

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Synthesis and Properties of Stereoregular Polymethacrylates with Azobenzene Moiety as a Photoreactive Side-Chain Mesogenic Group

Koichi Hatada<sup>a</sup>; Tatsuki Kitayama<sup>a</sup>; Takafumi Nishiura<sup>a</sup>; Makoto Tawada<sup>a</sup>; Tsutomu Harazono<sup>a</sup>; Takahiko Sugaya<sup>a</sup>

<sup>a</sup> Department of Chemistry Faculty of Engineering, Science Osaka University, Toyonaka, Osaka, Japan

**To cite this Article** Hatada, Koichi , Kitayama, Tatsuki , Nishiura, Takafumi , Tawada, Makoto , Harazono, Tsutomu and Sugaya, Takahiko(1997) 'Synthesis and Properties of Stereoregular Polymethacrylates with Azobenzene Moiety as a Photoreactive Side-Chain Mesogenic Group', *Journal of Macromolecular Science, Part A*, 34: 7, 1183 – 1194

**To link to this Article:** DOI: 10.1080/10601329708009378

**URL:** <http://dx.doi.org/10.1080/10601329708009378>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## SYNTHESIS AND PROPERTIES OF STEREOREGULAR POLYMETHACRYLATES WITH AZOBENZENE MOIETY AS A PHOTOREACTIVE SIDE-CHAIN MESOGENIC GROUP

KOICHI HATADA,\* TATSUKI KITAYAMA,  
TAKAFUMI NISHIURA, MAKOTO TAWADA,  
TSUTOMU HARAZONO, and TAKAHIKO SUGAYA

Department of Chemistry  
Faculty of Engineering Science  
Osaka University  
Toyonaka, Osaka 560, Japan

### ABSTRACT

Two kinds of methacrylates having a photoreactive and mesogenic ester group, 6-[4-(4'-methoxyphenylazo)phenoxy]hexyl methacrylate **1** and 6-[4-(4'-butoxyphenylazo)phenoxy]hexyl methacrylate **2**, were synthesized and polymerized. Polymerization with phenylmagnesium bromide in  $\text{CH}_2\text{Cl}_2$  at  $0^\circ\text{C}$  gave isotactic (*it*-) polymers (*mm* ~ 94%) and that with  $\text{Ph}_3\text{P-Et}_3\text{Al}$  in  $\text{CH}_2\text{Cl}_2$  at  $-40^\circ\text{C}$  syndiotactic (*st*-) polymers (*rr* ~ 84%). Syndiotactic poly(**1**) exhibited a liquid-crystalline (LC) phase, while *it*-poly(**1**) did not. Both *st*-poly(**2**) and *it*-poly(**2**) showed an LC phase, their transition temperatures differing from each other. The *trans*-to-*cis* isomerization by UV-light irradiation of the azobenzene moiety of the polymers, except *it*-poly(**1**) in the LC phase, induced phase transition of the LC phase into the isotropic phase. Using this phenomenon, image storage was examined. Image storage with a resolution up to  $0.5\text{--}1\ \mu\text{m}$  was achieved, and the stored image was quite stable at room temperature for at least one year.

## INTRODUCTION

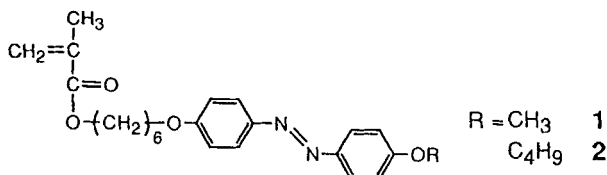
Polymethacrylate with a photoreactive ester group, such as the azobenzene derivative, is one of the most widely studied classes of photoresponsive polymers [1–5]. Ikeda and his coworkers copolymerized acrylates containing photoreactive azobenzene units with other acrylates having the biphenyl or phenyl benzoate group and studied a photoinduced phase transition phenomenon of the resulting liquid-crystalline (LC) copolymers. They utilized these copolymers for photorecording materials [1, 2]. They studied the effects of the molecular weight and the ratio of azobenzene moieties to whole mesogenic groups of the copolymers on the properties of the LC phase. However, the effects of stereoregularity of the polymer backbone have not been discussed. Since the origin of liquid crystallinity is attributed to orientation of mesogenic groups, stereoregularity of side-chain LC polymers is expected to be an important structural feature that affects the liquid crystallinity and LC properties. Okamoto and his coworkers found a remarkable tacticity dependence of LC phase formation of stereoregular polymethacrylate having a biphenyl-type mesogen, and ascribed it to the conformational difference between isotactic (*it*-) and syndiotactic (*st*-) polymers [6–8].

