BUTTERWORTH
HEINEMANN

Polymer Vol. 36 No. 4, pp. 849–855, 1995

0032-3861/95/$10.00+0.00

Synthesis and polymerization of liquid-crystalline monomers having diene groups

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(Received 18 July 1994; revised 5 September 1994)

Biphenyl compounds having diene groups were synthesized. In the first class of compounds, the diene groups were directly attached to one end or both ends of the biphenyl through ester bonding. In the second class of compounds, the diene groups were attached to one end or both ends of the biphenyl through methylene spacers. Only the first class of compounds were found to show a liquid-crystalline phase. The bulk thermal and photopolymerizations of the first class of compounds were carried out in the crystalline phase, liquid-crystalline phase and isotropic phase. It was found that the morphology of the systems strongly affected the polymerization rate and conversion. The polymerization behaviour is discussed in relation to the morphology of the system.

(Keywords: liquid-crystalline monomers; bulk polymerization; biphenyl dienes)

INTRODUCTION

The effect of monomer organization on polymerization and the resulting polymer properties has been investigated from both scientific and industrial points of view[1–7]. One of the typical monomer organizations is based on thermotropic liquid-crystalline systems. Thermotropic liquid crystals (LCs) are of increasing interest in the fields of electronics, optoelectronics, optical image recording and self-reinforced materials. In particular, polymer liquid crystals (PLCs) are becoming a candidate for applications based on both their anisotropic properties and their good film-forming property.

The macroscopic orientation of PLCs has been achieved by several methods[8–10]. Recently, Broer *et al.*[11–15] have reported the photopolymerization of the oriented low-molecular-weight liquid-crystalline acrylate to provide uniaxially ordered liquid-crystalline polymers by the use of photoinitiators. We have also reported the bulk photopolymerization of biphenyl compounds with diene groups and the formation of a gel network with molecular orientation[16]. Many studies on the polymerization of monomers with diene groups in monolayers, Langmuir–Blodgett (LB) films or lipid membranes have been reported[17–19], but polymerization of liquid-crystalline monomers with diene groups has not yet been reported. In this paper we describe the synthesis of various biphenyl compounds with diene groups and discuss their liquid-crystalline properties and the morphology effect of the compounds on the bulk thermal and photopolymerizations.

EXPERIMENTAL

Materials

The biphenyl compounds used in this study were synthesized according to schemes shown in *Figure 1*. In the first class of compounds, the diene groups were directly attached to one end or both ends at the 4-position of the biphenyl through ester bonding. They are abbreviated as SBX (X = H, M or C) and *n*SBS*n*, where X represents the substituents at the 4′-position of the biphenyl and *n* is the number of methylene groups at the end of the diene groups. In the second class, the diene groups were attached to one end or both ends of the biphenyl through methylene spacers between the biphenyl and diene groups. They are abbreviated as S*n*BC and S*n*B*n*S, where *n* represents the number of methylene groups of the spacers.

Synthesis of 0SBS0

First, 4×10^{-2} mol of sorbic acid, 1.2×10^{-2} mol of 4,4′-dihydroxybiphenyl and 4×10^{-3} mol of 4-pyrrolidinopyridine were dissolved in 100 ml of dimethylformamide (DMF). To the DMF solution was added dropwise a solution of 3×10^{-2} mol of dicyclohexylcarbodiimide (DCC) in 20 ml of DMF with stirring in an ice bath. The DMF solution was allowed to warm up to room temperature and followed by further stirring for 90 h. Precipitated dicyclohexylcarbodiurea was filtered off and evaporation was carried out *in vacuo*. The crude product was purified by recrystallization from ethanol.

^{1}H n.m.r. ($CDCl_3$) δ (ppm): 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) and 7.6 (d, 4H of biphenyl).

