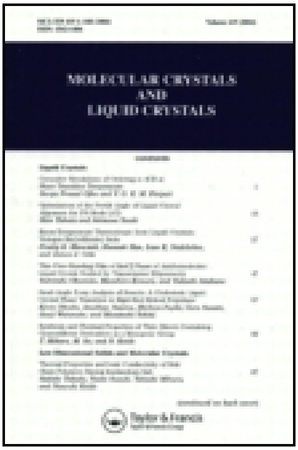

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Thermal Transition Behavior and Second Nonlinear Optical Properties of Polymers Containing Mesogenic Side Chains

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Thermal Transition Behavior and Second Nonlinear Optical Properties of Polymers Containing Mesogenic Side Chains

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Azo-type nonmesogenic monomer and mesogenic monomers which tend to be arranged in homogeneous or in homeotropic alignment were synthesized. Copolymers were obtained using these monomers by radical polymerization. Thermal and nonlinear optical properties of these copolymers were investigated. The second order nonlinear optical susceptibility enhancement due to liquid crystalline orientation has been observed.

Keywords: azo-type, smectic, side chain polymers, nematic, nonlinear optical

INTRODUCTION

Liquid crystal polymers (LCP) containing dye molecule are of interest for applications of nonlinear optical (NLO) and device materials. Organic NLO materials have been investigated by many research groups, owing to their potential application in integrated electro-optic system. In order to obtain organic materials with large nonlinear coefficients, it is necessary to attach the following factors in the molecules[1]: (1) conjugated π-electron systems, (2) donor-acceptor systems having strong polarized structures, and (3) non-centrosymmetric chemical species. On the base of these necessities for NLO properties, liquid crystals would be considered as one candidate for NLO materials owing to their chemical structures and orientational properties. It has demonstrated that better results were obtained with a nematic liquid crystalline polymer as host instead of nonmesogenic amorphous polymer [polymethylmethacrylate] doped in low molecular compound with large molecular hyperpolarizability, such as 4-(dimethylamino)-4′-nitrostilbene as guest.[2] From this result, side chain type liquid crystalline polymers are attractive for NLO materials.[3-5]

In this study, we have synthesized copolymers containing the different compositions of nonmesogenic azo monomer having Disperse Red 1 as a NLO component and mesogenic monomers which tend to be oriented by application of an external field in homogeneous or in homeotropic alignment depending on the dielectric anisotropy of mesogenic group. Thermal transition behavior, electric optical properties and second harmonic generation (SHG) of these copolymers have been investigated.

EXPERIMENTAL

Materials

The molecular structures of monomers used as polymerized and abbreviation of the copolymers are shown in Figure 1. The monomers were synthesized according to the Figure 1. Structures of all compounds were identified by FT-IR and ^{1}H NMR. Their purity was confirmed by thin layer chromatography.

Homopolymers and copolymers were obtained by DMF solution with the use of AIBN as initiator. Copolymers were purified by reprecipitation using methanol. The content of the dye in the copolymer was identified by UV spectrum.

Method

DSC measurements were made by means of a differential thermal analyzer Mettler TA3000 (heating and cooling rate 10°C/min). Textures of polymeric mesophases were observed with a polarizing microscope equipped programmable heating stage Mettler FP52. Copolymer dissolved in THF and spin deposited onto indium-tin-oxide coated glass. The film thickness ranged from 0.4 to 0.8 μm. The sample was then corona poled or applied a DC field above its isotropic transition temperature. The samples were then cooled slowly to the room temperature with applying the electric field, and the maximum electric field strength was 0.125 MV/cm. The second order NLO susceptibility χ^2 was determined by second harmonic generation (SHG) measurement. A Q-switched Nd^{3+}YAG laser supplied 0.6 mJ per pulse of fundamental wave (1063 nm), which was focused on an approximately 500 nm spot on the sample. Verification of the SHG wave was provided by measurement of the signal intensities at 532 nm.

RESULTS AND DISCUSSION

Thermal Properties

The aim of the first one was to obtain the high concentration of guest monomer in the host liquid crystal polymer. The acryl and methacryl monomers and polymers having methoxy group in the end of the mesogen, AAMB and MAMB, tend to be oriented homogeneously, while methacryl monomer and polymer containing cyano group in the end of mesogen, MACB, tend to be arranged homeotropically on applying the voltage perpendicular to the glass plate.

