dose

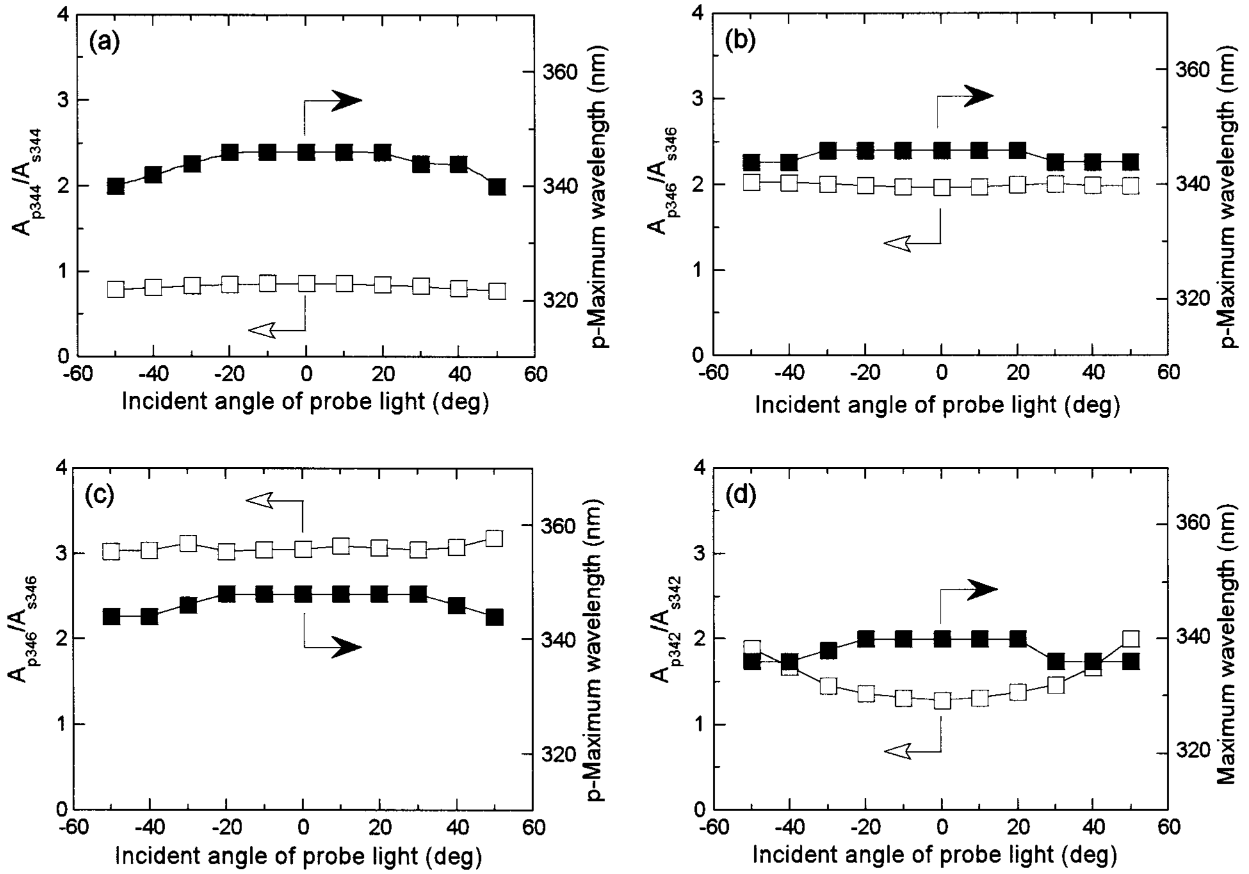

Figure 6. Changes in $A_{p\lambda_{max}}/A_{s\lambda_{max}}$ (□) and in p-maximum wavelength (p-λ_{max}) (■) taken by p-polarized probe light as a function of incident angle of probe light (θ_m) of the polymer films exposed to linearly polarized 436 nm light of a 3 J/cm^2 dose at room temperature: (a) pMAz2, (b) C2MeO, (c) C6MeO, and (d) C12MeO.

of 5 J/cm^2) may arise not only from *E*-to-*Z* photoisomerization but also from out-of-plane orientation of the chromophores toward surface normal.

To obtain information about the spatial orientation including in-plane and out-of-plane modes, absorption spectra of polymer films exposed to linearly polarized 436 nm light at room temperature were taken at various incident angles (θ_m) of linearly polarized probe light. We employ here $A_{p\lambda_{max}}/A_{s\lambda_{max}}$, whereas $A_{p\lambda_{max}}$ and $A_{s\lambda_{max}}$ denote the $\pi-\pi^*$ absorbances at the λ_{max} of polymer films taken by p-polarized and s-polarized probe light, respectively. Figure 6 shows the results illustrating the changes of $A_{p\lambda_{max}}/A_{s\lambda_{max}}$ and p-λ_{max} (p-maximum wavelength taken by p-polarized probe light) as a function of θ_m. The photoirradiated films of C2MeO and C6MeO display no marked θ_m dependence of A_{p346}/A_{s346} (open squares in Figure 6b,c), while A_{p342}/A_{s342} of C12MeO has a distinct minimum at $\theta_m = 0°$, accompanied by the appearance of the longest p-λ_{max} at $\theta_m = 0°$ (Figure 6d).

3.3. Irradiation at Elevated Temperatures. The photoirradiation of films of the polymers with the linearly polarized 436 nm light at elevated temperatures displays photoorientational behavior quite different from the results carried out at room temperature. The photoirradiation was performed at elevated temperatures, followed by immediate cooling to an ambient temperature to achieve absorption spectral measurements. The results are also given in Figure 4. Photoinduced orientation is generated for pMAz2 at 70 °C, lower than $T_g = 88$ °C (open triangles in Figure 4a), though the level of *S* is lower than that obtained by irradiation at room temperature. No dichroism is observed by irradiation at 105 °C much higher than T_g due to significant thermal relaxation in the amorphous polymer. As seen in Figure 5a, $A_\perp$, which is identical with $A_\parallel$, is reduced when compared with A_0, as a result of the redistribution due to random molecular motion above T_g and of the existence of *Z*-isomer in the photostationary state.