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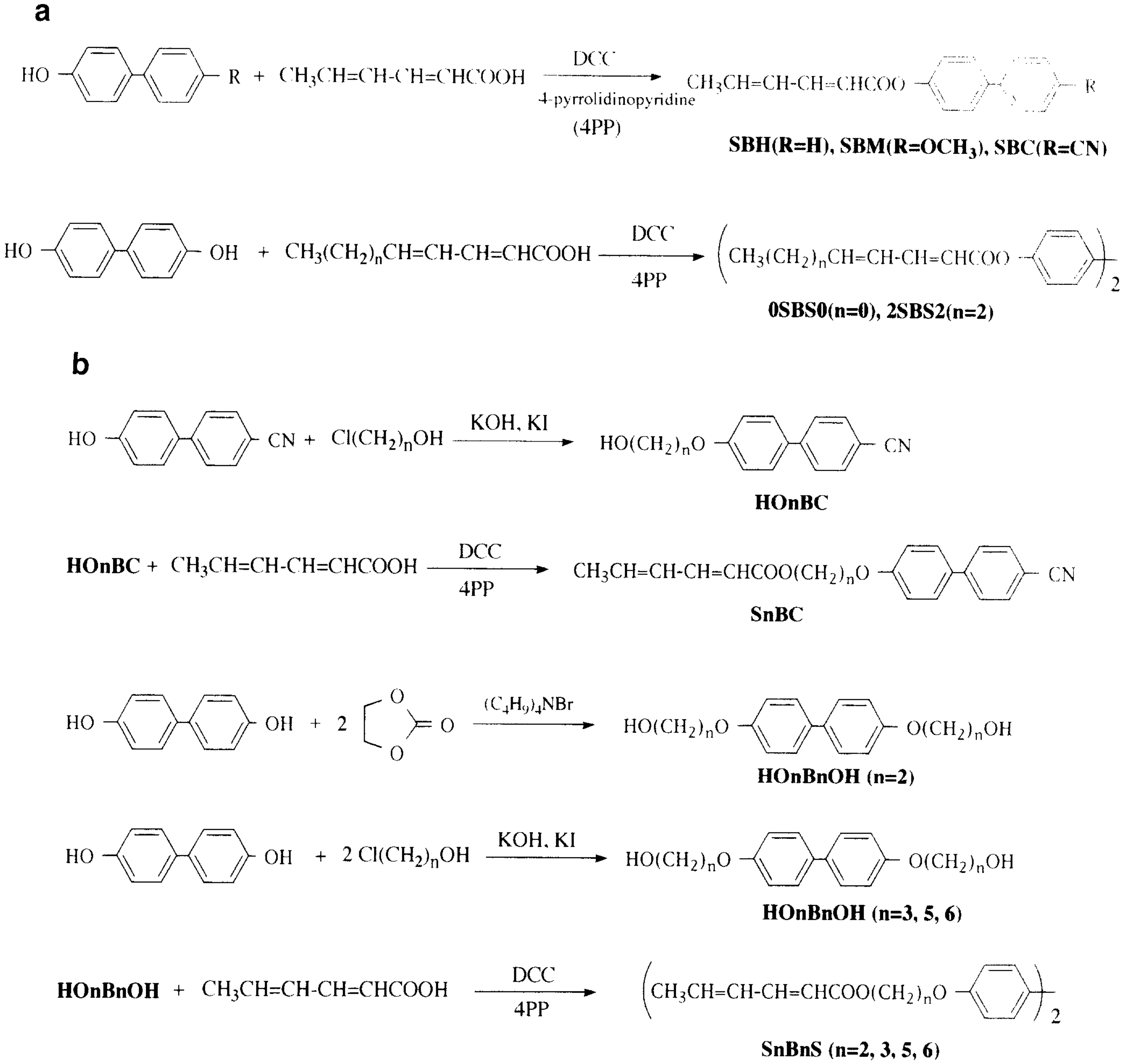

Figure 1 Synthetic routes of biphenyl compounds with diene groups attached (a) through ester bonding and (b) through methylene spacers

I.r. (KBr) (cm^{-1}): 1720 (ν_{CO}), 1640, 1610 ($\nu_{C=C}$). Elemental analysis: calculated for $C_{24}H_{22}O_4$, C 77.0, H 5.9; found, C 75.1, H 5.9.

Synthesis of 2SBS2

A mixture of 0.11 mol of *trans*-2-hexenyl aldehyde, 0.11 mol of malonic acid and 12 ml of pyridine was heated at 80 C for 3 h. The mixture was then cooled in an ice bath, and a solution of 4 ml of sulfuric acid and 10 ml of water was added with magnetic stirring. The precipitate was recovered by filtration and recrystallized from a mixture of water and ethanol to give 2,4-octadienoic acid; m.p. 76 C.

^{1}H n.m.r. (d-DMSO) δ (ppm): 0.9 (t, 3H of methyl), 1.45 (m, 2H of methylene), 5.8 (d, 1H of diene), 6.25 (m, 2H of diene) and 7.15 (m, 1H of diene). I.r. (KBr) (cm^{-1}): 2840 (ν_{OH}), 1685 (ν_{CO}), 1640, 1610 ($\nu_{C=C}$). Elemental analysis: calculated for $C_8H_{12}O_2$, C 68.6, H 8.6; found, C 68.6, H 8.7.

2SBS2 was prepared by reacting 2,4-octadienoic acid with 2,4-dihydroxybiphenyl in the presence of DCC in a similar manner as 0SBS0.

^{1}H n.m.r. (CDCl$_3$) δ (ppm): 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) and 7.6 (d, 2H of biphenyl). I.r. (KBr) (cm^{-1}): 1720 (ν_{CO}), 1635, 1610 ($\nu_{C=C}$). Elemental analysis: calculated for $C_{28}H_{30}O_4$, C 78.1, H 7.0; found, C 78.0, H 7.6.

Synthesis of SBX

SBH, SBM and SBC were synthesized by reacting sorbic acid with 4-hydroxybiphenyls that possess the corresponding substituents (H, OCH_3 or CN) at the 4′-position in the presence of DCC in a similar manner as 0SBS0. These compounds were purified by recrystallization from methanol. Analytical data are shown below:

SBH. ^{1}H n.m.r. ($CDCl_3$) δ (ppm): 1.9 (d, 3H of methyl), 6.0 (d, 1 H of diene), 6.25 (m, 2H of diene), 7.2–7.45 (m, 6H of biphenyl), 7.5 (m, 1H of diene) and 7.6 (m, 4H of biphenyl). I.r. (KBr) (cm^{-1}): 1720 (ν_{CO}), 1640, 1620 ($\nu_{C=C}$). Elemental analysis: calculated for $C_{18}H_{16}O_2$, C 81.8, H 6.1; found, C 81.7, H 6.1.

SBM. ^{1}H n.m.r. ($CDCl_3$) δ (ppm): 1.9 (d, 3H of methyl), 3.85 (s, 3H of methoxy), 6.0 (d, 1H of diene), 6.25 (m, 2H of diene), 7.0 (d, 2H of biphenyl), 7.18 (d, 2H of biphenyl), 7.45 (m, 1H of diene) and 7.55 (m, 4H of biphenyl). I.r. (KBr) (cm^{-1}): 1720 (ν_{CO}), 1640, 1620 ($\nu_{C=C}$). Elemental analysis: calculated for $C_{19}H_{18}O_3$, C 77.6, H 6.1; found, C 77.1, H 6.5.