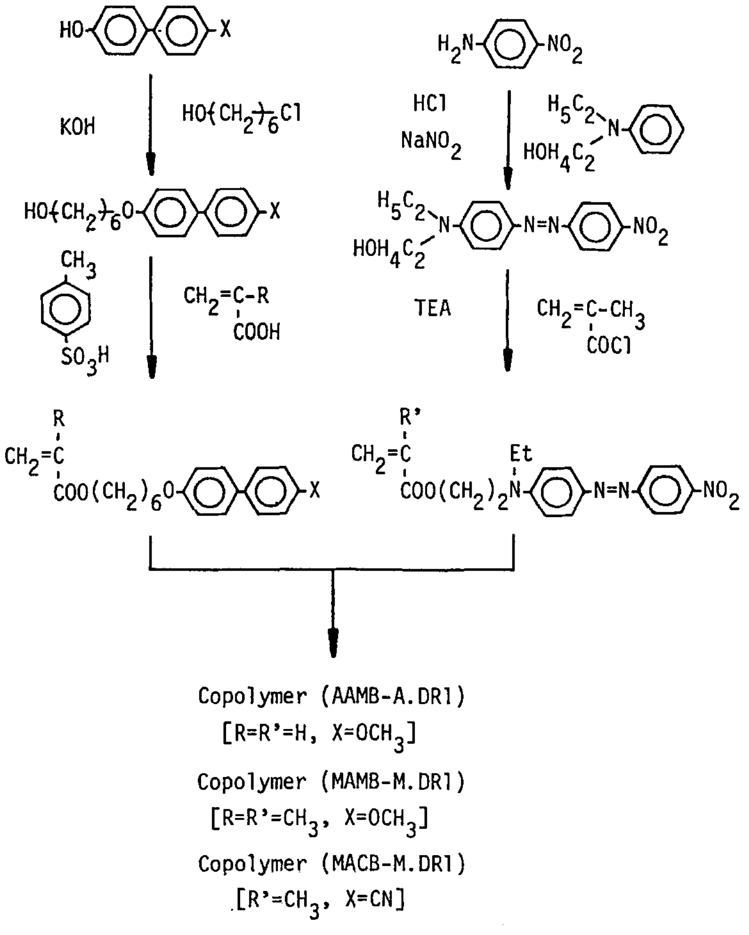

FIGURE 1 Reaction scheme of side chain type polymers and abbreviation of copolymers.

We have synthesized acryl type copolymers, AAMB-A.DR1, and methacryl type copolymers, MAMB-M.DR1 having methoxy group in the end of mesogen. Acryl type copolymers were obtained only at the contents of azomonomer, A.DR1, ranging from 0 to 15 mol%, while methacryl type copolymers were yielded any contents of azomonomer.

The molecular weight of copolymers, MAMB-M.DR1, were between 20,000 and 30,000 independent of azo monomer contents. Both acryl and methacryl type homopolymers and copolymers exhibited a fan type texture characteristic of smectic phase. The typical DSC curves are shown in Figure 2.

Transition temperatures and isotropization entropies of copolymers, AAMB-A.DR1, decreased rapidly with increasing of azo monomer contents. These results supported that the ordering of the liquid crystallinity vanished with increasing content of azo monomer.

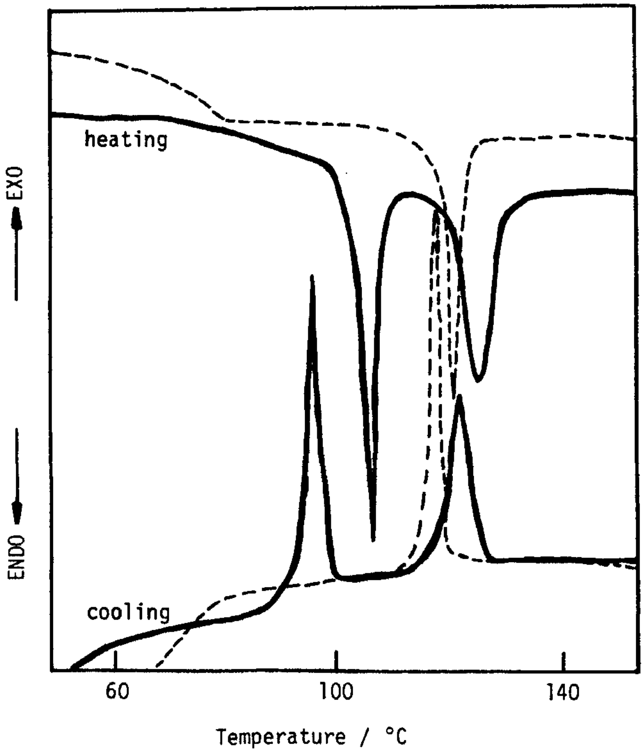

FIGURE 2 DSC Thermogram of Copolymer MAMB-M.DR1. ———: MAMB-M.DR1 (10%); -----: MAMB-M.DR1 (25%).

Thermal transition temperatures and entropies of acryl type copolymers, AAMB-A.DR1, are shown in Table I.

