Photoinduced Alignment of Polymer Liquid Crystals Containing Azobenzene Moieties in the Side Chain. 2. Effect of Spacer Length of the Azobenzene Unit on Alignment Behavior

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ABSTRACT: By irradiation with linearly polarized light at 366 nm, alignment change was generated in polymer liquid crystals (**MACB-AB*n***, $n = 3$, 6, and 11) with different spacer lengths of the azobenzene units but the same enthalpic stability of the liquid-crystalline phase. Polarized IR spectra revealed that the polymer main chain did not reorient while the mesogens were aligned perpendicular to the polarization direction of the writing light. The effect of the spacer length on alignment behavior was investigated by measuring the transmittance through the polymer liquid-crystal film and the induced order parameters. Results show that alignment change is more difficult to be induced in a polymer liquid crystal, having a short spacer. The spacer length does not affect the *trans*−*cis* photoisomerization and consequent *cis*−*trans* thermal isomerization behavior. The restriction of the polymer main chain on azobenzene moieties through the spacer affects the alignment efficiency of azobenzene mesogens and, therefore, affects the alignment behavior of the polymer liquid crystals.

Introduction

It is well-known that linearly polarized light can induce reorientation of azobenzene groups through photochemically induced *trans*−*cis*−*trans* isomerization. By using this property, polymers containing azobenzene groups are being developed for optical storage media, such as a polymer matrix dispersed with azodyes,[1] amorphous high T_g polymers with azobenzene groups,[2,3] and polymer liquid crystals containing azobenzene moieties in the side chain.[4,5]

Side group liquid-crystalline polymers show a unique combination of the functionality of conventional liquid crystals and the properties of macromolecules. They offer the possibility for modification of the order state by external fields and in this way the variation of optical properties. Since Wendorff demonstrated reversible optical storage properties in side-chain polymer liquid crystals with azobenzene moieties in 1987,[4,5] there has been a lot of interest in this area.[6−8] It was reported that optical anisotropy could be achieved in polymer liquid crystals with azobenzene moieties in a side chain by using linearly polarized light. The mechanism for alignment involves the photochemical *trans*−*cis* isomerization and consequent thermal *cis*−*trans* isomerization. By repetition of these *trans*−*cis*−*trans* isomerization cycles and motion of its transition moment, the optic axis of azobenzene groups becomes aligned perpendicular to the electric vector of polarized actinic light. Nonphotoactive mesogens underwent alignment together with the azobenzene groups for cooperative motion of the neighboring groups. The induced anisotropy was fairly stable below the clearing temperature of the polymer liquid crystals; hence, the material has long-term stability.

Both polymer liquid crystals with azobenzene groups and amorphous azo polymers were used in these storage processes. In the former it was implied that the presence of some spacer was needed between the rigid polymer main chain and the azo groups, since the spacer would allow the flexibility necessary for the required movement. Even the amorphous copolymers contained relatively long spacers.[9] On the contrary, in the latter it was reported that the presence of spacers was not necessary, and it is preferable to have materials with shorter or no spacers.[10] Stumpe and co-workers studied the effect of spacer length of a nonphotoactive unit or azobenzene unit on reorientation behavior of polymer liquid crystals.[11,12] The orientational order increased or decreased, depending on the enthalpic stability of the mesophase which changed with change in the spacer length. Since both the spacer length and the enthalpic stability of the mesophase have an effect on the photoinduced alignment behavior, it is preferred to study the effect of spacer length under the same enthalpic stability of the mesophase.

In this study, we used three polymer liquid crystals which have nearly the same change in enthalpy from nematic to isotropic phase but different spacer lengths of azobenzene units. The real effect of the spacer length, without the contribution of the enthalpic stability of the mesophase, on the alignment behavior of the polymer liquid crystals was investigated in detail.