SBC. ^{1}H n.m.r. ($CDCl_3$) δ (ppm) 1.9 (d, 3H of methyl), 6.0 (d, 1H of diene), 6.3 (m, 2H of diene), 7.25 (d, 2H of biphenyl), 7.45 (m, 1H of diene), 7.6 (d, 2H of biphenyl), 7.65 (d, 2H of biphenyl) and 7.7 (d, 2H of biphenyl). I.r. (KBr) (cm^{-1}): 2230 (ν_{CN}), 1715 (ν_{CO}), 1645, 1605 ($\nu_{C=C}$). Elemental analysis: calculated for $C_{19}H_{15}O_2N$, C 78.9, H 5.2, N 4.8; found, C 78.7, H 5.5, N 4.8.

Synthesis of S2B2S

First, 0.1 mol of 4,4′-dihydroxybiphenyl was reacted with 0.22 mol of ethylene carbonate in the presence of 0.01 mol of t-butylammonium bromide at 150–155°C for 8 h. After cooling to room temperature, the reaction mixture was poured into 1% aqueous sodium hydroxide (NaOH) solution with stirring. After filtration, the white solid was washed with water and acetone. The crude product was recrystallized from dioxane to give 4,4′-bis(2-hydroxyethyloxy)biphenyl.

4,4′-Bis(2-hydroxyethyloxy)biphenyl was reacted with sorbic acid in the presence of DCC in a similar manner as 0SBS0. S2B2S was purified by recrystallization from ethanol.

^{1}H n.m.r. ($CDCl_3$) δ (ppm): 1.9 (d, 6H of methyl), 4.2–4.6 (m, 8H of methylene), 5.8 (d, 2H of diene), 6.2 (m, 4H of diene), 6.95 (d, 4H of biphenyl), 7.2 (m, 2H of diene) and 7.5 (d, 4H of biphenyl). I.r. (KBr) (cm^{-1}): 1715 (ν_{CO}), 1645, 1605 ($\nu_{C=C}$). Elemental analysis: calculated for $C_{28}H_{30}O_6$, C 72.7, H 6.5; found, C 72.5, H 6.6.

Synthesis of SnBnS (n = 3,5,6)

A mixture of 4.6×10^{-2} mol of 4,4′-dihydroxybiphenyl, 0.18 mol of trimethylene chlorohydrin, 0.13 mol of NaOH and a small amount of potassium iodide in 200 ml of ethanol was refluxed for 30 h. After concentration to half the volume, the reaction mixture was poured into 1% aqueous NaOH solution. The white solid was washed with water and acetone. Recrystallization from dioxane yielded 4,4′-bis(3-hydroxypropyloxy)biphenyl. Sorbic acid was reacted with 4,4′-bis(3-hydroxypropyloxy)biphenyl in the presence of DCC in DMF. Recrystallization from ethanol yielded S3B3S. S5B5S and S6B6S were prepared in a similar manner as S3B3S.

S3B3S. ^{1}H n.m.r. ($CDCl_3$) δ (ppm): 1.9 (d, 6H of methyl), 2.1, 4.1, 4.4 (m, t, t, 12H of methylene), 5.8 (d, 2H of diene), 6.2 (m, 4H of diene), 7.0 (d, 4H of biphenyl), 7.2 (m, 2H of diene) and 7.4 (d, 4H of biphenyl). I.r. (KBr) (cm^{-1}): 1715 (ν_{CO}), 1645, 1605 ($\nu_{C=C}$). Elemental analysis: calculated for $C_{30}H_{34}O_6$, C 73.5, H 6.9; found, C 72.9, H 6.9.

S5B5S. ^{1}H n.m.r. ($CDCl_3$) δ (ppm): 1.9 (d, 6H of methyl), 1.7, 4.0, 4.2 (m, t, t, 20H of methylene), 5.8 (d, 2H of diene), 6.2 (m, 4H of diene), 6.95 (d, 4H of biphenyl), 7.2 (m, 2H of diene) and 7.5 (d, 4H of biphenyl). I.r. (KBr) (cm^{-1}): 1715 (ν_{CO}), 1645, 1605 ($\nu_{C=C}$). Elemental analysis: calculated for $C_{34}H_{42}O_6$, C 74.7, H 7.7; found, C 74.3, H 7.7.

S6B6S. ^{1}H n.m.r. ($CDCl_3$) δ (ppm): 1.9 (d, 6H of methyl), 1.6, 4.0, 4.1 (m, t, t, 24H of methylene), 5.8 (d, 2H of diene), 6.2 (m, 4H of diene), 6.95 (d, 4H of biphenyl), 7.2 (m, 2H of diene) and 7.5 (d, 4H of biphenyl). I.r. (KBr) (cm^{-1}): 1715 (ν_{CO}), 1645, 1605 ($\nu_{C=C}$). Elemental analysis: calculated for $C_{36}H_{46}O_6$, C 75.2, H 8.0; found, C 74.7, H 8.0.

Thermotropic properties

The thermal phase transition behaviour of biphenyl compounds was examined by means of differential scanning calorimetry (d.s.c.; Seiko I&G SSC-5020) and polarizing microscopic observation (Olympus BHSP polarizing microscope; Mettler FP80 and FP82 hot stage and controller).