For this work, stereoregular polymethacrylates having azobenzene moieties in the side-chains were prepared, and in this work the effects of stereoregularity on the liquid crystallinity are discussed. Among the polymethacrylates, LC-phase-forming polymers were used for image storage based on photoinduced phase transition via *trans*-to-*cis* isomerization of the azobenzene moieties.

## EXPERIMENTAL

### Reagents

6-[4-(4'-Methoxyphenylazo)phenoxy]hexyl methacrylate **1** was synthesized according to the literature [9]. 6-[4-(4'-Butoxyphenylazo)phenoxy]hexyl methacrylate **2** was synthesized in a similar manner. The methacrylates were recrystallized from tetrahydrofuran, dried under vacuum for 6 hours at 25°C, and stored in a desiccator with CaH<sub>2</sub> in the dark. The structures were identified by mass spectrometry and <sup>1</sup>H-NMR spectroscopy.



6-[4-(4'-alkoxyphenylazo)phenoxy]hexyl methacrylate

Methacrylate 1, mp 86.2–86.8°C,\* MS(FD):  $m/z$  396 ( $M^+$ ),  $^1\text{H NMR}$  (5 wt%, 35°C,  $\text{CDCl}_3$ ):  $\delta$  = 7.83–7.90 (m; aromatic), 6.96–7.02 (m; aromatic), 6.10 (s; vinylidene methylene), 5.54 (s; vinylidene methylene), 4.17 (t; oxymethylene), 4.03 (t; oxymethylene), 3.88 (s; methoxy), 1.94 (s;  $\alpha$ -methyl), and 1.47–1.86 (m; methylene).

Methacrylate 2, mp 91.7–92.1°C, MS(FD):  $m/z$  438 ( $M^+$ ),  $^1\text{H NMR}$  (5 wt%, 35°C,  $\text{CDCl}_3$ ):  $\delta$  = 7.84–7.87 (m; aromatic), 6.96–7.00 (m; aromatic), 6.09 (s; vinylidene methylene), 5.54 (s; vinylidene methylene), 4.17 (t; oxymethylene), 4.03 (t; oxymethylene), 1.94 (s;  $\alpha$ -methyl), 1.47–1.83 (m; methylene), and 0.99 (t; methyl).

Dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) was purified by a usual manner [10], dried over  $\text{CaH}_2$ , and distilled under high vacuum just before use. Phenylmagnesium bromide ( $\text{PhMgBr}$ ) was prepared from magnesium turnings and bromobenzene in diethyl ether. Triethylaluminum ( $\text{Et}_3\text{Al}$ ) was purchased from Nippon Aluminum Alkyls and used as a heptane solution. Triphenylphosphine ( $\text{Ph}_3\text{P}$ ) was purchased from Aldrich Chemical Company, recrystallized from hexane, dried under vacuum, and used as a toluene solution.

### Polymerization

The monomer was placed in a glass ampule under nitrogen. The ampule was evacuated on a vacuum system and then filled with dried nitrogen. After this procedure was repeated three times, a three-way stopcock was attached to the ampule and  $\text{CH}_2\text{Cl}_2$  was added with a hypodermic syringe to dissolve the monomer. In the polymerization with  $\text{PhMgBr}$ , the reaction was initiated by adding the initiator solution with a syringe slowly to the monomer solution at 0°C. In the polymerization with  $\text{Ph}_3\text{P-Et}_3\text{Al}$ ,  $\text{Et}_3\text{Al}$  solution was added to the monomer solution at room temperature, the solution was then cooled to  $-40^\circ\text{C}$ , and  $\text{Ph}_3\text{P}$  solution was added slowly to the solution. The polymerization reaction was quenched by adding a small amount of methanol, and the reaction mixture was poured into a large amount of hexane to precipitate a polymeric product. The precipitate was collected by filtration, washed with hexane and subsequently with water several times, and dried under vacuum for 6 hours at 50°C.