Experimental Section

Monomers, 4′-[6-(methacryloyloxy)hexyloxy]-4-cyanobiphenyl and *n*-[4-(4-ethylphenyl)diazenylphenyloxy]-alkyl methacrylate, were prepared by using a procedure similar to the literature.[13] Polymerization was performed as reported previously.[8] The feed ratio of the azobenzene monomer was 7 mol %. Conversion was 90% in each case and a good agreement between the initial comonomer ratio and copolymer composition was obtained. The structure of polymer liquid crystals **MACB-AB*n*** is detailed in Figure 1. The molecular weight was measured by gel permeation chromatogra-

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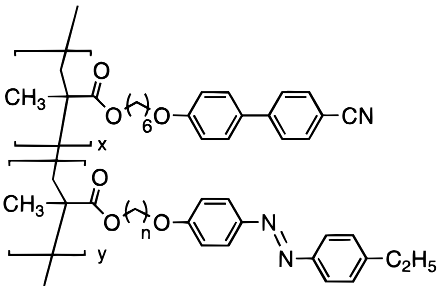

MACB-ABn

Figure 1. The structure of polymer liquid crystals, **MACB-AB*n***, used in this study. $n = 3$, 6, and 11.

phy (GPC; Toyo Soda HLC-802; column, GMH6 × 2 + G4000H8 + G500H8; eluent, chloroform) calibrated with standard polystyrenes. Thermotropic properties were obtained with a differential scanning calorimeter (Seiko I&E SSC-5200 and DSC220C) at a heating rate of 10 °C/min. Three scans were performed to check the reproducibility. The content of the azobenzene units was calculated from UV spectra (Shimadzu UV-200S) of the copolymer and the monomer in tetrahydrofuran solution. The results are summarized in Table 1.

Thin polydomain films (about 2-μm thickness) were obtained as described before.[8] Optical experiments were performed with the setup similar to the literature,[14] which consists of a linearly polarized pumping light (366 nm) from a 500-W high-pressure mercury lamp and a probe light (He−Ne laser 633 nm) which is far from the absorption band of the azobenzene groups. The writing light was focused with a lens and then passed through a polarizer before it impinged on the film and induced anisotropy. The probe light, polarized at 45° with respect to the polarization direction of the writing light, passed through crossed polarizers, was used to probe the induced anisotropy. The intensity of the probe light was detected with a photodiode which was connected to a computer. A sample placed in a thermostated block was put between the two polarizers. The entire data acquisition was computer-controlled with a PC. The induced order parameter was obtained as described before by using polarized UV and IR (JASCO FTIR-3) spectroscopy.[8] The UV spectra for the dynamic behavior of azobenzene were measured in situ in the spectrometer. In this case, mesogens in the films were uniformly aligned by rubbing treatment of the poly(vinyl alcohol) alignment layer which had been prepared on the glass substrate. The absorbance at 360 nm was measured immediately after the irradiation light was switched off.

Results

Photoinduced Alignment Behavior. In the previous paper, we reported that alignment could be induced in the polymer liquid crystal, **MACB-AB6**, by irradiation with linearly polarized light at 366 nm.[8] Azobenzene moieties were oriented perpendicular to the electric vector of writing light, and cyanobiphenyl groups underwent alignment together with the azobenzene moieties. Figure 2 shows the polarized IR spectra of **MACB-AB6** film after exposure to linearly polarized light (2.8 mW/cm^2) at 366 nm for 30 min at 95 °C. The absorption band at 2225 cm^{-1}, and the bands at 1604 and 1495 cm^{-1} are attributed to the stretching vibration of cyano groups and the backbone stretching vibration of benzene groups, respectively. It was found that the absorbance of these groups changed with the polarization direction of the measurement beam. When the polarization direction of the measurement beam was parallel to that of the irradiation light, the absorbance of cyano and benzene groups decreased to the minimum value (**a**). On the other hand, when the two directions were perpendicular to each other, the absorbance of these bands reached the maximum value (**b**). This result indicates that alignment of the azobenzene and cyanobiphenyl mesogens was induced; the molecular long axis was aligned perpendicular to the polarization direction of the irradiation light.

One can see that the absorbance of carbonyl groups located at 1730 cm^{-1} did not change with the change of the polarization direction of the measurement beam. It revealed that the alignment of the carbonyl groups was not induced. Since the carbonyl groups were directly attached to the polymer main chain, it seems sensible to assume that the polymer main chain did not participate in the alignment. Therefore, we can imagine that the mesogens and a small part of the spacer directly attached to the mesogen take part in the alignment process, whereas the rest of the spacer and the backbone do not reorient. The similar behavior of side-chain polymer liquid crystals in an electric field was reported recently by Czarnecki and co-workers.[15] It sounds very likely that side-chain polymer liquid crystals behave in this way in external fields, such as electric field and light.