Quite different phenomenon is observed for C2MeO, even though the polymer is thought to be amorphous; the dichroism defined as *S* is considerably enhanced at elevated temperatures. It is worthy to note that the irradiation at 135 °C gives rise to a high saturated $S = 0.53$ while the film temperature is higher than the T_g (open squares in Figure 4b). Such high *S* values of C2MeO irradiated at higher temperatures stem from the pronounced increase of $A_\perp$ (open squares in Figure 5b), indicating that the azimuthal reorientation of *p*-methoxyazobenzene side chains in the *y*-direction perpendicular to the electric vector of light (*xz*-plane in Figure 1) takes place efficiently without any deterioration of the molecular order even above T_g. Polarized FT-IR spectra of a film of C2MeO before (initial) and after linearly polarized light irradiation at 135 °C exhibit marked changes of absorption bands in the range 1800−1100 cm^{-1} attributed to the azobenzene units oriented by polarized visible light irradiation (Figure 7b) when compared with those of pMAz2 (Figure 7a). The bands at 1599, 1581, 1500, and 1471 cm^{-1} assignable to the in-plane vibration bands of the benzene rings[28] undergo drastic increase in perpendicular absorbances ($A_\perp^{IR}$) and decrease in parallel absorbances ($A_\parallel^{IR}$) in the polarized absorption spectra after the irradiation. Both the Ph−O

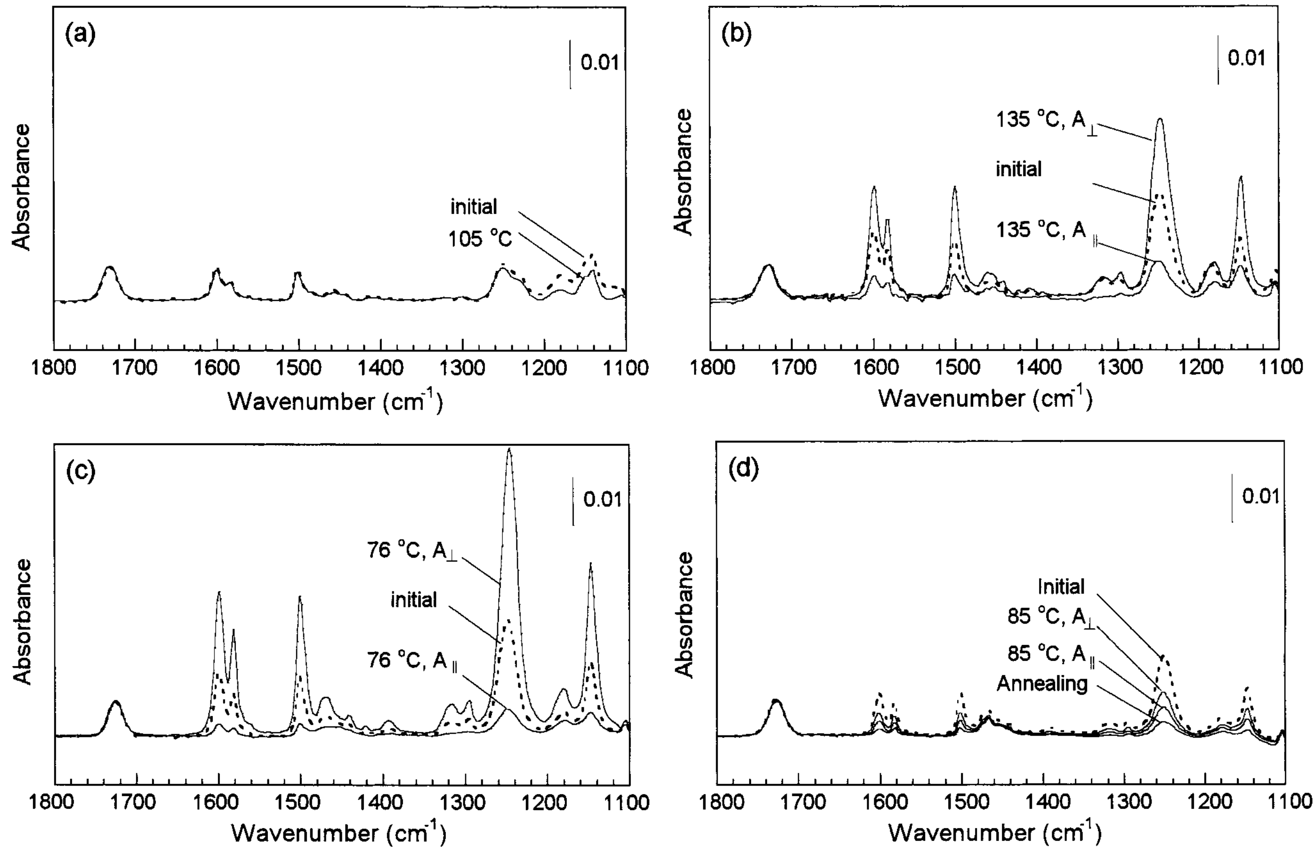

Figure 7. Polarized FT-IR spectra of polymer films before (dotted lines) and after (solid lines; $A_\perp$ and $A_\parallel$) irradiation with linearly polarized 436 nm light at different temperatures. (a) pMAz2 before and after irradiation at 105 °C, (b) C2MeO before and after irradiation at 135 °C, (c) C6MeO before and after irradiation at 76 °C, and (d) C12MeO before and after irradiation at 85 °C and after successive annealing at 100 °C without irradiation.

stretching mode at 1261 cm^{-1} and the =N−Ph stretching one at 1147 cm^{-1} display markedly enlarged $A_\perp^{IR}$ and reduced $A_\parallel^{IR}$, thoroughly in line with the results shown in Figure 5b.