Bulk thermal and photopolymerizations

The sample for bulk polymerization was prepared by loading 2 mg of a melt of each biphenyl compound into two quartz glass plates with ca. 15 μm gap and gradually cooling to the desired temperature. The sample thus prepared was placed in a thermostated block without or with photoirradiation with a 75 W high-pressure mercury lamp. After polymerization, the sample was removed from the quartz glass plates and was subjected to various measurements: i.r. (Jasco A-702) and gel permeation chromatography (g.p.c.; Jasco 880-PU, Shodex KF-80M + KF-80M column, tetrahydrofuran (THF) eluent).

The polymerization behaviour by heating or photoirradiation was directly followed on d.s.c. The sample films were cast by injecting a THF solution of monomeric biphenyl compound into aluminium d.s.c. pans. The d.s.c. cell was adapted with a quartz glass to allow u.v. light irradiation into the d.s.c. pan. The 75 W high-pressure mercury lamp was used to investigate the photopolymerization. The heat evolution was recorded as a function of time.

RESULTS AND DISCUSSION

Phase transition behaviour

D.s.c. thermograms of all biphenyl compounds were measured on heating at a rate of 2°C min^{-1}. The phase transition temperatures of these compounds are summarized in *Table 1*. Only the biphenyl compounds with diene groups attached through ester bonding without methylene spacers showed liquid-crystalline phases. SBH was found to be a monotropic liquid crystal that exhibited a liquid-crystalline phase only on cooling. Other biphenyl compounds, SBC, SBM, 0SBS0 and 2SBS2, showed an enantiotropic phase transition. On the basis of polarizing microscopic observation and X-ray powder pattern, the liquid-crystalline phases observed for the biphenyl compounds were assigned as a nematic phase.

The biphenyl compounds with diene groups attached through methylene spacers were synthesized to lower the phase transition temperature. Although the odd–even

Table 1 Phase transition temperatures of the biphenyl compounds[a]

Compounds	Transition temperature (°C) K	N	I
SBH		100	
	(78)		(82)
SBM	111		205
SBC	157		217
0SBS0	168	–	257
2SBS2	153	–	229
S3BC		126	
S6BC		79	
S2B2S		142	
S3B3S		127	
S5B5S		130	
S6B6S		119	

[a] K, crystalline phase; N, nematic phase; I, isotropic phase. The values in parentheses were obtained on cooling cycle

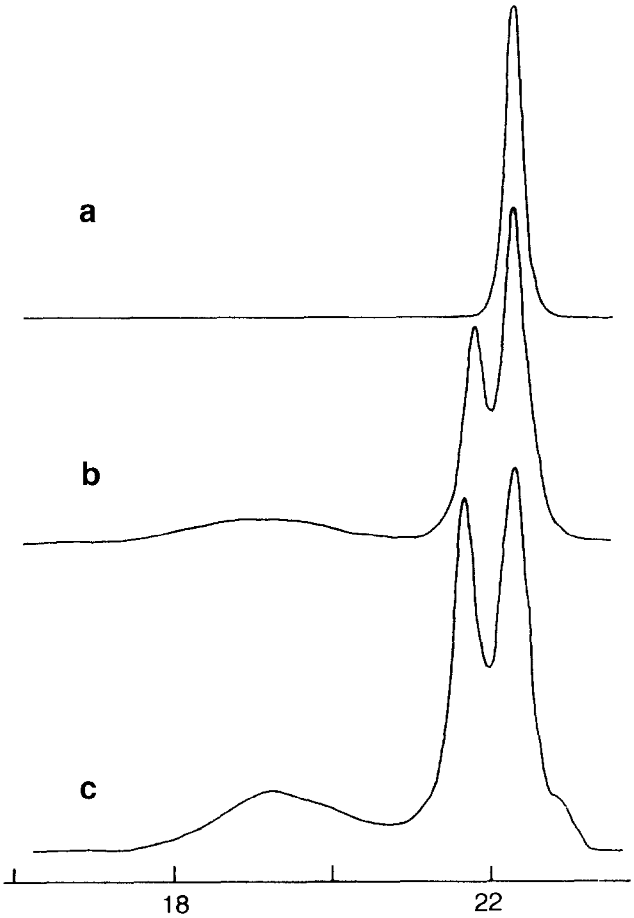

Figure 2 G.p.c. chromatograms of SBC (a) before and after heating at 200°C for (b) 30 min and (c) 60 min

effect of the methylene spacers on the melting points of S*n*B*n*S was recognized, no liquid-crystalline phase was observed. The result may be due to differences in the intermolecular forces between the ester bondings and ether bondings.

Bulk polymerization of SBC

Figure 2 shows g.p.c. chromatograms of SBC before and after heating at 200°C for 30 and 60 min. The molecular weight was calculated using a polystyrene calibration curve. Before heating, a sharp peak for monomeric SBC was observed at a retention time of 22.1 min. Although oligomers in the range < 20 min were observed after heating at 200°C for 60 min, the main product was dimer, which appeared at 21.7 min. To evaluate the efficiency of the bulk thermal polymerization, the conversion was defined as $P/(P+M)$, where P and M are the amounts of polymer including dimer and monomer determined by g.p.c. measurements, respectively. *Figure 3* shows the values of $P/(P+M)$ as a function of heating time. It is clearly seen that the conversion depends strongly on temperature. The bulk thermal polymerization rate increased with increasing temperature. The initial rate for the isotropic phase (230°C) was considerably higher than that for the nematic phase (170 and 200°C). On the other hand, there was little reaction for the crystalline phase (120°C). The results suggest that the bulk thermal polymerization of SBC is affected by the mobility of the mesogenic monomer.

