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Photoinduced alignment of polymer liquid crystals containing azobenzene moieties in the side chain. 4. Dynamic study of the alignment process

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Abstract

An anisotropy was induced in initial isotropic (polydomain) polymer liquid crystal **MACB-CNAB6** by using linearly polarized light at 366 nm. The alignment processes induced at various temperatures and various intensities of irradiation light were analyzed by using a biexponential function (as shown in text). It was found that the alignment process involved two response modes: a fast response mode and a slow one. The fast response mode was associated with the angular-dependent *trans–cis* photoisomerization and the preliminary alignment of mesogens, while the slow one was attributed to the position adjustment of the mesogens to obtain well-aligned monodomain. The writing rate and the induced anisotropy increased with increase in temperature and in light intensity at low intensity of the irradiation light. Combined with photochemical phase transition processes, optical switching and image storage were realized in the polymer liquid crystal. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Photoinduced alignment; Polymer liquid crystals containing azobenzene; Kinetics of orientation

1. Introduction

Polymer liquid crystals with azobenzene moieties are promising materials for optical switching and image storage because the orientation of mesogens in thin films of these materials may be modified by light [1,2]. It is well known that linearly polarized light can induce reorientation of azobenzene groups through photochemical *trans–cis–trans* isomerization [3,4]. By using this property, anisotropy could be achieved in initial isotropic polymer liquid crystals with azobenzene moieties in side chains by using linearly polarized light [5–8]. The mechanism for alignment involves the photochemical *trans–cis* isomerization and photochemical and/or thermal *cis–trans* isomerization of the azobenzene groups. By repetition of these *trans–cis–trans* isomerization cycles and motion of its transition moment, the optic axis of the azobenzene groups becomes aligned perpendicular to the electric vector of polarized actinic light. In the case of liquid-crystalline copolymers, non-photoactive mesogens undergo alignment together with the azobenzene groups for cooperative motion of the neighboring groups.

The alignment behavior is expected to depend on several factors such as the temperature and the intensity of irradiation light [6], the spacer length of azobenzene units [7], and the structure of the azobenzene groups [8]. Analysis of kinetic curves allowed us to evaluate the role of many factors influencing the photoinduced alignment process. Dynamic study of the alignment process in amorphous azo polymers has been well performed by Natansohn et al. [9], which gave an insight into the mechanism responsible for alignment processes. However, the dynamic study of the alignment process in polymer liquid crystals was seldom studied before. The aim of this work is to clarify the underlying mechanism responsible for the alignment behavior by analyzing the growth curves observed at various temperatures and various intensities of irradiation light.

2. Experimental

Monomers, 4′-[6-(methacryloyloxy)hexyloxy]-4-cyanobiphenyl and 6-[4-(4-cyanophenyl)diazenylphenyloxy]alkyl methacrylate, were prepared using a procedure similar to the literature [10]. Polymerization was performed as reported previously [6]. The feed ratio of azobenzene monomer was 7 mol%. Structure of the polymer liquid crystal **MACB-CNAB6** is detailed in Fig. 1. Molecular weight

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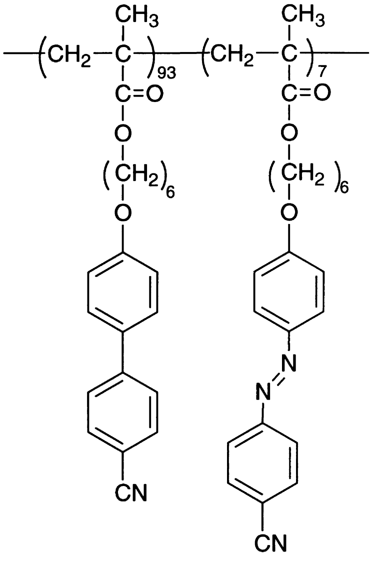

MACB-CNAB6

Fig. 1. Structure and composition of the polymer liquid crystal, **MACB-CNAB6**, used in this study.

was measured by gel permeation chromatography (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. Liquid-crystalline phase was determined by X-ray diffractometry (MAC Science MXP [3], model 5301; Cu Kα1 radiation from a 1.6 kW anode X-ray generator at 90°C). The content of the azobenzene units was calculated from UV spectra (Shimadzu UV-200S) of the copolymer and the monomer in tetrahydrofuran (THF) solution. The results are summarized in Table 1.