### Measurement

$^1\text{H-NMR}$  spectra were measured on a JEOL JNM GSX-270 spectrometer using  $\text{CDCl}_3$  as a solvent.  $^{13}\text{C-NMR}$  spectra were measured on a Varian UNITY INOVA600 spectrometer using  $\text{CDCl}_3$  as a solvent. Gel permeation chromatography (GPC) was performed on a JASCO 865-PU chromatograph equipped with Shodex KF-80M and KF-802.5 columns (0.8 cm  $\times$  30.0 cm) with maximum porosities of  $2 \times 10^7$  and  $2 \times 10^4$ , respectively, at 40°C, using tetrahydrofuran as an eluent. The

\*1 was reported to exhibit phase transition at 70.0°C (crystalline to nematic) and 74.4°C (nematic to isotropic) in DSC measurement [9]. DSC analysis of our sample showed a single endothermic peak at 87.4°C, which is close to the melting point determined by the usual method of melting the sample in a glass capillary tube. Repeated recrystallization of our sample did not cause a change of the melting point. The purity of 1 was higher than 98% as determined by  $^1\text{H-NMR}$  spectroscopy.

chromatograms were calibrated against standard polystyrene samples. Field desorption mass (FD-MS) spectra were taken on a JEOL JMS-DX303. Differential scanning calorimetry (DSC) analysis was performed on a RIGAKU DSC8230 calorimeter at a heating rate of 10°C/min under nitrogen flow (20 mL/min). The DSC patterns were recorded for the second heating scan. Optical microscopic investigation was performed with an OLYMPUS B061 polarized optical microscope equipped with Leitz Microscope Heating Stage 350.

### Preparation of Polymer Film

Polymer films for optical microscopic observation were made by casting the polymer solution. Toluene solutions of the polymers (30 mg/mL) were filtered using microporous filters (pore size 0.45  $\mu\text{m}$ ) and cast on quartz glass plates. The dried films of *st*-poly(1), *it*-poly(1), *st*-poly(2), and *it*-poly(2) were annealed for 30 minutes at 100, 110, 130, and 120°C, respectively.

Films for the image storage experiment were made by spin-coating using the same solutions and annealed similarly to the films for optical microscopic observation.

### Image Storage Experiment

A 500-W high-pressure mercury lamp was used as a light source. To obtain UV and visible lights, Toshiba color filters UV-D36C (400 nm >  $\lambda$  > 290 nm) and L-39 ( $\lambda$  > 390 nm) were used. The distance from the light source to the polymer film was set to be 25 mm.

## RESULTS AND DISCUSSION

### Polymerization of 6-[4-(4'-Alkoxyphenylazo)phenoxy]hexyl Methacrylates 1 and 2

Polymerizations of methyl methacrylate (MMA) with PhMgBr in toluene at 0°C [11] and with Ph<sub>3</sub>P-Et<sub>3</sub>Al in toluene at -78°C [12] are known to afford highly *it*-(*mm* ~ 100%) and highly *st*-(*rr* ~ 90%) polymers, respectively. The monomers 1 and 2 showed quite low solubilities in toluene, but the solubilities in CH<sub>2</sub>Cl<sub>2</sub> were much better than in toluene even at low temperature (Table 1). It has been known

TABLE 1. Solubility of Methacrylates 1 and 2

Monomer	Solvent	Solubility, g/mL	
		25°C	-40°C
1	Toluene	0.14	~0
	CH <sub>2</sub> Cl <sub>2</sub>	0.57	0.051
2	Toluene	0.080	~0
	CH <sub>2</sub> Cl <sub>2</sub>	0.33	0.043

that anionic polymerizations of MMA with Grignard reagents [11] and with  $\text{Ph}_3\text{P-Et}_3\text{Al}$  [13] proceed in halogenated solvents without losing high stereospecificity. Thus the polymerizations of monomers **1** and **2** were carried out in  $\text{CH}_2\text{Cl}_2$ .

Table 2 shows the results of the polymerizations of monomers **1** and **2**. Triad tacticities of the polymers were determined by  $^{13}\text{C-NMR}$  spectroscopy. Figure 1 illustrates the quaternary carbon NMR spectra of poly(**1**)s prepared with AIBN,  $\text{Ph}_3\text{P-Et}_3\text{Al}$ , and  $\text{PhMgBr}$ . In the spectrum of poly(**1**) prepared with AIBN, the signals clearly split into three groups of peaks which are assigned to triads: *rr* (44.8–45.3 ppm), *mr* (45.3–45.6 ppm), and *mm* (45.9–46.1 ppm). The assignments were made on the basis of the similarity of the spectral pattern and the knowledge that most radically prepared polymethacrylates are predominantly syndiotactic [14]. It is clear that poly(**1**) prepared with  $\text{PhMgBr}$  is highly isotactic (Fig. 1 and Table 2) and that poly(**1**) prepared with  $\text{Ph}_3\text{P-Et}_3\text{Al}$  is highly syndiotactic. The triad signals show further splittings due to pentad sequences, as in the cases of polymethacrylates, though the quantification of pentad fractions is hindered by insufficient peak separation as well as the lack of polymer samples with appropriate tacticity such as isotactic-rich ones instead of highly isotactic ones. The detailed analysis at the pentad level will be reported in the near future.