Fairly similar orientational behavior was observed for C6MeO when the irradiation was made at 76 °C (open and closed triangles in Figure 5c), though changes of $A_\perp$ and $A_\parallel$ occurred more rapidly than those for a C2MeO film irradiated at 135 °C. Polarized FT-IR spectra of C6MeO before and after linearly polarized light irradiation (Figure 7c) resemble those of C2MeO, revealing that the in-plane orientation is exclusively involved under the irradiation conditions. On the contrary, the irradiation of a C6MeO film at the higher temperatures of 90 and 120 °C (open squares and diamonds in Figure 4c) results in quite different changes of S, displaying the appearance of maximum values leading to the gradual decrease to give finally saturated S values which are rather smaller than that at 76 °C. The smaller anisotropy at the higher temperatures seems to be related to the change in the mesophase from smectic to nematic phases.[29] Changes of $A_\perp$ and $A_\parallel$ of films irradiated at 120 °C are shown in Figure 5c as open and closed diamonds, indicating the peculiar alteration of S during the illumination. Detailed discussion will be made later.

The aspect of the photogeneration of S of a C12MeO film at 85 °C to give a smectic phase displays the rapid appearance of the photodichroism (open squares in Figure 4d) in a linear manner similar to that of a C6MeO film irradiated at 76 °C. It is noteworthy that the saturated $S = 0.18$ for a C12MeO film is much smaller than those of films of C2MeO and C6MeO. Figure 5d shows considerable decreases of both $A_\perp$ and $A_\parallel$ (open and closed squares), consequently of A_{av}, under the irradiation conditions, suggesting the homeotropic reorientation of the azobenzene side chains. This kind of homeotropic orientation of the azobenzene side chains is supported by polarized FT-IR spectra, which display the marked reduction of both $A_\perp$ and $A_\parallel$ in the range 1800−1100 cm^{-1} attributable to the azobenzene moiety (Figure 7d).

p-Polarized absorption spectra of films irradiated at elevated temperatures were taken to reveal the spatial orientation of the azobenzenes. It is evident that C12MeO irradiated at 85 °C displays the marked θ_m dependence of absorption spectra, when compared with the other polymers. This situation was more clearly visualized by plotting $A_{p\lambda_{max}}/A_{s\lambda_{max}}$ as well as p-λ_{max} of films irradiated at elevated temperatures as a function of incident angle (θ_m) of p-polarized probe light (Figure 8). As presented in Figure 8d, C12MeO displays marked θ_m dependence of both A_{p342}/A_{s342} and p-λ_{max} relative to the other polymers, demonstrating that the azobenzene side chains in a C12MeO film irradiated at 85 °C orient toward the incident light, accompanied by the self-aggregation.

As mentioned above, a film of C6MeO irradiated at 90 as well as 120 °C exhibits the peculiarity in the photoorientational behavior (Figures 4c). Since the changes in photogenerated S are more pronounced at the 90 °C heating when compared with the irradiation at 120 °C, the film temperature was set at 90 °C to achieve detailed measurements of spectral alterations. Figure 9a shows polarized absorption spectra of a

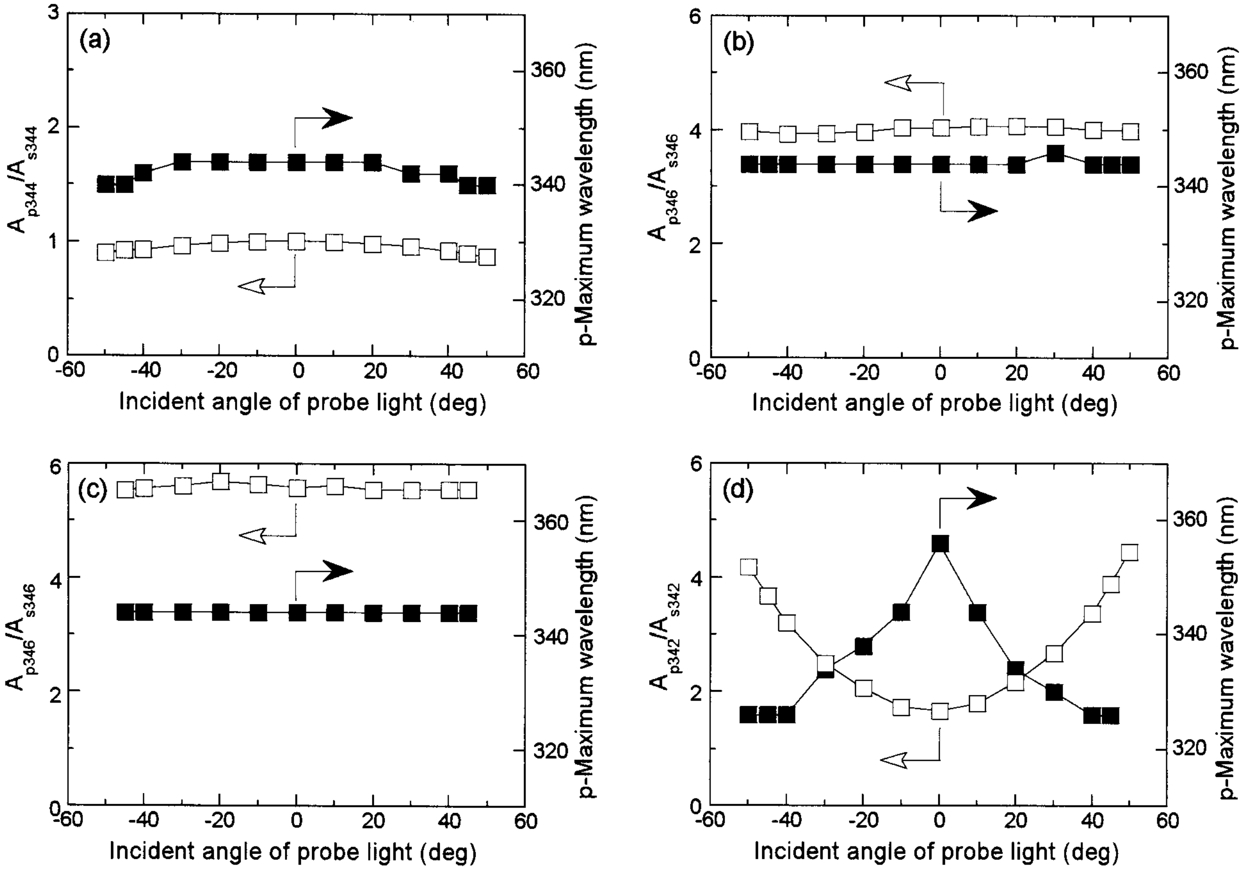

Figure 8. Changes in $A_{p\lambda_{max}}/A_{s\lambda_{max}}$ and in p-maximum wavelength (p-λ_{max}) as a function of incident angle of probe light (θ_m) of the polymer films exposed to linearly polarized 436 nm light at elevated temperatures: (a) pMAz2 irradiated at 105 °C, (b) C2MeO at 135 °C, (c) C6MeO at 76 °C, and (d) C12MeO at 85 °C.