Thin polydomain films (about 2 μm thickness) were obtained as described before [6]. Optical experiments were performed with the setup similar to the literature [11]. A sample placed in a thermostatic block was put between two crossed polarizers. Light at 366 nm from a 500 W high-pressure mercury lamp was chosen as irradiation light after it passed through a polarizer. The probe light came from a He–Ne laser at 633 nm, which is far from the absorption band of the azobenzene groups. To obtain the maximum birefringence, the probe light was polarized at 45° with respect to the polarization direction of writing light. Induced anisotropy was evaluated by polarizing microscopy with monitoring light at a wavelength longer than 630 nm. The concentration of *cis*-azobenzene was measured with an unpolarized beam in situ in the spectrometer. The concentration was estimated as $[cis]\% = 100 \times (A_0 - A_t)/A_0$, where A_0 and A_t are the maximum absorbance of the polymer before irradiation and at irradiation time *t*. The induced order parameter was obtained as described before by using polarized UV spectroscopy [6].

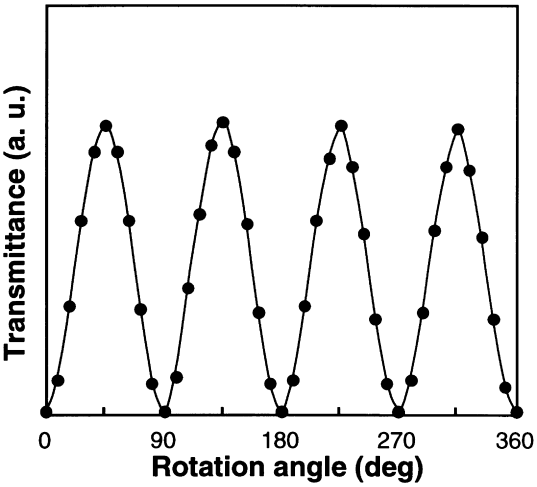

Fig. 2. Angular-dependent transmittance of **MACB-CNAB6** film evaluated by polarizing microscopy after irradiation at 106°C with 366 nm polarized light (2.8 mW/cm^2) for 30 min.

3. Results and discussion

3.1. Photoinduced alignment of MACB-CNAB6

The absorption maximum in the UV spectrum of polymer liquid crystal **MACB-CNAB6** film is located at around 370 nm due to a π–π^* transition of the azobenzene groups. There exists a weak absorption band at around 450 nm due to an n–π^* transition. The absorbance at 370 nm was reduced by irradiation of UV light at 366 nm owing to *trans–cis* photoisomerization, and was increased slowly due to *cis–trans* thermal isomerization when the irradiated

Table 1
Thermodynamic properties and molecular weight of the polymer liquid crystal used in this study[a]

Polymer	Phase transition temperature (°C)	ΔH_{NI} (kJ/mol)	ΔS_{NI} (J/mol·K)	Mn	Mw/Mn
MACB-CNAB6	G 45 N 112 I	1.9	4.8	7200	1.3

[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; Mn, number-average molecular weight; Mw, weight-average molecular weight.