Thermal transition temperature from solid to mesophase (Tm) and from mesophase to isotropic fluid (Ti) decreased with increasing content of azo type monomers, and mesomorphic temperature range became narrow. Copolymer, AAMB-A.DR1, did not exhibit the mesomorphic nature in concentration of dye monomer above 20%. Acryl type copolymer with cyano group in the end of mesogen gave no typical optical texture owing to their homeotropic alignment even though the glass surface treatment did not carry out. This behavior was detected by the conoscopic observation.

The transition temperature of copolymers, MAMB-M.DR1, are shown in Figure 3. The transition temperature of Tm disappeared and the glass transition temperature (Tg) appeared in the copolymers containing azo monomer above 20%. The Tg increased with increasing azo monomer contents.

The methacrylic type copolymers, MAMB-M.DR1, at the contents of azo monomer ranging from 0 to 60 mol% exhibited batonnets like texture which is characteristic of smectic phase. Liquid crystallinity of copolymers, MAMA-M.DR1 was broader than that of copolymers, AAMB-A.DR1.

TABLE I

Thermal properties of copolymers, AAMB-A.DR1

Dye(%)	Transition temperature (°C)	MR (°C)	ΔSi(cal/mol.K)
0	K $\underset{125.0}{\overset{127.7}{\rightleftharpoons}}$ S $\underset{144.3}{\overset{144.3}{\rightleftharpoons}}$ N $\underset{145.7}{\overset{145.7}{\rightleftharpoons}}$ I	20.7	0.26
5	K $\underset{119.1}{\overset{122.9}{\rightleftharpoons}}$ S $\underset{136.0}{\overset{137.2}{\rightleftharpoons}}$ I	16.9	1.60
10	K $\underset{115.8}{\overset{119.7}{\rightleftharpoons}}$ S $\underset{131.8}{\overset{133.1}{\rightleftharpoons}}$ I	16.0	1.36
20	K $\underset{106.0}{\overset{110.9}{\rightleftharpoons}}$ S $\underset{120.3}{\overset{122.0}{\rightleftharpoons}}$ I	14.3	0.72

K: solid, S: smectic, N: nematic, I: isotropic.
MR: mesomorphic temperature range.

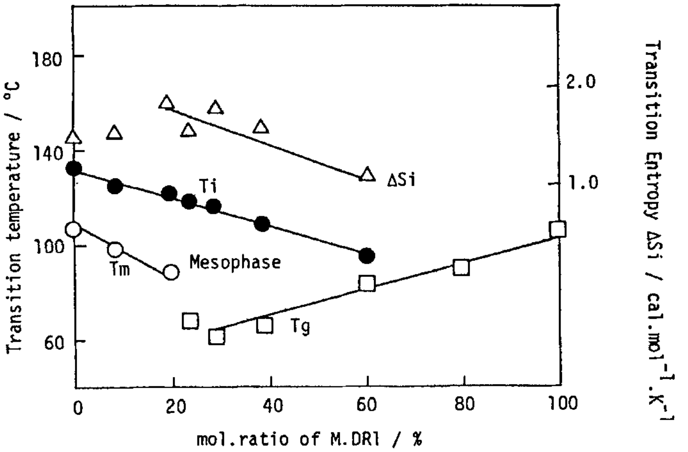

FIGURE 3 Transition temperature and isotropization entropy of copolymer (MAMB-M.DR1) as a function of azo monomer composition.

Methacryl type copolymers, MACB-M.DR1, having cyano group in the end of mesogen have also synthesized. Thermal transition temperatures and entropies of methacryl type copolymers, MACB-M.DR1, are shown in Table II.

The copolymers could be easily spun at the molten state owing to the high molecular weight copolymers. MACB-M.DR1 showed nematic phase. The copolymers showed both Tg and Ti (transition temperature from mesophase to isotropic fluid), and between Tg and Ti these copolymers also exhibited nematic phase

TABLE II

Thermal properties of copolymers, MACB-M.DR1

Dye (%)	Transition temperature (°C)	MR[a] (°C)	Δ Si[b] (cal/mol.K)	$\overline{Mn}$
0	$Tg \xrightarrow{64.4} M \underset{114.9}{\overset{115.0}{\rightleftharpoons}} I$	50.6	1.14	
5	$Tg \xrightarrow{52.8} M \underset{106.1}{\overset{107.7}{\rightleftharpoons}} M \underset{110.6}{\overset{111.3}{\rightleftharpoons}} I$	58.5	0.97	37,300
10	$Tg \xrightarrow{61.4} M \underset{98.3}{\overset{98.4}{\rightleftharpoons}} M \underset{104.3}{\overset{105.1}{\rightleftharpoons}} I$	43.7	0.87	31,300
20	$Tg \xrightarrow{74.9} M \underset{99.6}{\overset{100.3}{\rightleftharpoons}} I$	25.4	0.42	31,400
100	$Tg \xrightarrow{74.9} I$			17,600

[a] Mesomorphic temperature range, [b] isotropization entropy.
M: Mesophase.

characterized by X-ray and texture observations. No peak was observed in the area of small angle x-ray scattering. Ti decreased with increasing contents of dye monomer. The isotropization entropy change also decreased with increasing contents of dye monomer. These results would suggest the ordering of these copolymers influenced by the incorporation with dye monomer.