C6MeO film after the irradiation of exposure doses of 0.05 and 5 J/cm^2. Note that the exposure dose of 0.05 J/cm^2 results in the appearance of a maximum $A_\perp$ and the saturation of reduced $A_\parallel$ while $A_\perp$ is leveled off finally at the dose of 5 J/cm^2, as seen in Figure 9b. A_{av} is leveled off to give a value much smaller than A_0, implying the out-of-plane reorientation. To gain further insight into the spatial orientation of azobenzene chromophores, measurements of electronic absorption spectra of the films with s- and p-polarized probe light were performed at various incident angles (θ_m). Figure 10 shows p-polarized absorption spectra of C6MeO films exposed to linearly polarized 436 nm light of 0.05 and 5 J/cm^2 doses at 90 °C as a function of θ_m. We employ here A_{p320}/A_{p360} as the measure of a level of H-aggregation, whereas A_{p320} and A_{p360} are absorbances corresponding to aggregated and monomeric species (Figure 10c,d). As seen in Figure 10a, p-polarized spectra of the film illuminated at a 0.05 J/cm^2 dose are considerably similar to that of monomeric azobenzene and not influenced by θ_m at all, indicating that the in-plane orientation occurs exclusively (Figure 10c). On the other hand, p-polarized spectra of the film exposed to a 5 J/cm^2 dose display contrastive dependence on θ_m, as shown in Figure 10b. The larger θ_m is, the larger becomes the intensity of the blue-shifted absorption band (Figure 10d). The results support that prolonged irradiation of the film leads to the out-of-plane reorientation of self-aggregated azobenzene moieties. Such self-aggregation of azobenzenes triggered by molecular reorientation has been observed also for compression of Langmuir monolayers at water−air interface[24b] and Langmuir−Blodgett films of azobenzenes.[30]

On the other hand, no homeotropic reorientation occurred even after prolonged irradiation with the linearly polarized light when a film temperature was 120 °C. As shown in Figure 11, essentially no clear θ_m dependence of p- and s-polarized absorption spectra of the film was observed, and the spectral shapes imply no marked occurrence of H-aggregation. The results indicate that the azobenzene orients in a random fashion in the *yz*-plane (Figure 1) while the azimuthal (toward *y*-direction showing in-plane) reorientation of azobenzene side chains takes place. The contrastive behavior of photoreorientation at 120 °C comes very likely from nematic phase possessing a larger free volume, which enhances the molecular mobility in a photostationary state with a minor component of *Z*-isomer.[31]

3.4. Thermal Enhancement of Photoorientation. It was reported that the annealing of spin-coated films of liquid crystalline polymers with azobenzene side chains leads to marked enhancement of the optical anisotropy generated by irradiation with linearly polarized light.[10,15] The thermal treatment (annealing) of spin-coated films of the present polymers at temperatures above T_g after the exposure to linearly polarized light at room temperature was carried out here, since they display a variety of molecular orders and are accordingly suitable for the systematic study on the annealing effect. The results are summarized in Figure 12. A spin-coated film of the amorphous polymer, pMAz2, suffers from the decrease in the photoinduced optical anisotropy presented by *S* at 70 °C below T_g = 88 °C and the thorough disappearance at 105 °C (Figure 12a). On the contrary, C2MeO demonstrates the ther-

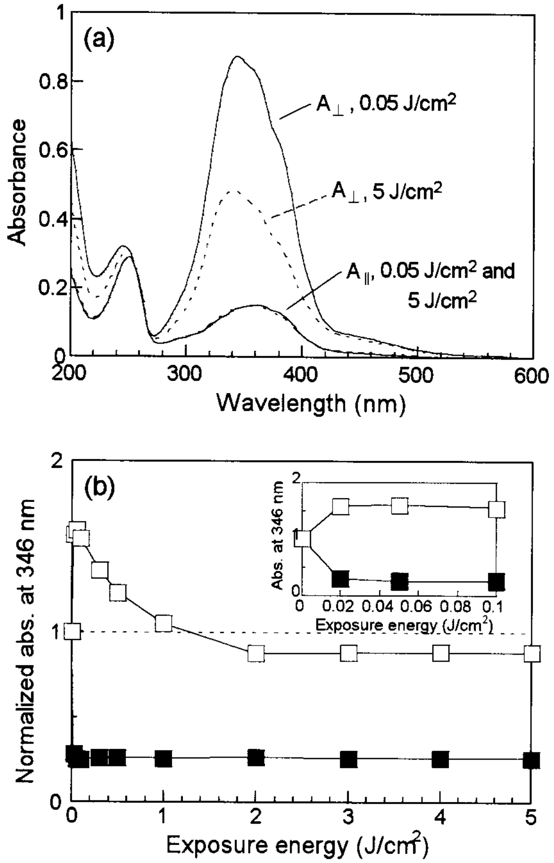

Figure 9. (a) Polarized absorption spectra of a C6MeO film taken at room temperature after irradiation with linearly polarized 436 nm light of exposure doses of 0.05 and 5 J/cm^2 at 90 °C, respectively. (b) Changes in normalized absorbances (□, $A_\perp$; ■, $A_\parallel$) of a C6MeO film at 346 nm as a function of exposure energy of linearly polarized 436 nm light at 90 °C. The inset shows a magnification of the exposure energy range (0−0.1 J/cm^2).

mal enhancement of S values in a manner quite different from pMAz2 (Figure 12b). S values are boosted at 115 °C slightly lower than the T_g (=120 °C) and markedly enhanced at 125 °C to give $S = 0.53$. Though no clear indication was obtained for the generation of any mesophase in C2MeO as stated above, the photoinduced dichroism was retained up to the melting temperature. In accordance with the literature,[10,15] C6MeO exhibits the pronounced enhancement of the photodichroism at elevated temperatures at 76 and 115 °C to give $S = 0.63$ ($\Delta n = 0.32$) (Figure 12c). Note that the polymer displays smectic and nematic phases at these temperatures. The highly ordered state of the annealed films was maintained even after heating at 78 °C for 4 h and 115 °C or below the clearing temperature and unchanged on prolonged storage for more than 1 year at room temperature.