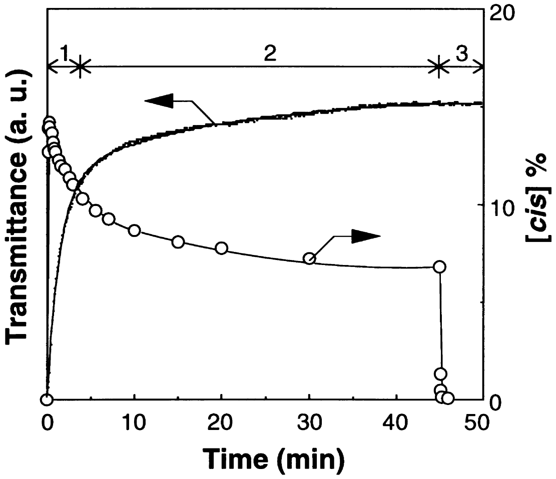

Fig. 3. Change in transmittance (points) and concentration of the *cis*-azobenzene (○) as a function of irradiation time. The solid line is a fit to Eq. (1). Film was irradiated with 366 nm polarized light (2.8 mW/cm^2) at 105°C. (1) fast alignment process; (2) slow alignment process; (3) relaxation process.

polymer film was kept in the dark. X-ray diffraction clearly showed that the polymer liquid crystal exhibited a typical nematic liquid-crystalline phase. By annealing the polymer film at a temperature just below T_{NI}, we obtained polydomain state film which was optically isotropic.

Anisotropy in a polymer film can be evaluated by polarizing microscopy by measuring the transmittance through two crossed polarizers with the polymer film between them as a function of rotation angle which is the direction of polarizer with respect to the direction of electric vector of irradiation light [6]. After exposing the polymer film to linearly polarized light at 366 nm (2.8 mW/cm^2) at 106°C for 30 min, clear homogeneous alignment was brought about. As shown in Fig. 2, the transmitted light intensity is lowest at 0°, 90° and so on, at every 90°, and highest at 45°, 135° and so on, at every 90°. This result clearly indicates that all the mesogens of the polymer liquid crystal were aligned into one in-plane direction to form a monodomain of nematic phase.

We also measured the continuous change in the transmittance through a pair of crossed polarizers with the polymer film between them as a function of irradiation time. Fig. 3 shows the change in transmittance (points) and concentration of the *cis*-azobenzene as a function of time. When the polarized light was turned on, the transmittance increased with time until a maximum level was reached. The growth of transmittance revealed that alignment change was generated in the polydomain polymer film. When the polarized light was turned off, no relaxation was observed, which was discussed in the previous paper [8]. The concentration of *cis*-azobenzene increased rapidly at first on irradiation due to photochemically induced *trans–cis* isomerization. After it reached a maximum, it decreased steeply at first, then slowly until a stable level was reached, corresponding to the saturation transmittance, because in some azobenzene moieties reorientation was induced perpendicular to the polarization direction of the actinic light and the resulting azobenzene became inactive. On irradiation of an unpolarized light at 366 nm with the same intensity, almost the same maximum value of the *cis*-azobenzene was produced, but no reduction of the concentration was observed on continuous irradiation. The change in the concentration produced by the polarized light revealed that azobenzene moieties were reoriented perpendicular to the polarization direction of the irradiation light through *trans–cis–trans* isomerization cycles.

3.2. Dynamic study of the alignment process

Dynamic study of the writing process in amorphous azo polymers revealed that it involved a fast response mode and a slow response mode. The writing curve was well fitted to a biexponential function as shown in the following [9,12]:

$$y = A(1 - \exp(-k_a t)) + B(1 - \exp(-k_b t)). \quad (1)$$

We found that the growth of the transmittance of the polymer liquid crystal could be adequately fitted to the biexponential function given by Eq. (1). A typical fitting curve (solid line) was also shown in Fig. 3. Similarly, it appears that the writing process in the polymer liquid crystal involves an initial ‘fast’ response mode and a subsequent ‘slow’ response mode. The parameter *An*, which is equal to $A/(A + B)$, represents the relative amplitude of the fast growth component with rate constant k_a, while the *Bn*, which is equal to $B/(A + B)$, represents the relative amplitude of the slow growth component with rate constant k_b.