Figure 2 shows the quaternary carbon NMR spectra of poly(**2**)s. The signals show splittings due to pentad sequences. The results indicate that the polymerizations of **2** with  $\text{PhMgBr}$  at  $0^\circ\text{C}$  and with  $\text{Ph}_3\text{P-Et}_3\text{Al}$  at  $-40^\circ\text{C}$  also gave highly isotactic and highly syndiotactic polymers, respectively. Tacticity values of poly(**2**) are quite similar to the corresponding poly(**1**).

### Thermal Properties of Stereoregular Poly(**1**) and Poly(**2**)

Figure 3 shows DSC thermograms of *st*- and *it*-poly(**1**)s. In the thermogram of *st*-poly(**1**) (Fig. 3A), glass transition at  $63^\circ\text{C}$  and two endothermic transitions at  $94$

TABLE 2. Polymerization of Methacrylates **1** and **2** in  $\text{CH}_2\text{Cl}_2$  for 24 hours<sup>a</sup>

Monomer	Initiator	Temperature, $^\circ\text{C}$	Yield, $\%$	$\bar{M}_n^b$	$\bar{M}_w^b$		Tacticity, $\%$ <sup>c</sup>		
					$\bar{M}_n$	<i>mm</i>	<i>mr</i>	<i>rr</i>	
<b>1</b>	$\text{Ph}_3\text{P/ET}_3\text{Al}^d$	$-40$	84	16,800	1.94	0	16	84	
	$\text{PhMgBr}^e$	0	87	13,300	2.53	94	4	2	
	$\text{AIBN}^f$	60	38	27,400	2.20	3	30	67	
<b>2</b>	$\text{Ph}_3\text{P/Et}_3\text{Al}^d$	$-40$	100	15,000	1.24	1	15	84	
	$\text{PhMgBr}$	0	29	12,400	2.47	93	5	2	
	$\text{AIBN}^f$	60	62	12,900	1.50	2	34	64	

<sup>a</sup>Monomer **1**, 0.5 g; **2**, 0.25 g; solvent, 10 mL,  $[\text{Monomer}]/[\text{Initiator}] = 10$  mol/mol.

<sup>b</sup>Determined by GPC.

<sup>c</sup>Determined by  $^{13}\text{C}$  NMR.

<sup>d</sup> $[\text{Ph}_3\text{P}]/[\text{Et}_3\text{Al}] = 1$ .

<sup>e</sup> $[\text{Monomer}]/[\text{Initiator}] = 20$  mol/mol.

<sup>f</sup>Solvent, benzene;  $[\text{Monomer}]/[\text{Initiator}] = 90$  mol/mol.