On the other hand, as shown in Figure 12d, S values of a C12MeO film photoirradiated at room temperature are slightly reduced at 70 °C and decreased drastically at 100 °C though the polymer is still of a smectic phase. The reduction of the dichroism at the higher temperature stems from homeotropic orientation, as mentioned above on the basis of the results shown in Figures 7d and 12d. This situation is confirmed by conoscopic observation as shown in the inset of Figure 12d.

4. Discussion

It has been well accepted that the decay of photoinduced optical anisotropy of amorphous polymers with azobenzene side chains occurs efficiently at temperatures above T_g due to the thermal randomization to increase a free volume and the high mobility of the side chains.[32] pMAz2 as an amorphous polymer presents the trivial results showing that no optical anisotropy is generated by polarized light irradiation at 105 °C much higher than the T_g (88 °C) whereas dichroism is induced at 70 °C though at a lower level (Figure 5a). An order parameter S of a film exposed at room temperature decreases markedly at 70 °C and disappears thoroughly at 105 °C (Figure 12a). The low-level photogeneration and the reduction of S by heating at 70 °C below the T_g arise from the increasing mobility of the side chains in a polymer film. As shown in Figure 6a, there is no clear dependence of A_{p344}/A_{s344} on θ_m, indicating that polar angle (θ) remains unchanged before and after the photoirradiation at room temperature to lead to no marked out-of-plane orientation of the unsubstituted azobenzene side chains.

It is to be noticed that an amorphous as-coated film of C2MeO exhibiting no mesophase shows the entirely contrastive temperature dependence of photoorientation behavior at elevated temperatures. The irradiation at 115 °C slightly lower than the T_g (120 °C) gives rise to a considerable enhancement of S. At temperature (135 °C) higher than the T_g, the rate of the appearance of the photodichroism increases remarkably. Quite similar acceleration of the photogeneration of dichroism is observed for the liquid crystalline C6MeO when a film of the polymer is heated at 76 °C close to the transition temperature between glassy state and smectic phase. The enhancement of photodichroism generated at room temperature by annealing at elevated temperatures is observed not only for C6MeO but also for C2MeO (Figure 12). Consequently, it is reasonable to refer C2MeO as a polymer exhibiting “potential liquid crystallinity”, as suggested by Stumpe et al.[33] The shorter ethylene spacer length of C2MeO results in the restriction of the molecular mobility to give rise to less side-by-side interactions of the mesogenic side chains linked to the main chain, while the photoinduced orientation of the chromophoric residues triggers the enhancement of uniaxially oriented state which may be thermodynamically more stable. It should be mentioned that both C2MeO and C6MeO display no remarkable dependence of A_{p346}/A_{s346} upon incident angles of probe light (Figures 6 and 8), indicative of the exclusive photoorientation in an in-plane manner at both room and elevated temperatures.

The irradiation of a C12MeO film at 63 °C in glassy state and 85 °C exhibiting the smectic phase causes the generation of dichroism in a linear manner to give a saturated S value, which is much smaller than both C2MeO and C6MeO. This is because of the homeotropic (perpendicular) orientation of the azobenzene residues to reveal the peculiar situation of C12MeO. A film displays a noticeable blue-shift of p-λ_{max} owing to the formation of H-aggregation and the increase of A_{p342}/A_{s342} as the increase in θ_m, in particular, when the film is exposed to light at higher temperatures (Figure 8d). This means that the in-plane photoorientation of the azobenzene is accompanied by the out-of-plane orientation in the C12MeO film, while the in-plane orientation occurs for the other three polymers at elevated temper-

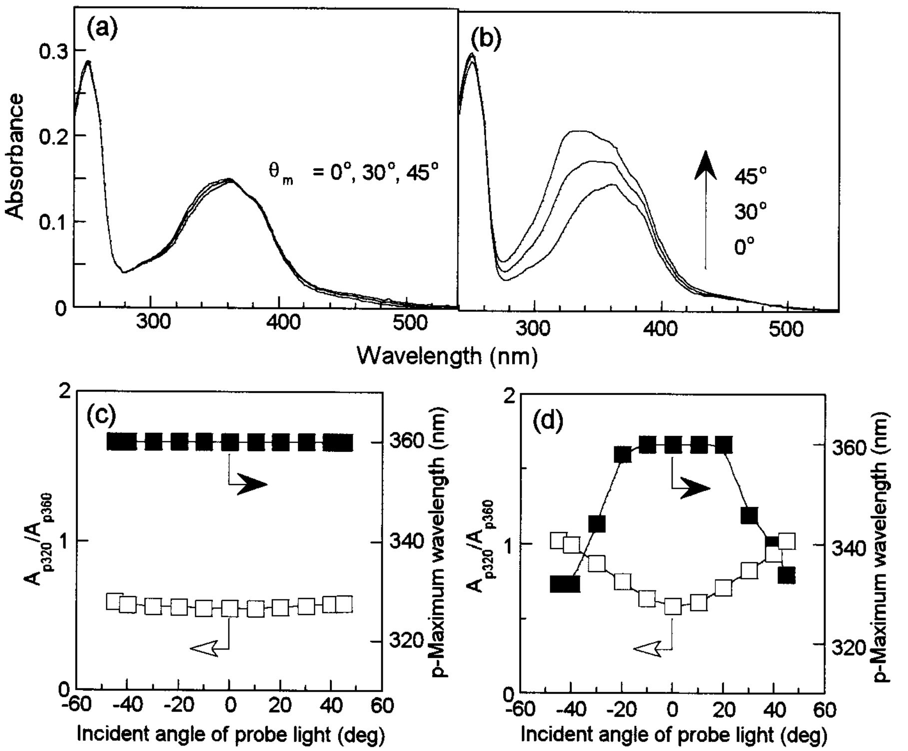

Figure 10. Polarized absorption spectra of a C6MeO film exposed to linearly polarized 436 nm light of exposure doses of (a) 0.05 J/cm^2 and (b) 5 J/cm^2, respectively, at various incident angles (θ_m) of p-polarized probe light. Changes in A_{p320}/A_{p360} and in p-maximum wavelength (p-λ_{max}) as a function of incident angle of probe light (θ_m) of the polymer films exposed to linearly polarized 436 nm light of exposure doses of (c) 0.05 J/cm^2 and (d) 5 J/cm^2, respectively.