Although it is in agreement that two processes exist in the photoinduced alignment process of azo polymers, the assignment of the two processes was different [9,12,13]. Comparing the growth of the transmittance with the change in concentration of the *cis*-azobenzene produced during the alignment process, the fast response was associated with the *trans–cis* photoisomerization and the steep decrease of the concentration, while the slow process corresponded to the slow decrease of the concentration of the *cis*-azobenzene. *Trans–cis* photoisomerization induced by polarized light results in a decrease in *trans*-azobenzene with the molecular long axis in the polarization direction of writing light, while no change in the amount of *trans*-azobenzene in the direction perpendicular to the polarization direction of incident light occurs, therefore a macroscopic anisotropy due to the angular-dependent photoselective isomerization was induced. Subsequently, *trans–cis–trans* isomerization cycles of azobenzene moiety accompanied by motion of its transition moment as well as by motion of inactive mesogens results in a long-term stable anisotropy. The rate for alignment change would decrease with decrease of the concentration of the *cis*-azobenzene. This process is not only responsible for the ‘slow’ process but also the ‘fast’ response, as shown in Fig. 3. Therefore, the ‘fast’ response may be attributed to the formation of the *cis* isomer and a

Table 2
Parameters obtained by fitting the transmittance growth curves at various temperatures to Eq. (1)[a]

Temperature (K)	k_a (s^{-1})	A	k_b (s^{-1})	B	An	Bn
381	0.0533	51.6	0.0042	3.9	0.93	0.07
379	0.0276	45.5	0.0009	11.1	0.80	0.20
377	0.0089	40.4	0.0004	15.4	0.72	0.28
375	0.0046	30.8	0.0009	17.9	0.63	0.37
372	0.0010	18.1	0.0008	28.5	0.39	0.61

[a] $An = A/(A+B)$; $Bn = B/(A+B)$.

preliminary alignment of the mesogens, at which the mesogens were not aligned quite perpendicular to the polarization direction of writing light, while the 'slow' response is connected with the position adjustment of the mesogens to obtain a well-aligned monodomain phase.

3.3. Temperature dependence of the alignment change

The photoinduced alignment behavior was performed at various temperatures with 366 nm polarized light at an intensity of 2.8 mW/cm^2. We observed that the alignment change in **MACB-CNAB6** could be induced from 90°C to a temperature just below T_{NI}. The growth rate of the transmittance increased with increase in temperature. It took about 90 s to reach the saturated transmittance at optimized temperature. To discuss the effect of temperature quantitatively, the rate constants and the amplitudes were obtained by fitting the experimental data obtained at various temperatures to Eq. (1) (Table 2). One can see that the rate constant k_a and the corresponding relative amplitude An increased with temperature, while the rate constant k_b showed no dependence on temperature. This means that the fast process becomes more dominant with increase of temperature. We note that the writing curve obtained at relatively low temperature, such as 92°C, could not be fitted by Eq. (1), which grew linearly with the irradiation time.

In Fig. 4, the Arrhenius plot for the fast response process of the polymer liquid crystal is given, which shows fairly good linearity. We obtained a value of 520.5 kJ/mol as activation energy for the alignment process, which is much higher than that obtained in amorphous polymer [12]. As described before [7], by using UV spectroscopy, we measured the rate constants of *cis–trans* thermal isomerization of the azobenzene groups at various temperatures within the liquid-crystalline phase. Then the activation energy of 84.5 kJ/mol was obtained for the thermal *cis–trans* back-isomerization. The value is comparable to those reported for the *cis–trans* isomerization of azobenzene groups [14]. However, the activation energy for the alignment process was much higher than that for *cis–trans* isomerization. This indicates that the fast response process is not a simple *trans–cis* or *cis–trans* isomerization process but a complex process. The activation energy obtained is only an apparent activation energy for many steps, such as the *trans–cis* photoisomerization, *cis–trans* thermal isomerization of azobenzene groups, and the motion of the azobenzene moieties and inactive mesogens. This is in agreement with the assignment of the fast response mode.