Effect of Spacer Length on Alignment Behavior. The three polymer liquid crystals used in this study have the same maximum absorption in UV/vis spectra at around 350 nm and show nearly the same extinction coefficiency at 366 nm. Before irradiation, the thin polymer film showed polydomain. There was no light passed through the crossed polarizer. If alignment is induced in the polymer film, light can pass through the polarizer and reach the detector due to birefringence of liquid crystals. Figure 3 shows the change in transmittance as a function of irradiation time. The intensity of the irradiation light was 2.8 mW/cm^2. An alignment change was induced in **MACB-AB6** film when the temperature was higher than 90 °C, while **MACB-AB3** exhibited the alignment change only when temperature was above 97 °C. **MACB-AB11** exhibited a similar behavior in the alignment change to **MACB-AB6**. Although the spacer length of azobenzene units in **MACB-AB11** is nearly twice as long as that in **MACB-AB6**, the difference in behavior in the alignment change between them is not so obvious as that between **MACB-AB6** and **MACB-AB3**. In addition, the transmittance of **MACB-AB3** increased more slowly than that of **MACB-AB6** and **MACB-AB11**, between which little difference was observed. For example, it took about 15 min to achieve the saturated transmittance for **MACB-AB6** and **MACB-AB11** at 97 °C, while about 25 min for **MACB-AB3** at 100 °C. This figure clearly shows that the spacer length of azobenzene units had a significant effect on the alignment behavior of the polymer liquid crystals. The results indicate that alignment change is more difficult to be generated in the polymer liquid crystal having a short spacer length of azobenzene units. When the spacer length is longer than six methylene units, the effect is not obvious. A similar dependency on spacers was reported previously by Finkelmann and Rehage.[16]

As reported previously,[8] we can use the induced order parameters to evaluate the efficiency of photoinduced

Table 1. Thermodynamic Properties and Molecular Weights of MACB-AB*n*[a]

polymer	x:y	phase transition temp. (°C)	ΔH_{NI} (kJ/mol)	ΔS_{NI} (J/mol·K)	M_n	M_w/M_n
MACB-AB3	93:7	G 51 N 114 I	1.9	4.8	31 000	1.6
MACB-AB6	94:6	G 44 N 115 I	1.8	4.6	25 000	2.0
MACB-AB11	93:7	G 36 N 113 I	2.0	5.0	26 000	1.8

[a] G, glass; N, nematic; I, isotropic; ΔH_{NI}, change in enthalpy of N–I phase transition; ΔS_{NI}, change in entropy of N–I phase transition; M_n, number-average molecular weight; M_w, weight-average molecular weight.

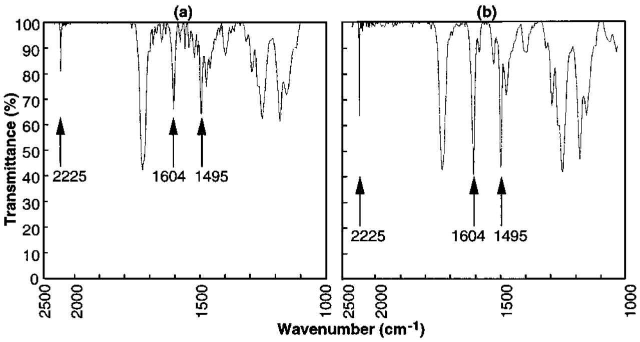

Figure 2. Polarized IR spectra of **MACB-AB6** film after irradiation with 366-nm linearly polarized light (2.8 mW/cm^2) at 95 °C for 30 min. Spectrum was measured at room temperature with polarized IR beam parallel to (a) and perpendicular to (b) the polarization of the irradiation light.