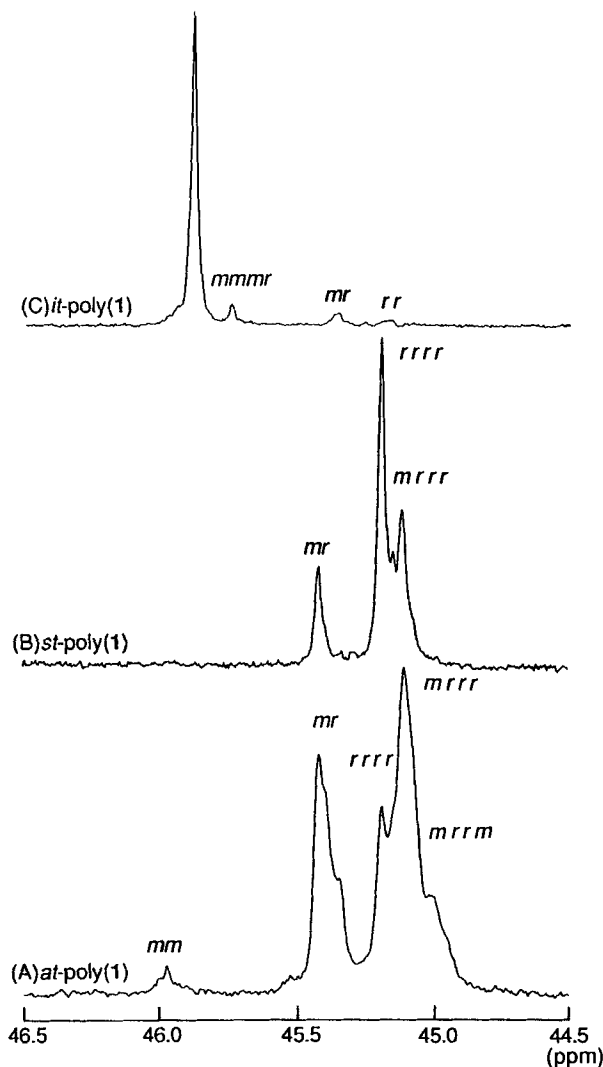


FIG. 1. Quaternary carbon NMR spectra of *at*-poly(1) (A), *st*-poly(1) (B), and *it*-poly(1) (C) prepared with AIBN,  $\text{Ph}_3\text{P-Et}_3\text{Al}$ , and  $\text{PhMgBr}$ , respectively, measured in  $\text{CDCl}_3$  at  $55^\circ\text{C}$  and 150.8 MHz.

and  $134^\circ\text{C}$  were observed. An LC phase was observed under a polarizing microscope in the temperature range from  $94$  and  $134^\circ\text{C}$ . From measurement of the wide-angle x-ray diffraction, it was confirmed that the phase transition at  $94^\circ\text{C}$  is crystalline to LC and that at  $134^\circ\text{C}$ , it is LC to isotropic phase, and that the LC phase is nematic [15].

On the other hand, *it*-poly(1) exhibited glass transition at  $34^\circ\text{C}$ , an exothermic peak at  $100^\circ\text{C}$ , and an endothermic peak at  $128^\circ\text{C}$  (Fig. 3B). Polarizing microscopic observation revealed that *it*-poly(1) did not form an LC phase in the  $30$ – $130^\circ\text{C}$  temperature range. By means of DSC and x-ray analyses, the exothermic and endo-

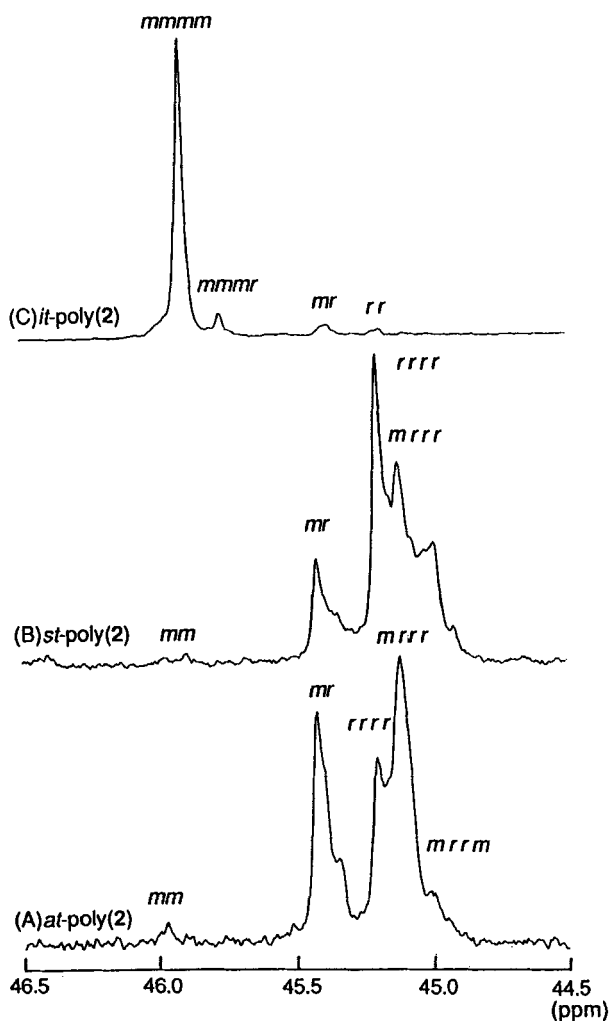


FIG. 2. Quaternary carbon NMR spectra of *at*-poly(2) (A), *st*-poly(2) (B), and *it*-poly(2) (C) prepared with AIBN,  $\text{Ph}_3\text{P-Et}_3\text{Al}$ , and  $\text{PhMgBr}$ , respectively, measured in  $\text{CDCl}_3$  at  $55^\circ\text{C}$  and 150.8 MHz.

thermic peaks in the DSC thermogram were found to be due to crystallization and melting, respectively [15].