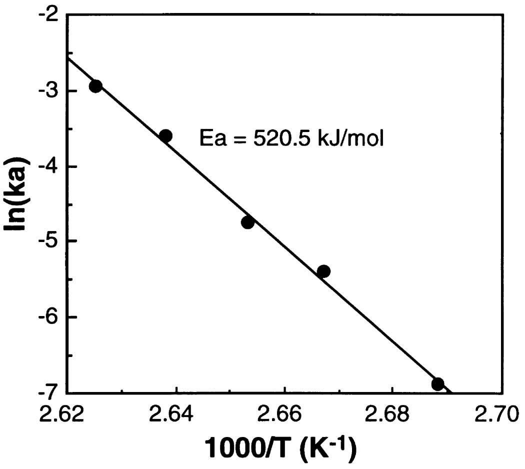

Fig. 4. Arrhenius plot of the rate constants in alignment process.

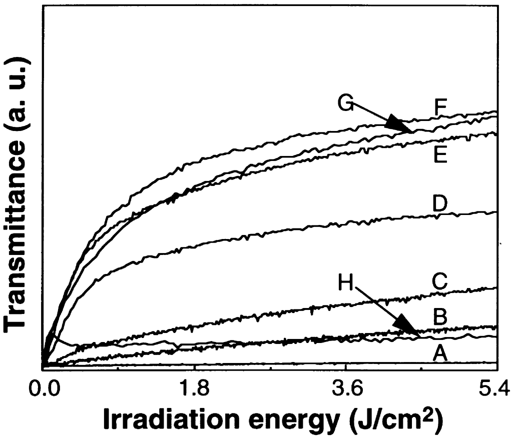

Fig. 5. Change in transmittance as a function of irradiation time. Film was irradiated with 366 nm polarized light at 100°C at various light intensities. (A) 1.0 mW/cm^2; (B) 2.0 mW/cm^2; (C) 3.0 mW/cm^2; (D) 4.5 mW/cm^2; (E) 6.0 mW/cm^2; (F) 7.0 mW/cm^2; (G) 9.0 mW/cm^2; (H) 10.5 mW/cm^2.

3.4. Light intensity dependence of the alignment change

Recently, Song and co-workers reported that the rate constants k_a and k_b were not dependent on the intensity of the writing laser, while the amplitude A and B showed dependence [12]. However, some of the literature states that the writing rate is proportional to the intensity of writing light [6,15]. To clearly understand the effect of light intensity on alignment behavior, we examined the alignment process at a wide range of light intensity and analyzed the dynamic behavior by fitting the transmittance to Eq. (1). Fig. 5 shows the writing curves of **MACB-CNAB6** at 100°C with 366 nm polarized light at different intensity. When the intensity of irradiation light was lower than 1.0 mW/cm^2, alignment change could not be generated in the polymer