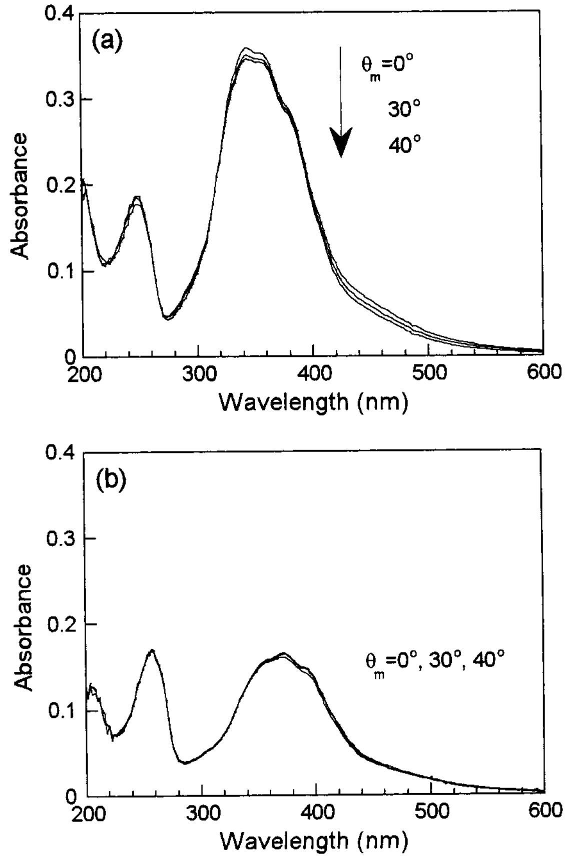

Figure 11. Polarized absorption spectra of a C6MeO film exposed to linearly polarized 436 nm light of an exposure dose of a 5 J/cm^2 at 120 °C at various incident angles (θ_m) of (a) p- and (b) s-polarized probe light.

atures except for a C6MeO film irradiated at 90 °C. Significant information concerning the out-of-plane orientation of a C12MeO film at elevated temperatures is obtained by an FT-IR spectrum of the film after annealed at 100 °C without linearly polarized light irradiation. As shown in Figure 7d, the bands due to the azobenzene including the Ph—O stretching at 1261 cm^{-1} and the =N—Ph stretching at 1147 cm^{-1} are reduced outstandingly, revealing that the homeotropic orientation of the azobenzene is readily induced thermally. This situation suggests that the concurrence of the in-plane and out-of-plane orientations of the azobenzene in C12MeO films at elevated temperatures arises from both photochemical and thermal events.

As shown in Figure 4c, the photoinduced change of S values of C6MeO films in smectic phase at 90 °C is quite unique when compared with those observed for the other polymers. The predominant contribution of $A_\perp$ to S values gives rise to a rapid increase in S (Figure 9b), followed by a gradual decrease through the maximum value of 0.64 at a 0.05 J/cm^2 exposure dose to give a saturated $S = 0.44$. The fact that absorption spectra of the dichroic film at the exposure dose of 0.05 J/cm^2 taken by using p-polarized light are insensitive to θ_m (Figure 10a) indicates evidently that polar angles (θ) of the molecular axis from the surface normal are randomly distributed in the yz-plane perpendicular to the polarization xz-plane of light. In other words, the in-plane orientation is completed to give the maximum S value at this point. The subsequent decrease in $A_\perp$ is accordingly assumed to be due to the out-of-plane reorientation of the perpendicularly oriented chromophores.[15]

On the other hand, the shape of p-polarized absorption spectra of a C6MeO film irradiated at a 5 J/cm^2 exposure dose depends significantly on θ_m, as illustrated in Figure 10b,d; the larger θ_m is, the more p-λ_{max} is blue-shifted, accompanied by the increment of absorbances.