Recently, Okamoto and his coworkers reported that the liquid crystallinity of several types of side-chain LC polymethacrylates depended on their stereoregularity [6-8]. The dependence has been attributed to the conformational difference between *st*- and *it*-polymers; *st*-polymer tends to assume a zigzag conformation, in which the side groups are aligned in the same direction and placed zigzag each other, and *it*-polymer tends to take a helical conformation, in which the side groups radiate from the helical main chain. They assume that these conformational differences affect the assembly of the mesogenic groups [8].



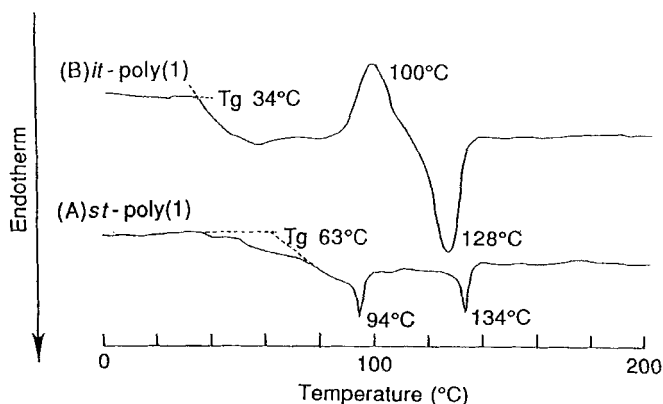


FIG. 3. DSC thermograms of *st*-poly(1) (A) and *it*-poly(1) (B) (heating rate 10°C/min).

Since the LC phase of side-chain LC polymers is generally formed above the glass transition temperature ( $T_g$ ) [1–4] at which the polymer chains begin to undergo segmental motion, flexibility of the main chain may affect the formation of the LC phase and its stability. Chain flexibility of polymethacrylate is known to depend on the tacticity (main-chain configuration) and is generally larger for *it*-polymer than for *st*-polymer [14]. This is also the case for poly(1), as evidenced from the lower  $T_g$  of the *it*-poly(1) than the *st*-poly(1). As described above, the *st*-poly(1) forms an LC phase and the *it*-poly(1) does not. This fact implies that excessive flexibility disfavors LC phase formation although chain flexibility is necessary for LC phase formation. Appropriate chain flexibility is an important factor for LC phase formation. Thus the main-chain configuration affects LC phase formation not only by restricting the alignment of the side chain but also by affecting chain flexibility.

On the other hand, in the case of poly(2), both *it*- and *st*-polymers formed LC phases as seen from the DSC thermograms shown in Fig. 4. Both *st*- and *it*-poly(2)s show three endothermic peaks in the DSC thermograms. Polarizing microscopic observations revealed that both polymers exhibited LC phases in the temperature ranges between three endothermic peaks. From wide-angle x-ray diffraction measurement it was confirmed that these three peaks correspond to the phase transitions of crystalline to LC(smectic), LC(smectic) to LC(nematic), and LC(nematic) to isotropic phase, respectively [15].

Monomer 2 has a higher melting point than monomer 1. This suggests that the mesogen in monomer 2 itself exhibits a stronger mesogen–mesogen interaction than that in monomer 1, which favors the formation of an LC phase, the difference in main-chain flexibility of *it*- and *st*-poly(2)s being a less dominant factor. The temperatures for the three transitions of the *st*-poly(2) are all higher than those for the corresponding transitions of the *it*-poly(2) (Fig. 4). The higher flexibility of *it*-poly(2) apparently lowers the phase transition temperatures, giving rise to the wider temperature range of the LC phase.

The effect of main-chain flexibility varies depending on the nature of mesogenic group in terms of its mesogenic interaction. In other words, by modifying the

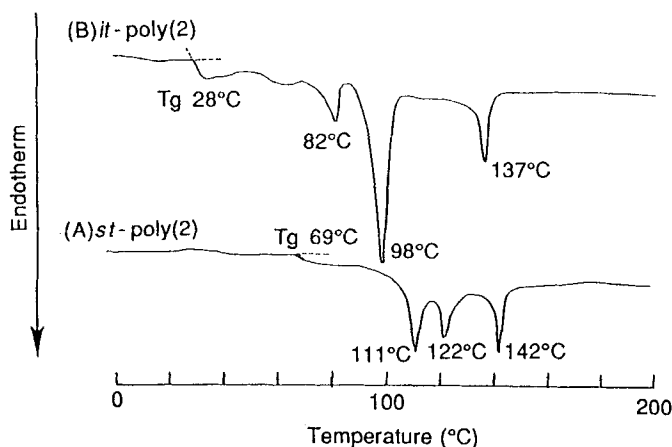


FIG. 4. DSC thermograms of *st*-poly(2) (A) and *it*-poly(2) (B) (heating rate 10°C/min).

main-chain flexibility through the control of tacticity, one can optimize the mesogenic interaction to obtain the proper LC phase. In this regard, stereospecific polymerization of mesogenic monomer should provide a useful means for designing LC polymers.