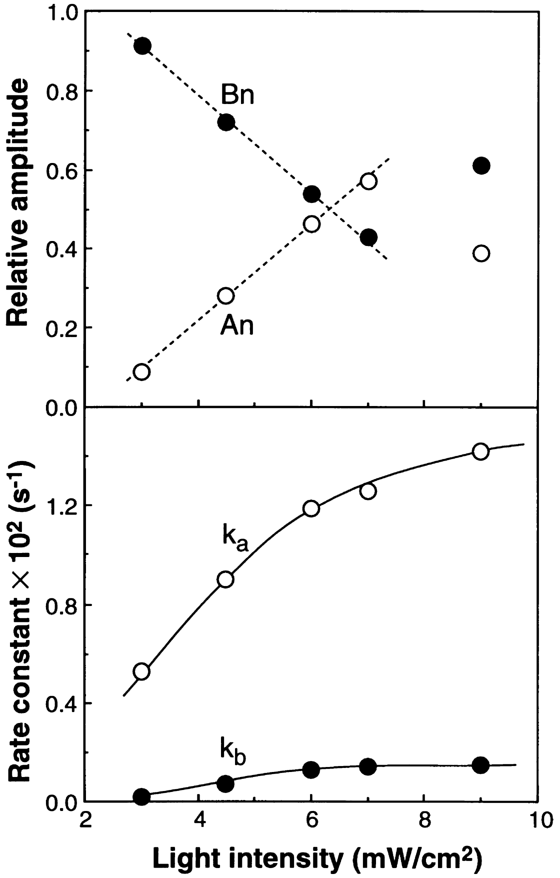

Fig. 6. Effect of writing light intensity on rate constants and amplitudes of the alignment process. Experiments were performed at 100°C.

liquid crystal. Threshold intensity was reported in some of the literature [6,16,17], but the reason for the threshold intensity was not yet clear. Recently, mean-field theory was applied to explain the experimental phenomenon observed in photoinduced alignment processes of azobenzene side-chain liquid-crystalline polymers [18]. The threshold was suggested to be determined by the excitation rate. With the increase in the intensity (from 1 to 7 mW/cm^2), at first, the growth rate as well as the saturated transmittance increased at the same irradiation energy. On further increase in intensity, both the growth rate and the maximum level showed no further increase, such as the curve G. When the intensity was 10.5 mW/cm^2, the transmittance increased rapidly at first, then decreased to a stable level (curve H). By observation under polarizing microscopy, it was proved that a photochemical phase transition took place locally.

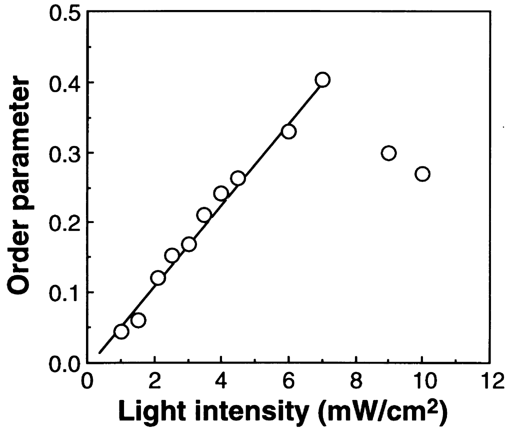

Fig. 7. Induced order parameters of azobenzene moieties at various light intensities. Film was irradiated with 366 nm polarized light at 100°C at the same irradiation energy, 4.0 J/cm^2.

We obtained the parameters by fitting the experimental data to Eq. (1). As shown in Fig. 6, the relative amplitudes as well as the rate constants exhibited dependence on the intensity of irradiation light at the intensity range in the present work. Relative amplitude of the fast process increased while that of the slow process decreased linearly with intensity at low intensities of irradiation light. In the case of high intensity (9 mW/cm^2), the amplitude of the fast process decreased unexpectedly. The reason may be ascribed to the occurrence of a photochemical phase transition, which made the alignment process more complex. Both k_a and k_b increased with increase in intensity of the irradiation light. It seems that there exists a saturation value of the intensity of irradiation light, above which the rate constants did not increase further. The saturation intensity may also be determined by the excitation rate of the azobenzene moieties.

As described before [6], the induced order parameter $S = (R - 1)/(R + 2)$ was calculated to characterize the anisotropy. Fig. 7 shows the induced order parameters of the azobenzene moieties at various intensities of irradiation light. One can see that the induced order parameter increased linearly with intensity of irradiation light at the low intensity region [16,18]. We expected that the order parameter would reach a saturated value on high intensity region. However, experimental results showed that the order parameter reduced on further increase in intensity of irradiation light. This is due to the occurrence of the photochemical phase transition caused by higher concentration of *cis*-azobenzene which was produced by higher intensity of the irradiation light. Overall, the writing rate increases with increase of intensity of writing light until a saturation value is reached; the induced order parameter or the amplitude increases with intensity of writing light at first, then decreases due to photochemical phase transition.