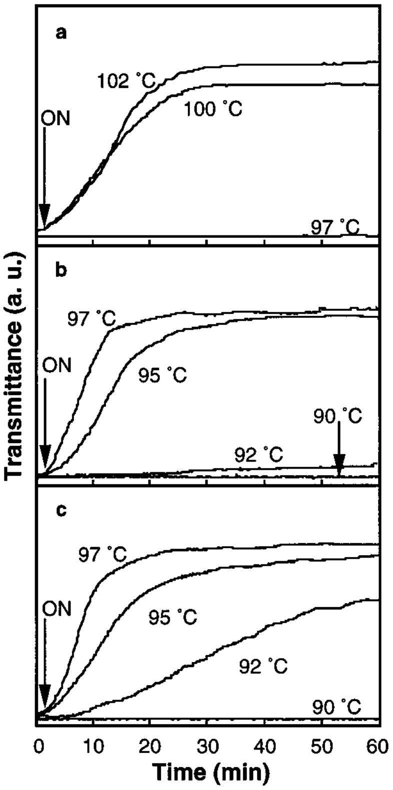

Figure 3. The transmittance as a function of irradiation time. Films were exposed to linearly polarized light (366 nm) at 2.8 mW/cm^2 at various temperatures. (a) **MACB-AB3**; (b) **MACB-AB6**; (c) **MACB-AB11**.

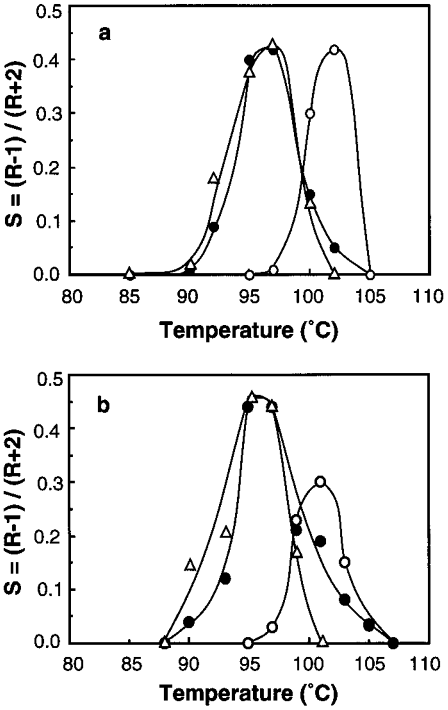

Figure 4. Induced order parameters of azobenzene (a) and cyanobiphenyl (b) moieties of **MACB-AB*n*** at various temperatures. Films were irradiated with linearly polarized light (366 nm) at 2.8 mW/cm^2 at 95 °C for 30 min. △, **MACB-AB11**; ●, **MACB-AB6**; ○, **MACB-AB3**.

alignment change. The order parameters of azobenzene moieties and cyanobiphenyl mesogens can be determined by polarized UV spectra at 360 nm and polarized IR spectra at 2225 cm^{-1}, respectively. Figure 4 shows the induced order parameters in **MACB-AB*n*** films after exposure to polarized light (2.8 mW/cm^2) at 366 nm for 30 min at various temperatures. Compared with **MACB-AB3**, alignment was induced in **MACB-AB6** and **MACB-AB11** at a relatively low temperature. Little difference in the behavior was observed between **MACB-AB6** and **MACB-AB11**. With an increase of temperature, the order parameter increased at first until a maximum level and then decreased. As reported previously,[8] the increase of order parameter is attributed to the increase of the *cis*–*trans* isomerization rate as well as the mobility of mesogens for an alignment change, and the decrease of order parameter is due to the phase transition induced by *trans*–*cis* isomerization of azobenzene groups.[14,17,18] The induced order parameters at various temperatures confirmed the effect of the spacer length on alignment change again.

***Trans*–*cis*–*trans* Isomerization Behavior of Azobenzene Groups.** The composition and the clearing temperature are nearly the same for the polymer liquid crystals used in this study. The change in enthalpy from nematic to isotropic phase which is dominated by nonphotoactive mesogens is also nearly the same (Table 1). The only difference in the three polymer liquid crystals is the length of the flexible alkyl spacer between the backbone and the mesogenic azobenzene group. To clearly understand the effect of spacer length on alignment behavior, the photoinduced *trans*–*cis* isomerization and the thermal *cis*–*trans* isomerization behavior of azobenzene groups were investigated. To compare the *trans*–*cis* photoisomerization rate, we measured the concentration of *cis*-azobenzene produced by 366-nm unpolarized light in the films at various