### Image Storage Experiment

Ikeda and his coworkers reported the photoinduced phase transition of polyacrylates having a mesogenic azobenzene moiety as a trigger and its application to image storage material [1–4]. Azobenzene moiety changes its molecular shape from the “rodlike” *trans*-form to the “bent” *cis*-form upon UV light irradiation. The *trans*-form of azobenzene moiety works as mesogen while the *cis*-form does not. Moreover, a small amount of *cis*-azobenzene moieties in the LC phase of *trans*-azobenzene moieties does not stabilize the LC phase. Therefore, the isomerization of azobenzene moieties from *trans* to *cis* causes phase transition from the LC to the isotropic phase.

The photoinduced phase transition is applicable to the photorecording process by using polarized light as the reading light [1–4]. The polymers obtained in this work are expected to be applicable to such a photorecording process. Polymer films for image storage experiments were made by spin-coating. The films were annealed for 30 minutes at temperatures from 100 to 130°C depending on the polymers, as described in the Experimental Section. UV light was irradiated on films covered by a photomask which had 7 lines of different widths (0.5–50 μm), and the pattern was stored on the films. Visual inspection of the stored pattern with a polarizing microscope indicates that resolution up to 0.5–1 μm has been achieved on the film of *st*-poly(1), as shown in Fig. 5. The stored pattern did not change for at least one year at room temperature, and it could be erased by heating the film above 134°C or by irradiating with visible light above 100°C for 4 minutes.

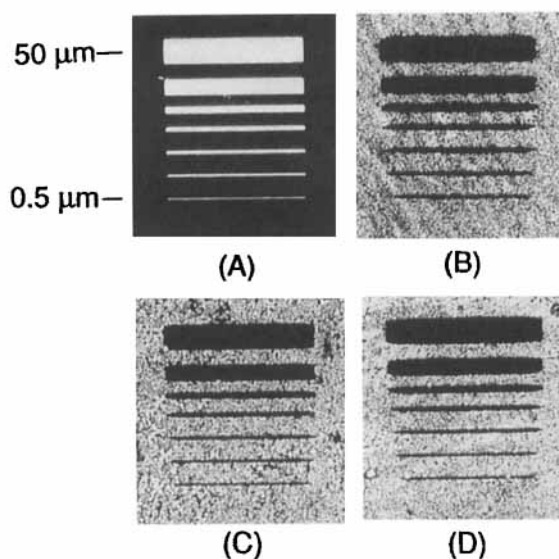


FIG. 5. A photomask used for replicating test pattern (A) and the pattern stored on *st*-poly(1) (B), *st*-poly(2) (C), and *it*-poly(2) (D) films at 100, 112, and 90°C, respectively, observed under a polarizing optical microscope (magnification  $\times 25$ ).

Similar experiments were carried out using *it*- and *st*-poly(2). Both of these polymers also gave stored images with high resolution. The tacticity dependence of the thermal stability of the stored images was examined by annealing the film samples at 85°C. Figure 6 shows polarized optical micrographs of the stored images on *it*- and *st*-poly(2)s at 25°C before (Fig. 6A) and after (Fig. 6B) annealing at 85°C

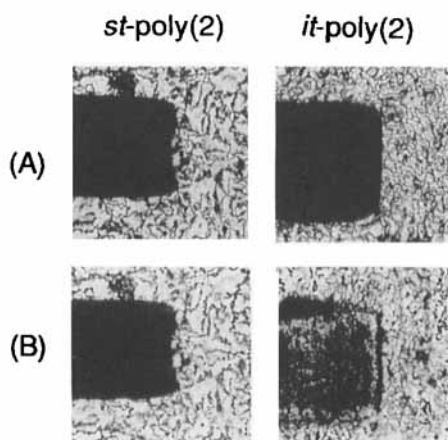


FIG. 6. Test patterns stored on the polymer films before annealing (A) and after annealing at 85°C for 21 hours (B), observed under a polarizing optical microscope (magnification  $\times 100$ ).

for 21 hours. After annealing, the stored image on the film of *it*-poly(2) became partly transparent due to thermal reorientation of the mesogenic group to form an anisotropic phase.

