

Polymerization of Liquid Crystalline Monomers with Diene Groups and Formation of a Polymer Network with Uniaxial Molecular Alignment

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SYNOPSIS

Two biphenyl compounds with diene groups at both ends of the biphenyl group were synthesized. A nematic phase was observed for both the biphenyl compounds. Bulk photopolymerization was investigated by differential scanning calorimetry. Reactivity and formation of a polymer network with uniaxial molecular alignment are discussed in relation to the molecular ordering of the biphenyl compounds. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The effects of monomer organization on polymerization and resulting polymer properties are becoming of interest from scientific and industrial points of view. Recently, several studies have reported on the polymer membranes with anisotropic molecular alignment in relation to the bulk polymerization of liquid crystalline monomers such as acrylate, methacrylate, vinyl ether, and epoxide derivatives.¹⁻³ On the other hand, we have reported the liquid crystalline properties and bulk photopolymerization of biphenyl compounds with diene groups.⁴ The 1,4-addition polymerization of the biphenyl compounds was brought about by irradiation in the whole temperature range of the liquid crystalline phase. No liquid crystalline properties, such as anisotropic molecular ordering, were observed for the polymers obtained by photopolymerization of biphenyl compounds with diene groups at one end of the biphenyl group, while biphenyl compounds with two diene groups at both ends of the biphenyl group were found to show birefringence by polymerizing in the liquid crystalline phase. In this article we discuss the bulk photopolymerization of the biphenyl compounds with two diene groups and the formation of a poly-

mer network with uniaxial molecular alignment with regard to a molecular ordering of the biphenyl compounds.

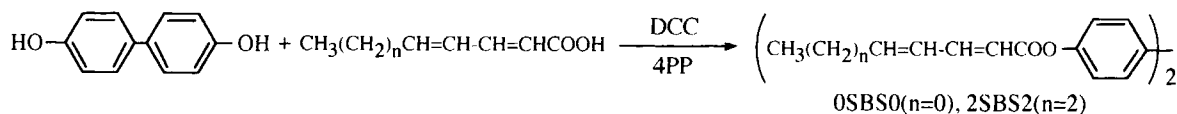
EXPERIMENTAL

The structure and the phase transition temperatures of the biphenyl compounds with two diene groups at both ends of the biphenyl group, 0SBS0 and 2SBS2, are shown in Figure 1. 0SBS0 and 2SBS2 were synthesized as follows.

The biphenyl compounds were synthesized by reacting 4,4'-biphenol with sorbic acid or 2,4-octadienoic acid in the presence of dicyclohexylcarbodiimide (DCC) and 4-pyrrolidinopyridine (4PP) in dimethylformamide (DMF) in an ice bath. The DMF solution was allowed to warm up to room temperature and followed by further stirring for 90 h. Precipitated dicyclohexylurea was filtered off, and evaporation was carried out *in vacuo*. The crude product was purified by recrystallization from ethanol. The structure of the biphenyl compounds was confirmed by infrared (IR), nuclear magnetic resonance (NMR), and elemental analysis.

DATA FOR 0SBS0: ¹H-NMR (CDCl₃) δ 1.9 (d, 6H of methyl), 6.0 (d, 2H of diene), 6.3 (m, 4H of diene), 7.2 (d, 4H of biphenyl), 7.4 (m, 2H of diene), 7.6 (d, 4H of biphenyl); IR (KBr, cm⁻¹) 1720 (ν_{CO}), 1640, 1610 (ν_{C=C}).

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	Phase transition temperature (°C)		
	Crystalline	Nematic	Isotropic
0SBS0	168		257
2SBS2	153		229

Figure 1 Structure and phase transition temperature of the biphenyl compounds with diene groups at both ends of the biphenyl group.

Elemental analysis: calculated for ($\text{C}_{24}\text{H}_{22}\text{O}_4$) C, 77.0, H, 5.9; found C, 75.1, H, 5.9.

DATA FOR 2SBS2: $^1\text{H-NMR}$ (CDCl_3) δ 0.95 (t, 6H of methyl), 1.5 (m, 4H of methylene), 2.1 (m, 4H of methylene), 6.0 (d, 2H of diene), 6.25 (m, 2H of diene), 7.2 (d, 4H of biphenyl), 7.45 (m, 2H of diene), 7.6 (d, 2H of biphenyl); IR (KBr, cm^{-1}) 1720 (ν_{CO}), 1635, 1610 ($\nu_{\text{C}=\text{C}}$). Elemental analysis: calculated for ($\text{C}_{28}\text{H}_{30}\text{O}_4$) C, 78.1, H, 7.0; found C, 78.0, H, 7.6.