These copolymers could be oriented easily to the homeotropic alignment on applying the electric field about 80 voltage than the copolymers of MAMB-M.DR1 containing the different dielectric anisotropy in the mesogenic group.

NLO Properties

The dielectric anisotropy ($\Delta\varepsilon$) is mainly determined by the dipolar properties of the mesogenic group. The applied electric field will align the mesogenic parts depending on their dipolar components. The sign of $\Delta\varepsilon$ would be estimated by the parallel dipole moment minus perpendicular dipole moment to the molecular long axis. Consequently, compounds such as cyano group (positive $\Delta\varepsilon$) in the end of mesogen can be easily oriented homeotropically and compounds such as methoxy group (negative $\Delta\varepsilon$) in the end of mesogen homogeneously, on applying the voltage perpendicular to the glass plate.

In guest-host polymer system, it is well known that the χ^2 value is proportional to the content of guest molecules. In order to get a high concentration of NLO materials in the polymer, copolymerization was carried out with dye monomer and liquid crystal monomer. The dependence of dye content on the χ^2 was investigated.

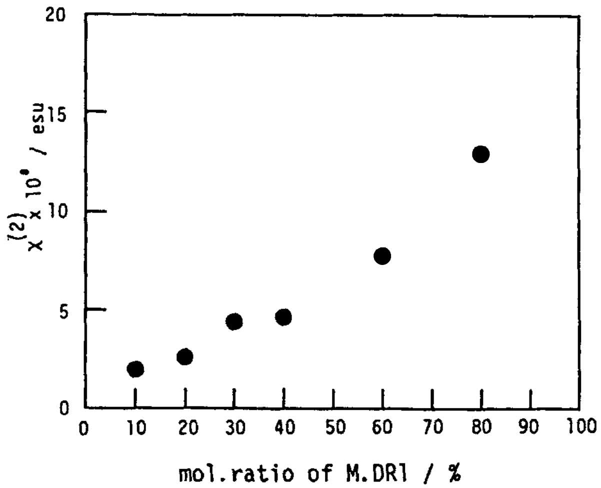

FIGURE 4 Relationship between χ^2 value and azo monomer composition of copolymer (MAMB-M.DR1).

The relationship between χ^2 and azo monomer contents is shown in Figure 4. The χ^2 value of copolymers increased linearly with increasing of azo monomer contents. At the content of azo monomer of 80 mol%, almost same χ^2 value was obtained as conventional nonmesogenic copolymers.

The reason why copolymers MAMB-M.DR1, did not exhibit higher value than we have expected. The SHG value is deeply influenced by the orientation behavior of the molecule.[6] In the case of the copolymer, a nematic phase observed at the content of azo monomer below 60%. However, the SHG value was larger in the nonmesomorphic phase than nematic phase. These results would be attributed to the different orientational behavior between mesogen and azo molecule or the orientation of these copolymers was not enough to show the χ^2 value. The methoxy containing mesogenic polymer (negative $\Delta\varepsilon$) can be easily oriented homogeneously, while nitro containing dye polymer (positive $\Delta\varepsilon$) would be oriented homeotropically on applying the voltage to the perpendicular to the glass plate.

Therefore, SHG was detected for the copolymers having the same dielectric anisotropy, MACB-M.DR1, after poling in a DC field under the same condition of copolymers, MAMB-M.DR1. This indicated that the microscopic structure of side chain dipole became non-centrosymmetrically on applying an electric field.

Liquid crystalline orientation induced by a DC field was observed for all copolymers, MACB-M.DR1, at the microscopic measurements. The photographs showed that the liquid crystalline orientation was parallel to the poling field direction. These results also supported by the measurements of χ^2_{333} and χ^2_{311}. The χ^2_{333} and χ^2_{311} value was 2.8×10^{-8} and 6.4×10^{-9}, respectively. The χ^2_{333} value is 4.4 times larger than the χ^2_{311} value. The χ^2 value of the copolymers, MACB-M.DR1, at the 20 mol% of azo monomer content was evaluated to be 1.2 times greater than that of nonmesogenic copolymer. The enhancement of the χ^2 value would be deeply attributed to the liquid crystalline orientation.

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