Figure 4 shows g.p.c. chromatograms of SBC before and after photoirradiation for 30 and 60 min at 170°C. The g.p.c. chromatograms under photoirradiation exhibited very similar changes to that for the bulk thermal polymerization, except that both the amount of polymer and the average molecular weight increased. *Figure 5* shows the conversion, $P/(P+M)$, as a function of irradiation time. The initial polymerization rate increased with increasing temperature, and the conversion for the isotropic phase became a plateau after 20 min similarly to the bulk thermal polymerization. *Figures 3* and *5* show that the time courses of the conversions for photopolymerization at 120, 200 and 230°C are similar to those for thermal polymerization at the same temperatures. Only the conversion at 170°C is strongly enhanced by photoirradiation. The extremely low conversion for the crystalline phase (120°C) suggests that the polymerization of SBC is not topochemical, i.e. molecular rearrangement or mobility is required for polymerization of SBC. On the other hand, the thermal reactivity above 200°C was much higher than that below 170°C as can be seen in *Figure 3*. The high thermal reactivity is attributed

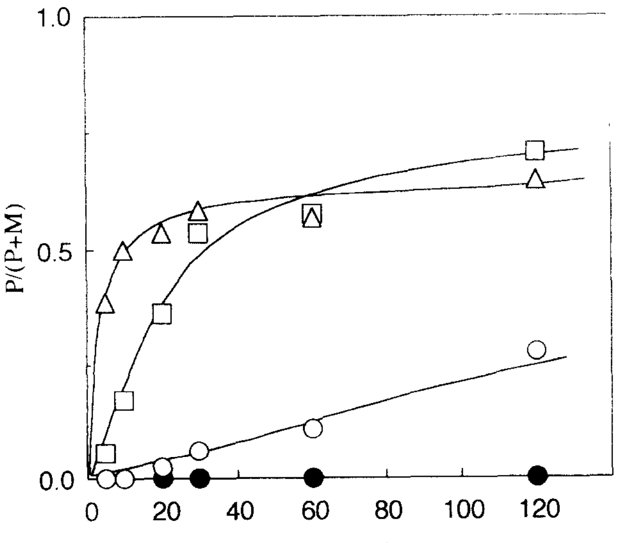

Figure 3 Time course of conversion $P/(P+M)$ for SBC by heating at various temperatures: (●) 120°C; (○) 170°C; (□) 200°C; (△) 230°C

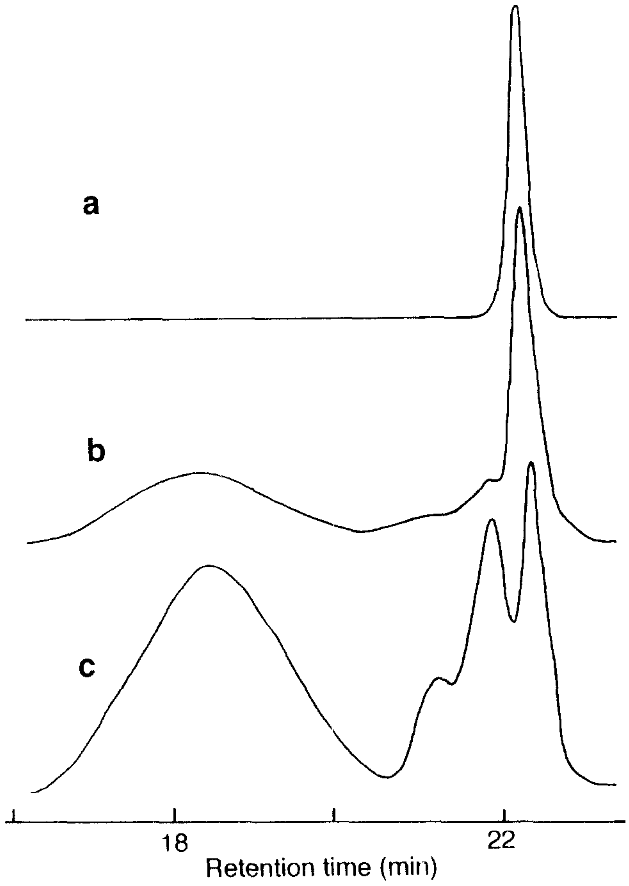

Figure 4 G.p.c. chromatograms of SBC (a) before and after photoirradiation at 170°C for (b) 30 min and (c) 60 min

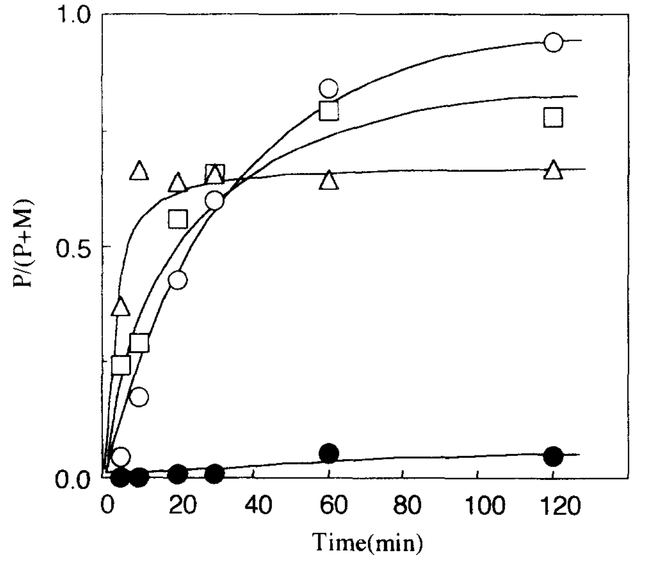

Figure 5 Time course of conversion $P/(P+M)$ for SBC by photoirradiation at various temperatures: (●) 120°C; (○) 170°C; (□) 200°C; (△) 230°C

to a small increase in conversion above 200°C by photoirradiation.