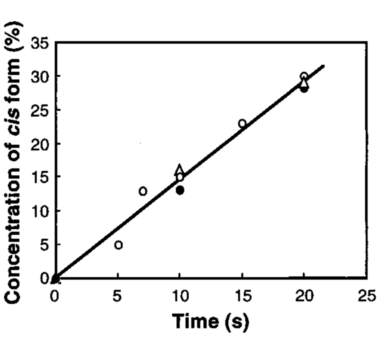

Figure 5. Concentration of *cis*-azobenzene produced by irradiation with 366-nm unpolarized light (2.0 mW/cm^2) at 95 °C as a function of irradiation time. △, **MACB-AB11**; ●, **MACB-AB6**; ○, **MACB-AB3**.

times. The concentration was estimated as $[cis]\% = 100 \times (A_0 - A_t)/A_0$, where A_0 and A_t are the absorbance at 360 nm of the polymer before irradiation and at irradiation time t. Unpolarized light was used to avoid any angular-dependent absorption of the irradiation light. Figure 5 shows the results obtained at 95 °C. The concentration of the *cis*-form azobenzene increased at the same rate against the irradiation time for the polymer liquid crystals. This indicates that the *trans*–*cis* photoisomerization is not affected by the spacer length between the backbone and the azobenzene moiety.

Although the non-first-order reaction was reported for glass-state polymers,[19,20] the general agreement is that the thermal *cis*–*trans* isomerization is the first-order reaction in a wide variety of media and phases; therefore, $\ln\{[cis]/[cis]_0\} = -kt$, where $[cis]$ and $[cis]_0$ are the concentration of *cis*-azobenzene at time t and time zero, respectively, and k is the rate constant for the thermal *cis*–*trans* isomerization. By measuring the UV spectra, the rate constant can be determined by fitting the experimental data to the following equation:[21]

$$\ln\{[A_\infty - A_t]/[A_\infty - A_0]\} = -kt \qquad (1)$$

where A_∞, A_t, and A_0 are the absorbance at 360 nm at time infinite, time t, and time zero, respectively. Before measuring the *cis*–*trans* isomerization of the azobenzene groups at high temperature with the films which were prepared on the rubbed poly(vinyl alcohol) alignment layer, the isomerization behavior was compared between the films on the rubbed poly(vinyl alcohol) layer and those on the nonrubbed poly(vinyl alcohol) layer at room temperature. No difference was observed between them. When the experimental data were fitted to eq 1, fairly good linearity of the first-order plots was observed for all samples. Although the spacer length is different, the rate constants of the three polymer liquid crystals were nearly equal to each other at the same temperature. For instance, we obtained the values as 8.44×10^{-3}, 8.48×10^{-3}, and 8.52×10^{-3} s^{-1} as the rate constants of the *cis*–*trans* isomerization at 95 °C for **MACB-AB3**, **MACB-AB6**, and **MACB-AB11**, respectively. Rate constants of *cis*–*trans* isomerization at various temperatures within the liquid-crystalline phase were measured. In Figure 6, the Arrhenius plots for the thermal *cis*–*trans* isomerization were given, which also show fairly good linearity. We obtained the values as 58.0, 58.5, and 57.7 kJ/mol as activation energy for **MACB-AB3**, **MACB-AB6**, and **MACB-AB11**, respectively. The activation energy obtained in the present system is comparable to those reported for *cis*–*trans* isomerization in liquid-crystalline matrices.[21] Both the same rate constant and the same activation energy mean that there is no difference in the *cis*–*trans* isomerization even though the spacer length is different. The spacer length of azobenzene units does not affect the dynamics of the *trans*–*cis*–*trans* isomerization of the azobenzene moieties.

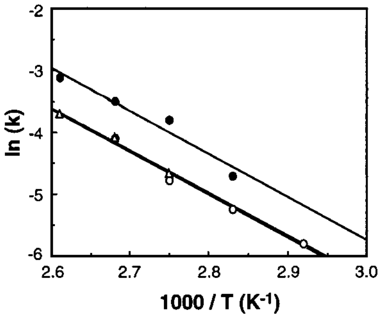

Figure 6. Arrhenius plots for *cis*–*trans* thermal isomerization of azobenzene moieties in **MACB-AB*n*** films. △, in **MACB-AB11**; ●, in **MACB-AB6**; ○, in **MACB-AB3**.