Phase transition temperatures of the monomeric biphenyl compounds were examined by means of differential scanning calorimetry (DSC; SEIKO I&G SSC-5020) and polarizing microscopic observation (polarizing microscope, Olympus BHSP; hot stage and controller, Mettler FP80 and FP82). DSC thermograms were measured on heating at a rate of $2^\circ\text{C}/\text{min}$, and the peak temperature was taken as the phase transition temperature. X-ray powder pattern was measured by using Rigaku RAD-1VB.

Photopolymerization of the biphenyl compounds was directly followed by DSC. The sample film was cast by injecting a tetrahydrofuran (THF) solution of each monomeric biphenyl compound into aluminum DSC pan, followed by vacuum drying at room temperature to constant weight. The DSC cell was adapted with a quartz glass to allow ultraviolet (UV) light irradiation into the DSC pan by a 75-W high-pressure mercury lamp. The heat evolution during the polymerization was recorded as a function of time. Molecular weights of compounds irradiated were measured by gel permeation chromatography (GPC; JASCO 880-PU; column, Shodex KF-80M + KF-80M; eluent, THF; calibrated with standard polystyrenes).

The oriented sample was prepared by injecting each molten monomeric biphenyl compound in a cell. The cell consisted of two parallel quartz glass plates which were coated with polyvinylalcohol and

rubbed to obtain homogeneous alignment. The cell gap was approximately $7\ \mu\text{m}$. Transmitted intensity as a function of the angle defined as the angle between the direction of molecular orientation, and the plane of polarization was measured.

RESULTS AND DISCUSSION

0SBS0 showed a large endothermic peak at 168°C and a broad exothermic peak centered around 245°C in a first DSC thermogram obtained by heating at a rate of $2^\circ\text{C}/\text{min}$. No clear peak was observed for 0SBS0 on a cooling cycle and second heating cycle. 2SBS2 exhibited two endothermic peaks and a broad exothermic peak in the DSC thermogram; the large endothermic peak at 153°C , the small endothermic peak at 229°C , and the broad exothermic peak centered around 245°C . Therefore, polarizing microscopic observation was performed by heating at a rate of $10^\circ\text{C}/\text{min}$. The shlieren texture was observed from 168 to 257°C for 0SBS0 and 153 to 229°C for 2SBS2. Both the X-ray powder patterns of 0SBS0 and 2SBS2 gave only a broad peak centered around 2θ of 20° ($d = 4.43\ \text{\AA}$) above their melting temperatures. Consequently, both the biphenyl compounds are considered to exhibit a nematic phase from 168 to 257°C for 0SBS0 and from 153 to 229°C for 2SBS2, respectively. However, a thermal reaction (decomposition or polymerization) was recognized for both the biphenyl compounds above 245°C .

The biphenyl compounds were investigated with regard to their ability to undergo solution or bulk radical polymerization by using 2,2'-azobisisobutyronitrile (AIBN) as a thermal radical initiator or 2,2-dimethoxy-2-phenylacetophenone as a radical photoinitiator. Trace amounts of polymer were obtained by all radical polymerization conditions attempted in this study. On the other hand, polymers

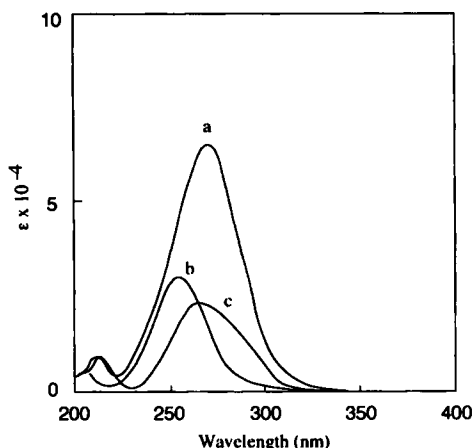


Figure 2 Absorption spectra of 0SBS0, sorbic acid, and 4,4'-biphenol in THF: (a) 0SBS0; (b) sorbic acid; (c) 4,4'-biphenol.

could be obtained by irradiation of light with wavelengths shorter than 300 nm on both the biphenyl compounds in the nematic phase and the isotropic phase. The product obtained by irradiation was found to dissolve hardly in any solvent. Gel permeation chromatography (GPC) measurements for extracts with THF exhibited two peaks: a larger peak corresponding to each monomeric biphenyl compound and a shoulder peak corresponding to dimer, respectively. Based on the calibration curve with respect to the concentration of monomeric biphenyl compounds, the maximum conversion to the polymers was more than 90% estimated by GPC measurements for the extracts with THF. Although the structure of the polymers cannot be determined due to their insolubility in any solvent, the previous study of biphenyl compounds with diene groups at one end of biphenyl groups suggests that the 1,4-addition polymerization occurs mainly by irradiation at 170°C, and a dimerization reaction is also brought about by heating above 200°C with or without irradiation.⁴ Therefore, the thermal reaction observed during DSC measurement above 245°C was likely related to the dimerization of diene groups.