Figure 6 shows the weight-average molecular weight (M_w) of SBC without or with photoirradiation for 1 h at various temperatures. The photoirradiation is clearly found to increase the M_w of polymers in the temperature range from 170 to 200°C. In addition, the M_w of polymers decreased with temperature for the nematic phase and isotropic phase. The reaction above 200°C is governed by the thermal kinetic factor as described above. The main product for the isotropic phase was dimer whether SBC was irradiated or not. Therefore, the decrease of the M_w of polymers with temperature is explained as a result of the increase of the amount of dimer in the product. On the other hand, thermal reactivity at 170°C is lower than that above 200°C. The increases in conversion as well as the M_w of polymers by photoirradiation are closely related to the low thermal reactivity, the longitudinal molecular orientation and mobility at lower temperature in the range of the nematic phase.

In order to reveal the reaction mechanism, n.m.r. and i.r. spectra were measured. I.r. spectra for SBC with various irradiation times at 170°C are shown in *Figure 7a*. As polymerization proceeded the peak at 1645 cm^{-1} decreased and the new peak at 1750 cm^{-1} increased owing to disruption of the conjugation of the carbonyl group with the diene group. N.m.r. spectra showed the loss of the peaks at 6 and 6.3 ppm due to the diene group and a new broad peak around 5.7 ppm. The results suggest that the photopolymerization proceed through 1,4-addition[18,19]. On the other hand, heating at 230°C gives the dimer as the main product as described above. Although heating caused the loss of the peak due to the diene group in the n.m.r. spectra, no peak due to 1,4-addition was observed around 5.7 ppm. In addition, the peak at 1715 cm^{-1} due to the conjugated carbonyl group remained in the i.r. spectra, as can be seen in *Figure 7b*. It is assumed that the heating product is formed through not only 1,4-addition but also 1,2-addition (dimerization and polymerization).

Bulk polymerization of 0SBS0 and 2SBS2

The products obtained by photoirradiation on bifunctional compounds, 0SBS0 and 2SBS2, did not dissolve in any organic solvents. To investigate the photopolymerization of bifunctional compounds the d.s.c. thermograms were measured. *Figure 8* shows d.s.c. exotherms for the photopolymerization of 0SBS0 and 2SBS2 at various temperatures (170, 200 and 230°C). The polymerization

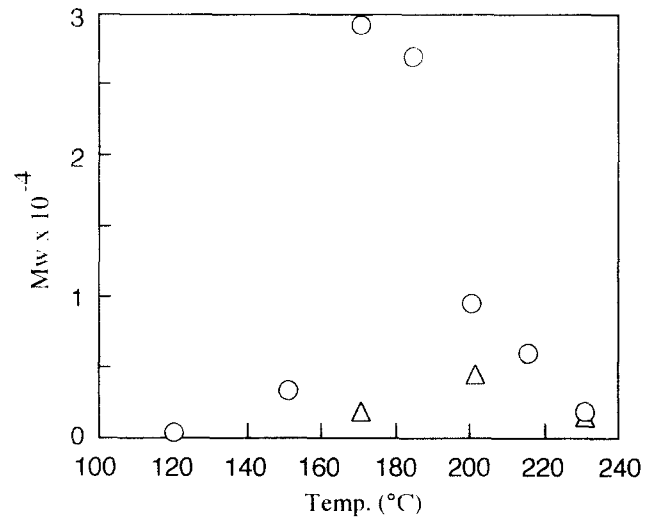

Figure 6 Weight-average molecular weight for SBC without (△) or with photoirradiation (○) for 1 h at various temperatures. The molecular weight was calculated using a polystyrene calibration curve