3.5. Optical switching and image storage

Photoinduced birefringence in amorphous polymers could be erased by using circularly polarized light or heating the polymers above glass transition temperatures [19]. It is obvious that photoinduced anisotropy in polymer liquid crystals can be erased by heating the polymer liquid crystals above clearing temperatures. Shibaev reported another method to erase the induced anisotropy by changing the polarization direction of the irradiation light by 90° with

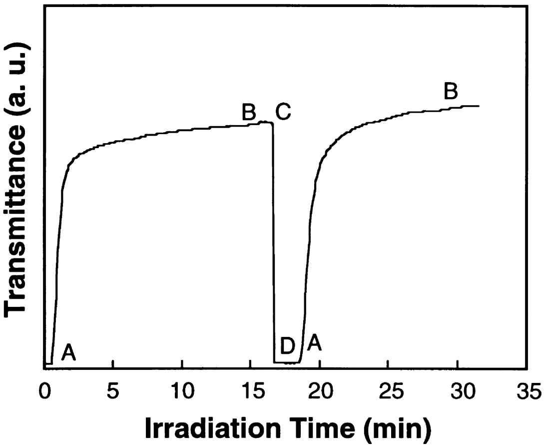

Fig. 8. A typical writing-erasing-rewriting curve of **MACB-CNAB6**. Experiment was performed at 106°C. The polarized light was turned on at point A, and turned off at point B; the unpolarized light was turned on at point C, and turned off at point D.

respect to that of the initial beam [20]. We found that the induced anisotropy could be easily erased by using unpolarized light due to the photochemical phase transition [1,14,21]. Fig. 8 presents a typical writing-erasing-rewriting curve of **MACB-CNAB6**. The linearly polarized light at 366 nm (3.1 mW/cm^2) was turned on at point A, and the transmittance rapidly increased until a maximum level was reached. When the writing light was turned off at point B, no relaxation was observed. When unpolarized light at 366 nm (25 mW/cm^2) was switched on at point C, the induced anisotropy was completely eliminated. The alignment was reintroduced when linearly polarized light was switched on again. After irradiation of 366 nm unpolarized light, we observed neither an initial polydomain state nor induced monodomain state, but an isotropic state in the polymer film by using polarizing microscopy. Photochemical phase transition took place. These results clearly indicate that reversible alignment can be induced in **MACB-CNAB6** film. In a combination of the photoinduced alignment process and photochemical phase transition process, optical switching was realized by means of polymer liquid crystal containing azobenzene moieties in the side chain, although the writing rate was not so satisfactory.

Image storage experiments with the use of a standard photomask were conducted on the polymer liquid crystal. The polymer films were prepared by casting as described before. After annealing, the photomask was directly placed on the polymer film and the resulting sample was irradiated at 106°C with polarized light at 366 nm from a mercury lamp. After exposure, resolution of the stored image was examined in the polarizing microscope. As shown in Fig. 9, a clear photoimage with good resolution was obtained. The highest resolvable group is found to be group 6. In fact the resolution of the image storage can be improved further by eliminating some experimental defects, such as poor spatial distribution of the Hg light intensity, irregular sample surface and distortion of the focus of the writing light. The image can be stably stored below T_{NI}. No image degradation was observed after more than one year at room temperature. These results reveal that polymer liquid crystals can be used as materials for optical switching and image storage.

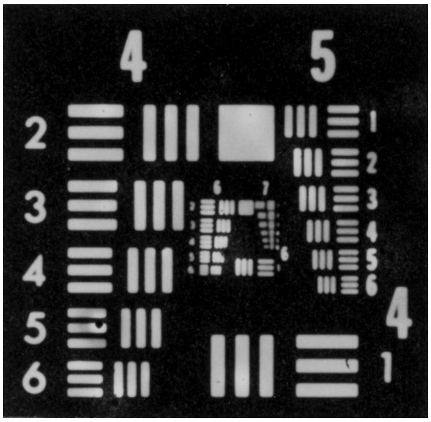

Fig. 9. Stored image in the polymer liquid crystal after 1 year. The thin film was covered with a standard photomask and irradiated with 366 nm polarized light (3.1 mW/cm^2) at 106°C for 30 min.