Figure 2 shows the absorption spectra of 0SBS0, sorbic acid, and 4,4'-biphenol in THF. The wavelengths of absorption maxima of sorbic acid and 4,4'-biphenol were 255 and 265 nm, respectively. The absorption spectrum of 0SBS0 was very similar to the sum of the absorption spectra of sorbic acid and 4,4'-biphenol. The spectrum of 2SBS2 was almost the same as that of 0SBS0. Therefore, the irradiation of light with wavelengths shorter than 300 nm on the biphenyl compounds can be considered to cause the polymerization of the biphenyl compounds.^{5,6}

To investigate the photopolymerization behavior of the biphenyl compounds, the heat evolution during polymerization was directly measured by DSC. Figure 3 shows the changes in the heat evolution of 0SBS0 with or without irradiation at 170, 200, and 230°C, at which 0SBS0 exists in the nematic phase. The irradiation on 0SBS0 caused an increase in the heat evolution and shift of the exotherms to shorter irradiation time, indicating an increase in reactivity of 0SBS0. In particular, the considerable increase in the reactivity was observed by irradiation at 170°C. However, no heat evolution was observed for 0SBS0 in the crystalline phase (120°C) with or without irradiation. The bulk thermal and photopolymerization of liquid crystalline monomers with acrylate or methacrylate groups have been reported to proceed in a few minutes,^{1,3} where the polymerization took place via radical reaction. The photopolymerization rate of 0SBS0 is much slower than that of acrylate and methacrylate liquid crystalline monomers. In addition, as described earlier, only trace amounts of polymer of 0SBS0 and 2SBS2 were obtained by all radical polymerization conditions attempted in this study. The result is consistent with

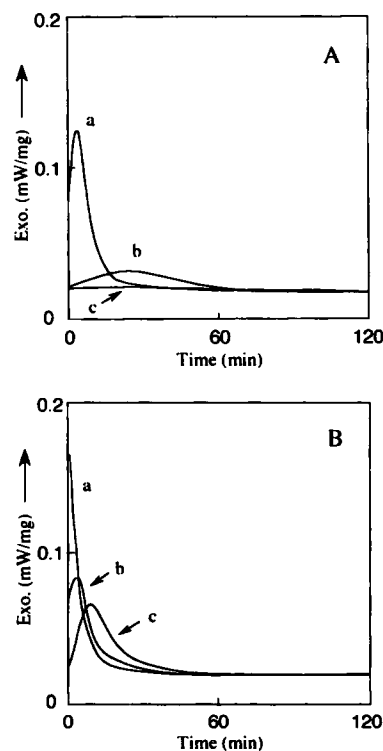


Figure 3 DSC exotherms for 0SBS0 with or without irradiation at various temperatures: (A) without irradiation; (B) with irradiation; (a) at 230°C; (b) at 200°C; (c) at 170°C.

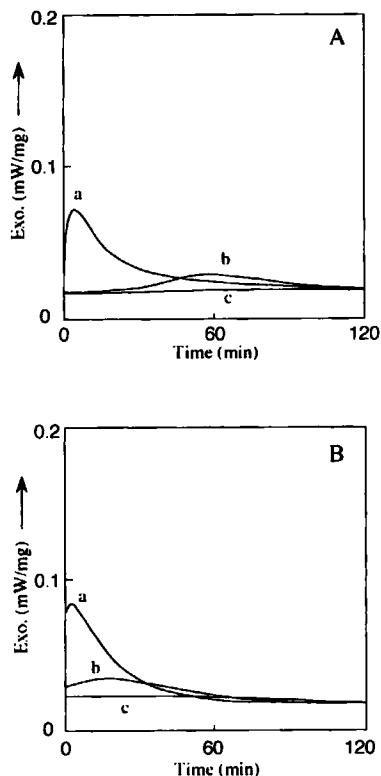


Figure 4 DSC exotherms for 2SBS2 with or without irradiation at various temperatures: (A) without irradiation; (B) with irradiation; (a) at 230°C; (b) at 200°C; (c) at 170°C.