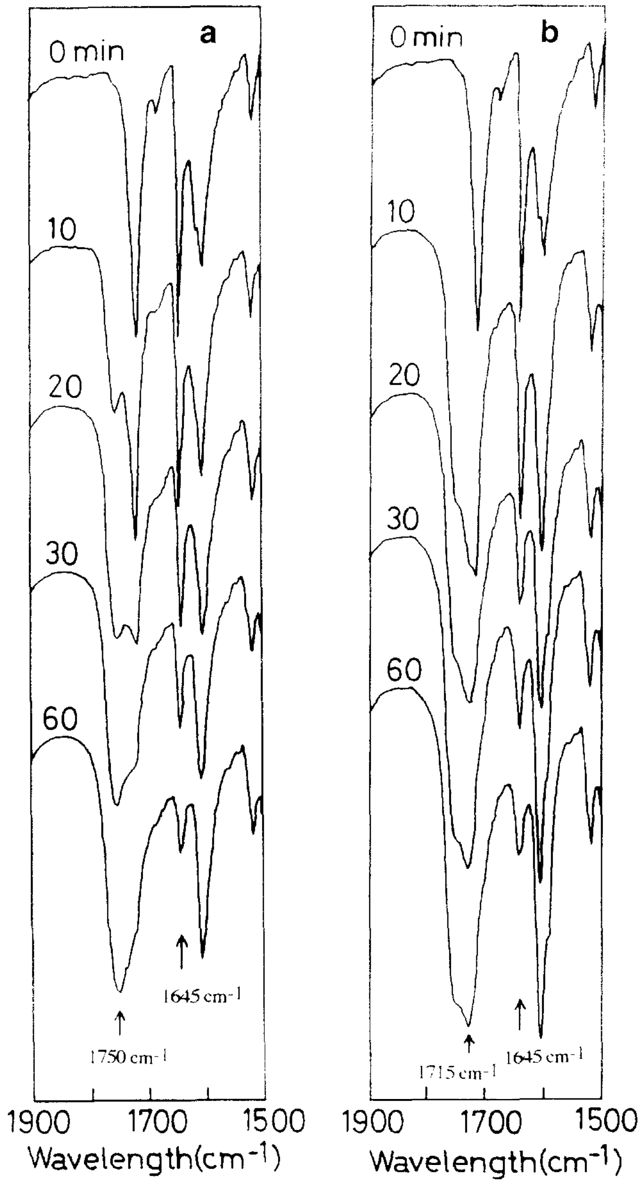

Figure 7 Changes of i.r. spectra of SBC at various time intervals (a) under photoirradiation at 170 C and (b) without photoirradiation at 200 C. The numerical values on the curves represent the time intervals (min)

rate increases with temperature. However, exotherms at higher temperatures do not unequivocally indicate whether polymerization or dimerization takes place. The polymerization rate of 2SBS2 is lower than that of 0SBS0. The molecular orientation of 0SBS0 and 2SBS2 was estimated by measuring the polarized absorption spectra of 4-dimethylamino-4′-nitroazobenzene doped in 0SBS0 or 2SBS2 at a concentration of 1 wt%. For a uniaxially symmetrical system, the dichroic ratio of the polarized absorption spectra is related to the order parameter as a measure of the molecular orientation. The result indicates that the molecular orientation of 0SBS0 is higher than that of 2SBS2. The difference in the polymerization rate may result from the orientational factor owing to a difference in the bulkiness of side chains.

It is worthwhile here to describe the effect of polymerization on the morphology of polymers. The transmitted intensity through the samples, which were prepared by placing a melt of biphenyl compounds into two quartz glass plates, between two crossed polarizers was measured. The sample was irradiated in the nematic phase. *Figure 9* shows the transmitted intensity as a function of temperature before and after photoirradiation on SBC, 0SBS0 or 2SBS2. It is clearly seen that the changes in the transmittance before photoirradiation correspond to the thermal phase transition. After photoirradiation, the transmittance was observed both for 0SBS0 and 2SBS2, while no transmittance was observed for SBC. The transmittance through 0SBS0 decreased abruptly above 330 C, while the gradual decrease in the transmittance was observed for 2SBS2 over the lower temperature range. In this photoirradiation experiment, 2SBS2 was irradiated for 4h, because of its lower polymerization rate compared to that for 0SBS0. The

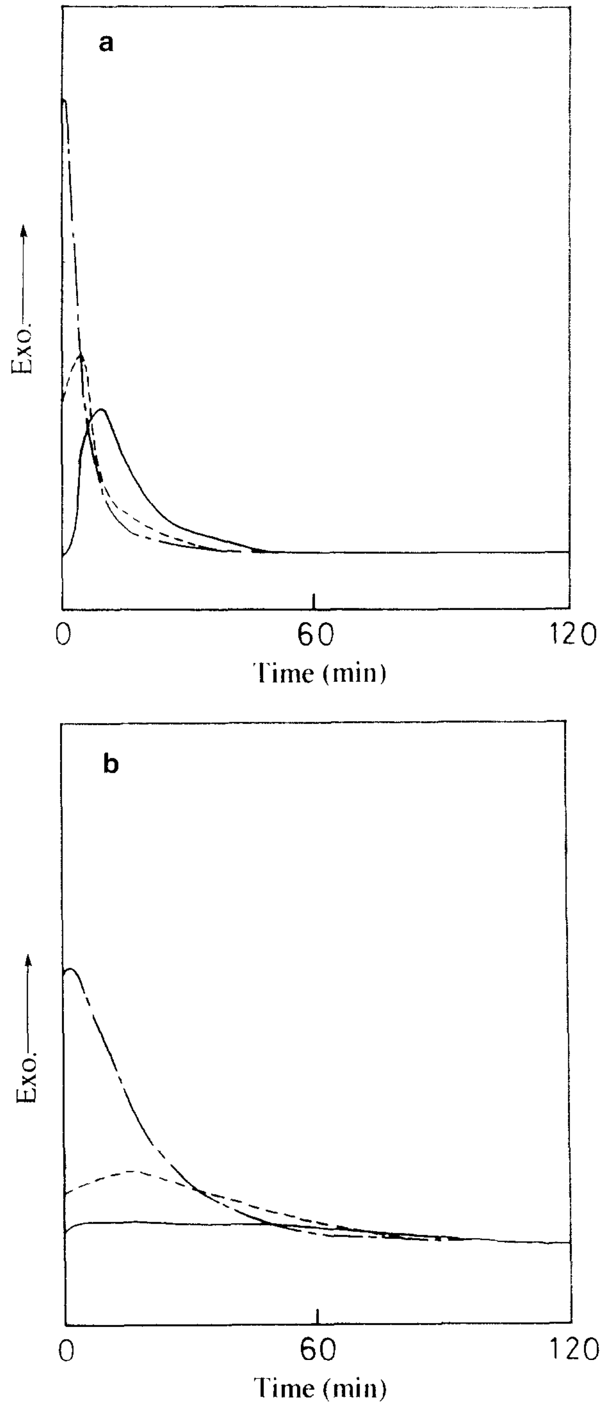

Figure 8 Bulk photopolymerization exotherms for (a) 0SBS0 and (b) 2SBS2: (   ) 170 C: (------) 200 C: (- -) 230 C