As Ikeda and his coworkers pointed out, one of the keys for stable image storage in a polymer is a high  $T_g$  of the material [1–4]; segmental motion of the main chain is frozen below  $T_g$ , and thus the recorded image can be stored for a long time. In this regard, side-chain LC polymethacrylate is usually better suited for stable image storage than the corresponding polyacrylate since the former has a higher  $T_g$  than the latter [16]. In addition,  $T_g$  values are tacticity-dependent, and *st*-polymer shows a higher  $T_g$  than *it*-polymer [14]. Therefore, tacticity control is an important factor for making a side-chain LC polymer for image storage.

## CONCLUSION

Methacrylates having an azobenzene group as a photoreactive and mesogenic entity were synthesized and polymerized. In addition to the structure of the mesogenic group, main-chain configuration (stereoregularity) was found to be an important factor for LC phase formation. The stereoregularity may govern not only the alignment of the mesogenic side chain but also the main-chain flexibility, which in turn affects LC phase formation. By modifying the main-chain flexibility through the control of tacticity, the mesogenic interaction can be optimized to favor LC phase formation.

By using phase transition due to UV-light irradiation, image storage on a polymer film was achieved. The stored image was stable at room temperature for at least one year and could be erased by heating the film or irradiating visible light. The thermal stability of the stored image depends on the tacticity of the polymer. Tacticity control is an important factor for the higher image-storage ability of a side-chain LC polymer.

## ACKNOWLEDGMENTS

The authors are grateful to Professor Jung-Il Jin of Korea University for his helpful discussion, to Professor M. Kobayashi and Professor K. Tashiro of the Faculty of Science of Osaka University for their help for x-ray measurement and helpful discussion, and also to Professor M. Takai, Dr. H. Aritome, and Mr. K. Mino of the Research Center for Extreme Science of Osaka University for their help for making the photomask.

## REFERENCES

- [1] T. Ikeda, S. Kurihashi, D. B. Karanjit, and S. Tazuke, *Macromolecules*, **23**, 3938 (1990).
- [2] T. Ikeda, S. Horiuchi, D. B. Karanjit, S. Kurihashi, and S. Tazuke, *Ibid.*, **23**, 36 (1990); **23**, 42 (1990).
- [3] T. Ikeda and O. Tsutsumi, *Science*, **268**, 1873 (1995).

- [4] K. Ueno, H. Shirai, O. Tsutsumi, and T. Ikeda, *Polym. Prepr. Jpn.*, **44**, 333 (1995); **44**, 334 (1995).
- [5] M. Eich and J. H. Wendorff, *Makromol. Chem., Rapid Commun.*, **8**, 59 (1987); **8**, 467 (1987).
- [6] K. Nishimura, T. Nakano, and Y. Okamoto, *Polym. Prepr. Jpn.*, **44**, E360 (1995).
- [7] Y. Okamoto, T. Asakura, and K. Hatada, *Chem. Lett.*, p. 1105 (1991).
- [8] T. Nakano, T. Hasegawa, and Y. Okamoto, *Macromolecules*, **26**, 5496 (1993).
- [9] K. Sugiyama and K. Shiraishi, *Res. Rep. Fac. Eng., Kinki Univ.*, **22**, 37 (1988).
- [10] J. A. Riddick and W. B. Bunger, *Organic Solvents*, vol. 2, 3rd ed., Wiley, New York, NY, 1970, p. 770.
- [11] A. Nishioka, H. Watanabe, K. Abe, and Y. Sono, *J. Polym. Sci.*, **48**, 241 (1960).
- [12] T. Kitayama, E. Masuda, M. Yamaguchi, T. Nishiura, and K. Hatada, *Polym. J.*, **24**, 817 (1992).
- [13] T. Kitayama, S. Ishi, N. Fujimoto, and K. Hatada, *Polym. Prepr. Jpn.*, **40**, 224, 1930 (*Engl. Ed.*, E65, E829) (1991).
- [14] K. Hatada, T. Kitayama, and K. Ute, *Prog. Polym. Sci.*, **13**, 251 (1988).
- [15] K. Hatada, T. Kitayama, T. Nishiura, and M. Tawada, *To Be Submitted*.
- [16] J. Brandrup and E. H. Immergut, *Polymer Handbook*, 2nd ed., Wiley, New York, NY, 1975, p. III146-148.

Received July 30, 1996

Revision received November 11, 1996