Ringsdorf and Schupp's work dealing with the polymerization of substituted butadienes at the gas-water interface.⁵ On the other hand, Ohno et al. reported that the polymerization of liposomes composed of diene-containing lipid in water was achieved by using a water-soluble radical initiator.⁶ Lamparski and O'Brien revealed that the AIBN-initiated thermal radical polymerization and photopolymerization of lipid bilayers having mono- or bis-hexadienoyloxy groups was dependent on the monomer structure, the mode of initiation, the monomer to initiator ratio, and the lateral diffusion of the monomer within the assembly.⁷ Although the polymerization mechanism for the biphenyl compounds, OSBS0 and 2SBS2, with diene groups is not well defined, the result suggests that the mobility of the molecules is considered to be an important factor in influencing polymerization behavior. To reveal the polymerization mechanism of the biphenyl compounds with diene groups, much data should be accumulated.

The changes in the heat evolution of 2SBS2 with or without irradiation are shown in Figure 4. An increase of the photopolymerization was also ob-

served by irradiation at 200 and 170°C, while little change in the heat evolution curve of 2SBS2 was recognized at 230°C, at which 2SBS2 was in an isotropic phase. Namely, the irradiation in the isotropic phase could not increase the polymerization of 2SBS2. The results imply that the spatial ordering is also important for the polymerization of the biphenyl compounds with diene groups. In addition, the product at higher temperature may be mainly attributed to thermoinitiated reaction. On the other hand, the reactivity at 170°C was lower than that of OSBS0 with or without irradiation. The bulkiness of propyl group as the terminal group of 2SBS2 may be one of the factors to influence the reactivity of diene groups attached to the biphenyl group.

In Figure 5, the transmitted intensity of 2SBS2 in the quartz cell with homogeneous alignment after irradiation at 170°C for 1 h was plotted as a function of the angle, θ , defined as the angle between the direction of molecular orientation and the plane of polarization. The transmitted intensity was measured at 300°C. The transmitted intensity was found to change as a function of angle: The curve showed the maximum around 45 and 135°, and the minimum around 0, 90, and 180°. This angle dependence of 2SBS2 irradiated was almost similar to that of 2SBS2 aligned homogeneously before irradiation. On the other hand, little transmitted intensity was observed for 2SBS2 irradiated at 230°C, at which 2SBS2 was in the isotropic phase. It is known that the transmitted intensity, I , of the uniaxially oriented sample with respect to θ can be written by an equation⁸:

$$I = I_0 \sin^2(2\theta) \sin^2\left(\frac{\pi d \Delta n}{\lambda}\right) \quad (1)$$

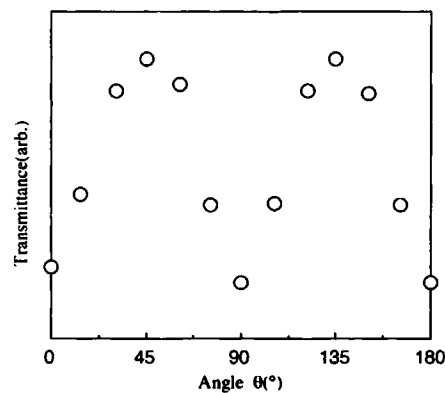


Figure 5 Change in transmittance intensity through 2SBS2 as a function of θ . Transmittance intensity was measured at 300°C.

where I_0 and λ are the intensity and the wavelength of incident light. The variables d and Δn are the sample thickness and the birefringence, respectively. The variables except for θ are constant in this study. Thus, the transmitted intensity is assumed to depend on θ only. The maximum transmitted intensity was observed at 45 and 135°, and the minimum transmittance intensity was observed at 0, 90, and 180°, respectively. Thus, the result shown in Figure 5 implies that the homogeneous parallel molecular alignment was maintained even at 300°C, which is above the isotropization temperature of 2SBS2. However, the birefringence monitored at room temperature was decreased considerably when the sample irradiated at 170°C was heated above 300°C due to thermal decomposition. Therefore, it can be assumed that the birefringence results from the formation of polymer networks with uniaxial molecular ordering, not from a crystalline or liquid crystalline phase of the polymers produced. The result demonstrates that the initial anisotropic molecular alignment can be frozen by the photopolymerization and photocrosslinking reaction of diene groups attached to both ends of the biphenyl group in the liquid crystalline phase.

CONCLUSION

Biphenyl compounds with diene groups at both ends of the biphenyl group were found to polymerize in the nematic phase and the isotropic phase by irradiation of light with wavelengths shorter than 300 nm. Comparison with the result of irradiation in the solid phase revealed that the mobility influenced the polymerization behavior of the biphenyl compounds with diene groups. In addition, the photopolymerization rate was related to the molecular ordering

and the bulkiness of diene groups. The polymer network films with uniaxial molecular alignment could be obtained by photopolymerization of biphenyl compounds with two diene groups in the liquid crystalline phase.

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