polymerization and crosslinking reaction of diene groups at both sides of biphenyl resulted in the formation of a polymer gel network having anisotropic molecular orientation at the beginning of the photoirradiation. The higher molecular orientation for 0SBS0 may be explained as a result of higher molecular orientation in the initial monomeric state and higher polymerization rate of 0SBS0. It is assumed that, in addition, side reactions such as decomposition cause the lower molecular orientation for 2SBS2. The prolonged photoirradiation actually decreased the molecular orientation even for 0SBS0. On the other hand, the polymerization of diene groups at one side of biphenyl is considered to disturb the molecular orientation owing to the strong coupling between the main chain formed and biphenyl side group[20,21].

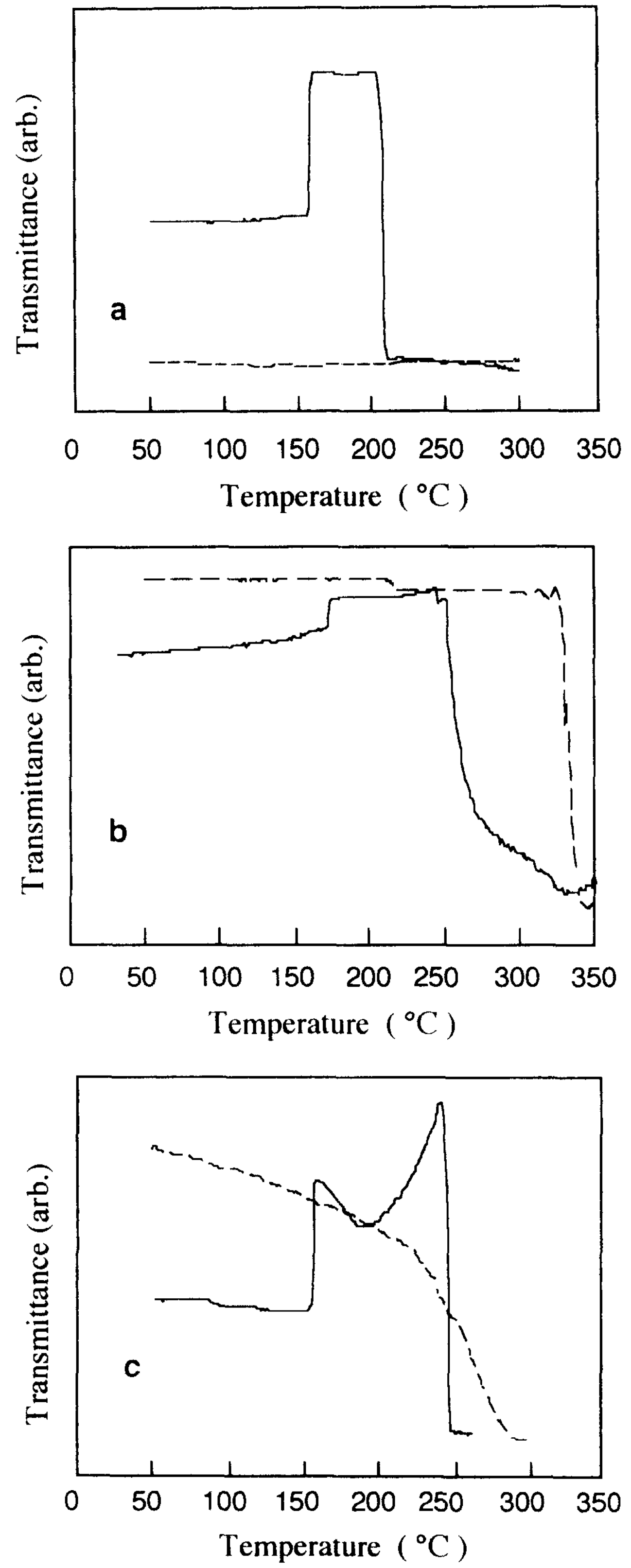

Figure 9 Changes in transmittance of (a) SBC, (b) 0SBS0 and (c) 2SBS2 through crossed polarizers before (——) and after photoirradiation (------). Irradiation was performed in the nematic phase for 2 h for SBC, 4 h for 0SBS0 and 1 h for 2SBS2

CONCLUSION

The biphenyl compounds with diene moieties at one end or both ends attached through ester bonding show the nematic phase. The conversion of bulk polymerization and the M_w of the resulting product depend strongly on the initial morphology of the system. Considerable increase in the conversion was achieved for the nematic phase by photoirradiation, while the conversion was very low without photoirradiation. The initial polymerization rate increased with temperature in the nematic and isotropic phases. However, the average molecular weight decreased with temperature in the nematic and isotropic phases. It has been demonstrated that the polymerization behaviour of the liquid-crystalline monomers was dependent on the longitudinal molecular orientation and mobility of the system.

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