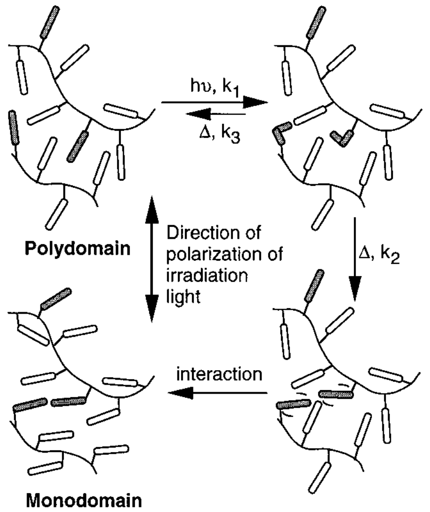

Figure 7. Illustration for the mechanism of photoinduced alignment in polymer liquid crystals. k_1, rate constant of *trans*–*cis* photoisomerization; k_2 and k_3, rate constants of *cis*–*trans* thermal isomerization.

Discussion

As shown in Figure 7, it seems reasonable to assume that the alignment process consists of three steps: the *trans*–*cis* isomerization of azobenzene moieties due to photoselection excitation, the alignment of azobenzene moieties through *trans*–*cis*–*trans* isomerization cycles, and the orientation of nonphotoactive moieties for cooperative motion. Therefore, the alignment process may be affected by the isomerization behavior of the azobenzene moiety and the enthalpic stability of the mesophase which dominates the mobility of the mesogens for an alignment change. As demonstrated before, the spacer does not affect the isomerization behavior of the azobenzene moiety; the same enthalpic stability of mesophase reveals the same mobility of mesogens for an alignment change. It seems that neither of them leads to the different efficiency of alignment change. If we analyze the *cis*–*trans* isomerization process in detail, we will realize that, after azobenzene was transformed to the *cis* form by linearly polarized light, there are two ways for the *cis* form to isomerize thermally to the *trans* form. One is to deviate from the initial state accompanied by a motion of its transition moment and finally to become perpendicular to the direction of irradiation light. This is an effective isomerization, which can induce the alignment change. The rate constant of this process is defined as k_2. The other way is to isomerize to the original state. This way cannot induce alignment change. We defined the rate constant of this process as k_3. Although the rate constants of *trans*−*cis* photoisomerization as well as those of *cis*−*trans* ($k_2 + k_3$) thermal isomerization are the same among the three polymer liquid crystals, the ratio of k_2 to k_3 may be different if the spacer length is different. For a polymer possessing short spacer lengths of azobenzene units, the azobenzene moieties cannot be regarded as being free from the polymer main chain; the restriction of the polymer main chain on azobenzene moieties increases the isomerization rate k_3 and decreases the effective isomerization rate k_2; therefore, the alignment change is more difficult to be achieved. In other words, although the polymer main chain does not affect the *trans*−*cis*−*trans* isomerization of the azobenzene moieties, it affects the motion of the transition moment of the azobenzene mesogen. If the spacer is long enough, such as six methylene units, the azobenzene moieties can be considered as being free from the polymer main chain; therefore, the alignment behavior for **MACB-AB6** and **MACB-AB11** is nearly the same. Unfortunately, we cannot measure the rate constants k_2 and k_3.

Conclusion

In summary, we have shown the effect of the spacer length of azobenzene units on the alignment behavior of polymer liquid crystals by measuring the transmittance through a polymer liquid-crystal thin film and the induced order parameters. An alignment change in a polymer liquid crystal possessing short spacer length was more difficult to be generated. When the spacer is long enough, such as six methylene units, the increase of the spacer length did not affect the alignment efficiency. It was found that the *trans*−*cis* photoisomerization rate and *cis*−*trans* thermal isomerization rate were not affected by the spacer length. The effect of the spacer length of azobenzene units on alignment behavior may be attributed to the effect of the polymer main chain through a spacer on the motion of the transition moment of the azobenzene moieties.

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