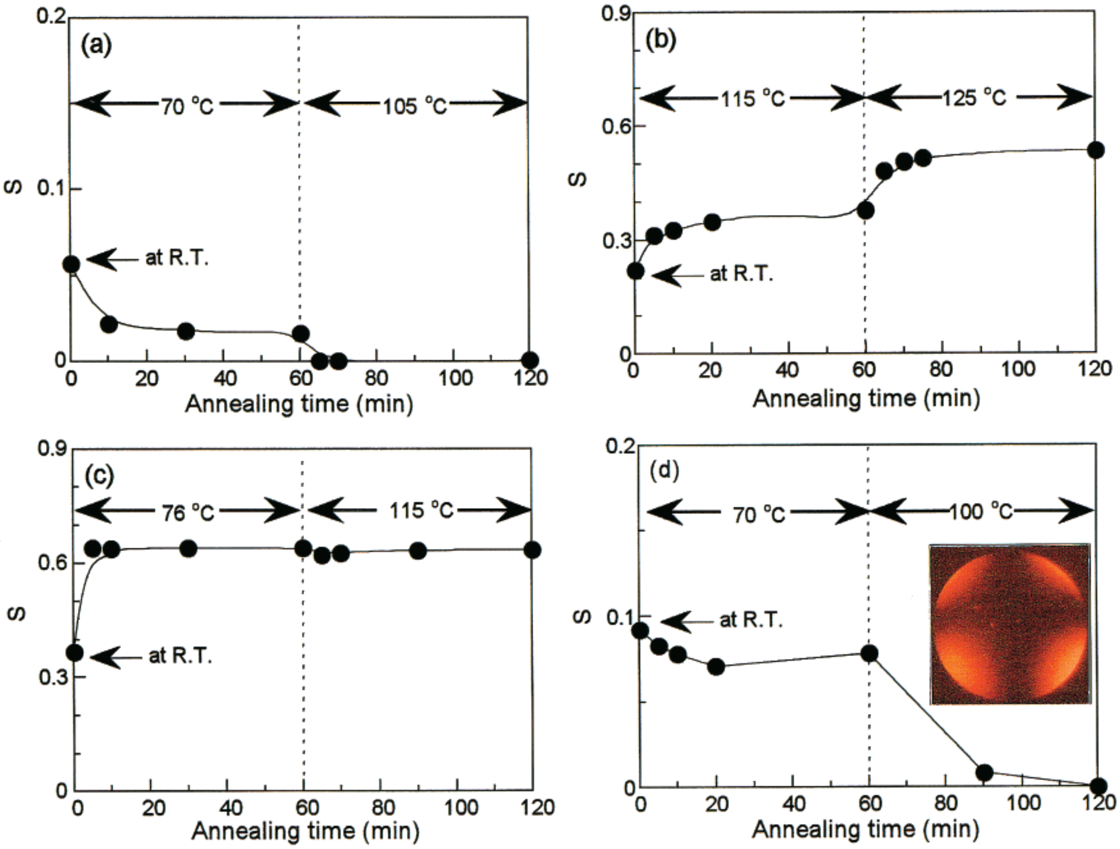

Figure 12. Changes in order parameter S by annealing of polymer films photoirradiated with linearly polarized 436 nm light at room temperature: (a) pMAz2, (b) C2MeO, (c) C6MeO, and (d) C12MeO. The inset in (d) corresponds to the conoscopic observation of out-of-plane orientation of C12MeO after annealing at 100 °C.

This θ_m dependence arises evidently from the reorientation to the surface normal and the concurrent self-organization of the azobenzene groups. In other words, the prolonged irradiation with linearly polarized light brings about the out-of-plane reorientation of the azobenzene, which is determined by the propagation direction (another perpendicular direction of the electric vector) of the actinic light, leading to the formation of H-aggregates. Changes in birefringence induced by irradiation with linearly polarized light at high temperatures were observed by Wang et al.[34] for liquid crystalline polymers with azobenzene side chains, though no clear mechanism has been provided. The successive out-of-plane reorientation occurs as a result of the repetition of photoisomerization in the same mechanism as that for the out-of-plane orientation induced by nonpolarized light to minimize light absorption.[35]

It is worthy to mention here that the thermal treatment without light irradiation of a C6MeO film above T_g gives rise to no measurable decrease of the $\pi-\pi^*$ absorption band, indicating that the out-of-plane reorientation is caused not thermally, but exclusively photochemically, in a sharp contrast to a C12MeO film.

A much slower rate of the subsequent out-of-plane reorientation stems from the markedly reduced $A_{\|}$ as a consequence of in-plane photoreorientation. But this interpretation is not enough, since no out-of-plane reorientation is observed for the same polymer when the illumination is carried out at 76 °C, where the in-plane orientation is leveled off at an exposure dose of about 0.4 J/cm^2 (Figure 4c). Figure 8c shows unequivocally that the in-plane photoorientation at 76 °C occurs without any out-of-plane orientation, as stated above. No marked occurrence of the out-of-plane is observed for the irradiation at 90 °C at the exposure dose of 0.05 J/cm^2, as evidence by the θ_m independence of absorption spectra (Figure 10a). These results mean that the in-plane orientation of each azobenzene consists solely of the modification of the azimuthal angle (ϕ) without change of a polar angle (θ) as a result of angular selective photoisomerization and angular redistribution. The in-plane molecular orientation of azobenzenes in polymer matrices has been thought to occur through the three steps involving angular-selective photoisomerization, angular redistribution of molecular axis, and rotational diffusion due to thermal agitation.[11] It follows that the angular redistribution in a smectic phase takes place preferentially in a plane determined by the electric transition dipole moments of E- and Z-isomers. The successive out-of-plane orientation at 90 °C is due to the high mobility of mesogens with the relatively long hexyl spacers and the interaction with incident light. As mentioned in the Introduction section, out-of-plane reorientation induced by prolonged irradiation with linearly polarized light has been occasionally observed. Such delayed occurrence of the out-of-plane photoreorientation comes very likely from the fact that azobenzene chromophores perpendicularly orientated as a result of the in-plane photoreorientation absorb the light at a far lower level because of the orthogonal direction of the electric vector of the light.

The biaxial photoorientation of an azobenzene molecule with electric transition dipole moment parallel to the polarization plane of the light is illustrated as shown in Figure 1. This is an extreme case. The photoorientation behavior of azobenzenes in films of C6MeO can

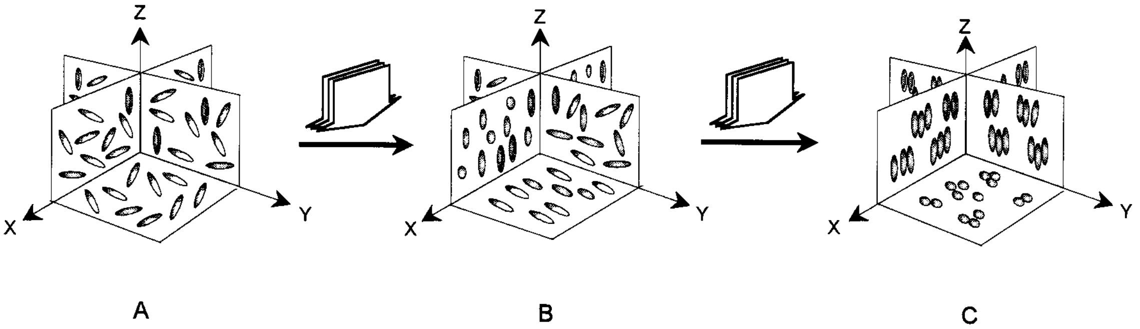

Figure 13. Illustrative presentation of the biaxial photoorientation. The electric vector of linearly polarized light is in parallel with the *xz*-plane.