4. Conclusion

In summary, we have demonstrated that the alignment change was induced in the initial polydomain polymer liquid crystal **MACB-CNAB6**. The alignment process could be fitted to a biexponential function. The fast response process was assigned to the *trans–cis* photoisomerization and a preliminary alignment of the mesogens, while the slow one was attributed to position adjustment of the mesogens. The rate constant k_a and the corresponding amplitude *An* exhibited dependence on temperature and on intensity of the irradiation light at low intensity. At high intensity of the irradiation light, the rate constants would reach a saturation value, but the amplitude became irregular due to phase transition. Experimental results also showed that the polymer liquid crystal can be used as a material for optical switching and image storage.

References

[1] Ikeda T, Tsutsumi O. Science 1995;268:1873.
[2] Gibbons WM, Shannon PJ, Sun ShT, Swetlin BJ. Nature 1991;351:49.
[3] Eich M, Wendorff JH, Reck B, Ringsdorf H. Makromol Chem, Rapid Commun 1987;8:59. Eich M, Wendorff JH. Makromol Chem, Rapid Commun 1987;8:457.
[4] Wiesner U, Reynolds N, Boeffel C, Spiess HW. Makromol Chem, Rapid Commun 1991;12:457. Wiesner U, Reynolds N, Boeffel C, Spiess HW. Liq Cryst 1992;11:251.
[5] Läsker L, Fischer Th, Stumpe J, Kostromin S, Ivanov S, Shibaev V, Ruhmann R. Mol Cryst Liq Cryst 1994;253:1.

[6] Wu Y, Demachi Y, Tsutsumi O, Kanazawa A, Shiono T, Ikeda T. Macromolecules 1998;31:349.
[7] Wu Y, Demachi Y, Tsutsumi O, Kanazawa A, Shiono T, Ikeda T. Macromolecules 1998;31:1104.
[8] Wu Y, Demachi Y, Tsutsumi O, Kanazawa A, Shiono T, Ikeda T. Macromolecules 1998;31:4457.
[9] Ho MS, Natansohn A, Rochon P. Macromolecules 1995;28:6124.
[10] Shibaev VP, Kostromin SG, Platé NA. Eur Polym J 1982;18:651.
[11] Ikeda T, Horiuchi S, Karanjit DB, Kurihara S, Tazuke S. Macromolecules 1990;23:42.
[12] Song OK, Wang CH, Pauley MA. Macromolecules 1997;30:6913.
[13] Stumpe J, Läsker L, Fischer Th, Rutloh M, Kostromin S, Ruhmann R. Thin Solid Film 1996;284–285:252.
[14] Tsutsumi O, Kitsunai T, Kanazawa A, Shiono T, Ikeda T. Macromolecules 1998;31:355.
[15] Rochon P, Bissonnette D, Natansohn A, Xie S. Appl Opt 1993;32:7277.
[16] Schonhöff M, Mertesdorf M, Lösche M. J Phys Chem 1996;100:7558.
[17] Geue Th, Ziegler A, Stumpe J. Macromolecules 1997;30:5729.
[18] Pedersen ThG, Johansen PM. Phys Rev Lett 1997;79:2470.
[19] Rechon P, Gosselin J, Natansohn A, Xie S. Appl Phys Lett 1992;60:4.
[20] Shibaev VP, Kostromin SG, Ivanov SA. Polym Sci, Ser A 1997;39:36.
[21] Tsutsumi O, Shiono T, Ikeda T, Galli G. J Phys Chem B 1997;101:1332.