be illustrated as shown in Figure 13. The spatial direction of a molecule exposed to linearly polarized light is defined by two angles: an azimuthal angle (ϕ) contained by the longitudinal axis of the molecule and the electric vector of light and a polar angle (θ) of the molecular axis from the surface normal. Before the photoirradiation of a spin-coated film, both ϕ and θ of azobenzenes are randomly distributed three-dimensionally so that a film is isotropic (state A). Irradiation with linearly polarized light at room temperature or 76 °C leads to a biased distribution of ϕ to provide a preferential orientation perpendicular to the electric vector ($\phi = 90°$) to give rise to the in-plane orientation (state B). Note that the in-plane orientation contains no modification of θ, indicating that the directions of azobenzene is randomly distributed in the *yz*-plane, as confirmed by the θ_m independence of absorbances of the azobenzene (Figure 8). The state B is also generated at the early stage of the photoirradiation at 90 °C, while prolonged irradiation at the same temperature induces the out-of-plane orientation (state C). When the film temperature is elevated at 120 °C, the in-plane orientation takes place rapidly at the early stage of photoirradiation (state B), followed by the gradual decline of S due to the enhancement of molecular mobility, which suppresses the out-of-plane photoreorientation.

Since the biaxial photoorientation takes place successively, the difference in the orientation modes can be visualized by photopatterning on the basis of the difference in exposure doses of the same light. A C6MeO film was first exposed to linearly polarized 436 nm light of the 0.05 J/cm^2 dose, followed by the exposure of the film through a photomask to light of the 5 J/cm^2 dose without the change of the polarization direction. Figure 14 shows the polarized micrographs of the film. Brighter and darker areas correspond to in-plane and biaxial orientations, respectively. The stored information is kept unchanged at room temperature for 1 year or longer. The erasure of the pattern is carried out by UV light irradiation or annealing over the clearing temperature of the polymer.

5. Conclusion

The photoorientation of azobenzene side chains in spin-coated films exposed to linearly polarized light is markedly influenced by the following factors. The first is the nature of polymers depending on whether the polymers are amorphous, liquid crystalline, potentially liquid crystalline, or semicrystalline. In accordance with previous reports,[2,4,5,32] it was confirmed that amorphous pMAz2 exhibits a low level of photodichroism that decays above T_g, while liquid crystalline C6MeO shows relatively large photodichroism, which is markedly enhanced at mesophases and disappears above the clearing temperature. It should be stressed that C2MeO displays quite a similar behavior to liquid crystalline C6MeO in the photoorientation even the former displays no mesophase. It is reasonable to refer the polymer as potentially liquid crystalline. As reported previously,[3] the photodichroism of semicrystalline polymers with azobenzene side chains generated by linearly polarized light displays anomalous thermostability owing to the crystalline nature. Second, the photoorientation is

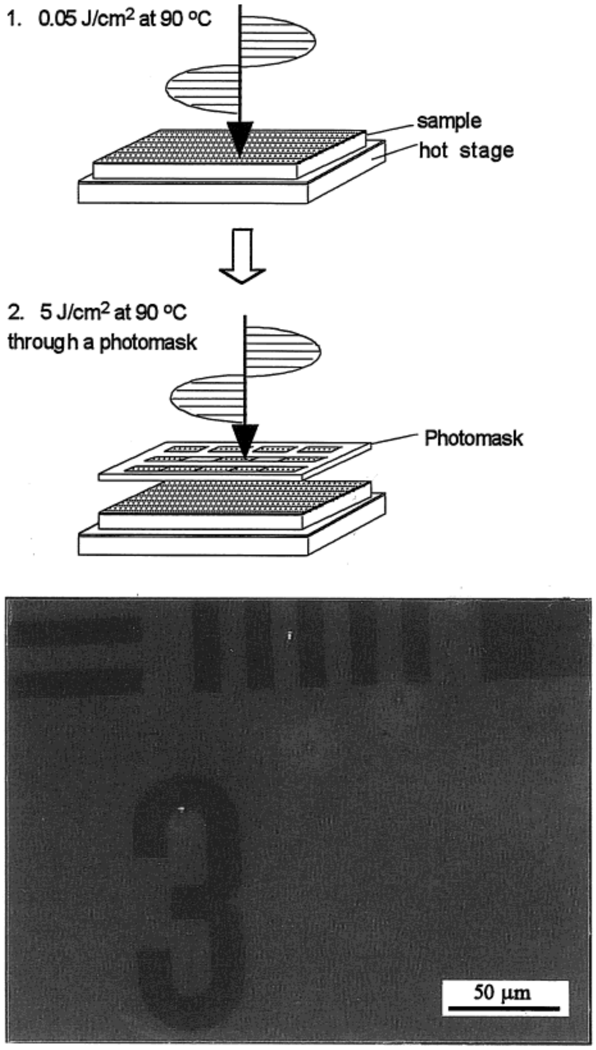

Figure 14. Polarized microscopic images of a C6MeO film irradiated with linearly polarized 436 nm light of a 0.05 J/cm^2 exposure dose and subsequently irradiated through a photomask with the same light of a 5 J/cm^2 dose.

markedly influenced by temperatures of films because of the difference in mesophases. As revealed by films of C6MeO, the in-plane orientation occurs preferentially in glassy state as well as at 76 °C, whereas it is followed by the out-of-plane orientation to demonstrate the distinctive succession of the biaxial photoreorientation at 90 °C. The out-of-plane reorientation is induced as a consequence of the minimization of light absorption. However, irradiation at much higher temperature of 120 °C showing nematic phase generates no homeotropic photoreorientation and gives rise to a lower value of order parameter after passing high optical anisotropy at the early stage as shown in Figure 5c. This fact results from enhanced molecular mobility of the mesogenic azobenzene in the nematic phase. Third, the concurrence of the in-plane and out-of-plane photoreorientation is efficiently generated for C12MeO with the long alkylene spacer, because of its hydrophobicity to induce homeotropic alignment efficiently upon heating.

Polymers substituted with azobenzenes in side chains as well as main chains are promising materials because of their multiple photonics applicabilities that require versatile performances and reliabilities. The present study suggests that the appropriate choice of chemical structures of azobenzene-containing polymers is a prerequisite for the practical applications.

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