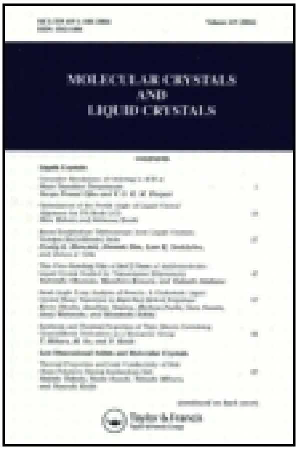

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis and thermal properties of new chalcone-based side-chain polymers

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To cite this article: T. Mihara, M. Tsutsumi & N. Koide (2002): Synthesis and thermal properties of new chalcone-based side-chain polymers, Molecular Crystals and Liquid Crystals, 382:1, 53-64

To link to this article: http://dx.doi.org/10.1080/713738754

Mol. Cryst. Liq. Cryst., Vol. 382, pp. 53–64
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1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290120288

SYNTHESIS AND THERMAL PROPERTIES OF NEW CHALCONE-BASED SIDE-CHAIN POLYMERS

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We synthesized two types of photocrosslinkable side-chain liquid crystalline polymers (SLCPs) with a chalcone derivative in the side chain. One is a polymer having the chalconyl moiety directly connected to the benzoate component, the other is a polymer with a spacer group introduced between the cyanobiphenyl and the chalconyl moiety. The thermal properties of these polymers were investigated by polarizing optical microscopy measurements and differential scanning calorimetry measurements. Mesophase structures of these polymers were examined by X-ray measurements. A smectic phase was exhibited for the polymers.

Keywords: chalcone; photodimerization; side-chain liquid crystalline polymer; smectic phase

INTRODUCTION

Liquid crystalline polymers (LCPs) have an anisotropic structure generated by self-organizing mesogenic groups. In some cases, the orientation of mesogenic groups in the LCPs can be locked-in by the photoreaction and/or crosslinking agent. Such anisotropic LCP networks have the possibility of application for electro-optic materials [1,2]. Several methods have been known to obtain anisotropic LCP networks. The in situ photopolymerization of the oriented LC monomers provided the highly oriented LCP networks. Various types of monomers such as bifunctional acrylates [3–5], epoxides [6,7], vinylethers [8,9], and so on [10] were used for the preparation of the highly oriented LCP networks.

Anisotropic LCP networks are also obtained by photocrosslinking of LCPs with photosensitive groups [11]. Lightly crosslinked LCPs have

Received 4 December 2001; accepted 9 April 2002.

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elastomeric properties and can be easily stretched to obtain oriented systems.

The cinnamoyl group is a very famous photosensitive group. Photodimerization of the cinnamoyl groups have already been studied in detail. Therefore many researchers have synthesized SLCPs with cinnamoyl groups in the side chain and investigated their photochemical properties [12–18].

The chalconyl group is known to be a good photosensitive group [19,20]. The photoreaction of chalconyl groups takes place by irradiation with relatively longer wavelength UV light than that of the cinnamoyl group. Photosensitive polymers containing chalcone derivatives have been studied for photoalignment film [21–24].

Makita et al. synthesized poly(4-methacryloyloxy chalcone) (PM4Ch) or poly(4′-methacryloyloxy chalcone) (PMCh) and investigated the photoreaction of their polymers. The authors also reported that PM4Ch and PMCh would be employed as a photoalignment film. Seo et al. reported copolymers composed of a cholesteryl monomer and a chalcone monomer [25]. However, all the chalcone based polymers did not display mesomorphic properties. SLCPs with chalcone groups are little reported.

The purpose of this study is to synthesize new chalcone-based SLCPs that are capable of photocrosslinking under relatively longer-wavelength UV light irradiation to avoid the degradation of polymer film. We have synthesized two types of side-chain polymers with a chalconyl moiety attached to a mesogenic group. One is a polymer having the chalconyl moiety directly connected to the benzoate component, the other is a polymer with a spacer group introduced between the cyanobiphenyl and the chalconyl moiety. The synthetic procedure and thermal properties of the polymers are described in detail.

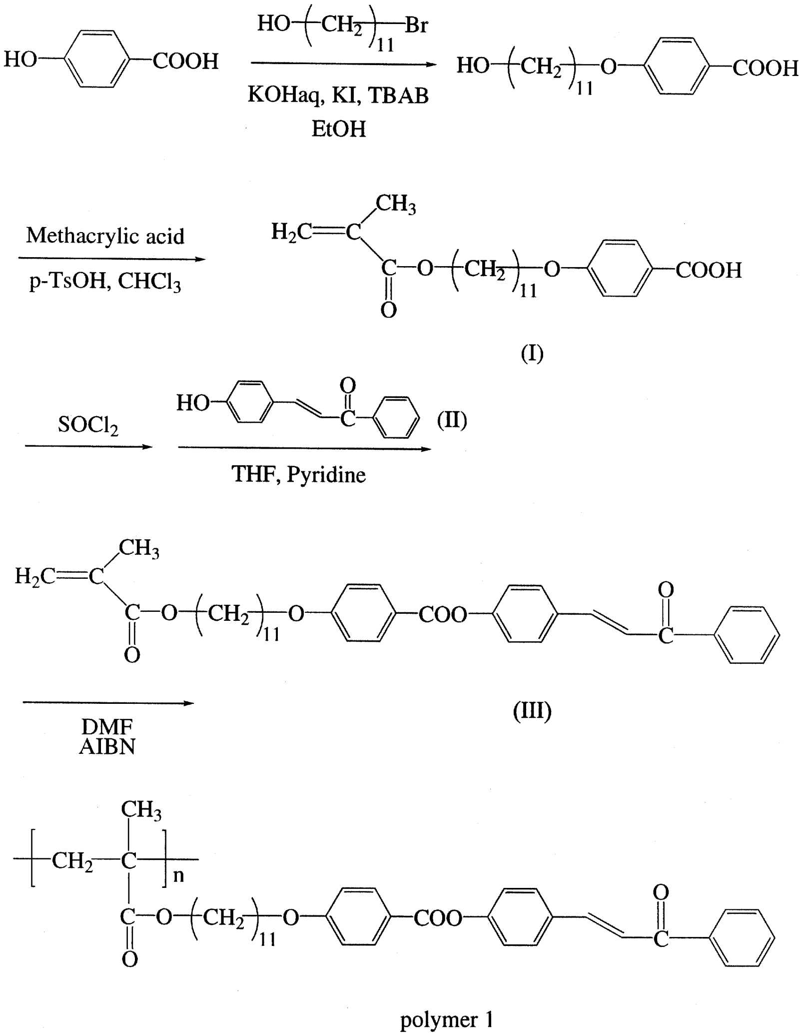
EXPERIMENTAL

Materials

Polymers 1 and 2 were prepared according to Schemes 1 and 2, respectively. The intermediates (I) and (II) for preparing polymer 1 were synthesized according to the literature [26]. The intermediate (I) exhibited an enantiotropic phase transition with a nematic phase between 106°C and 117°C on the heating run and between 99°C and 78°C on the cooling run. The melting point of the intermediate (II) was 185°C.

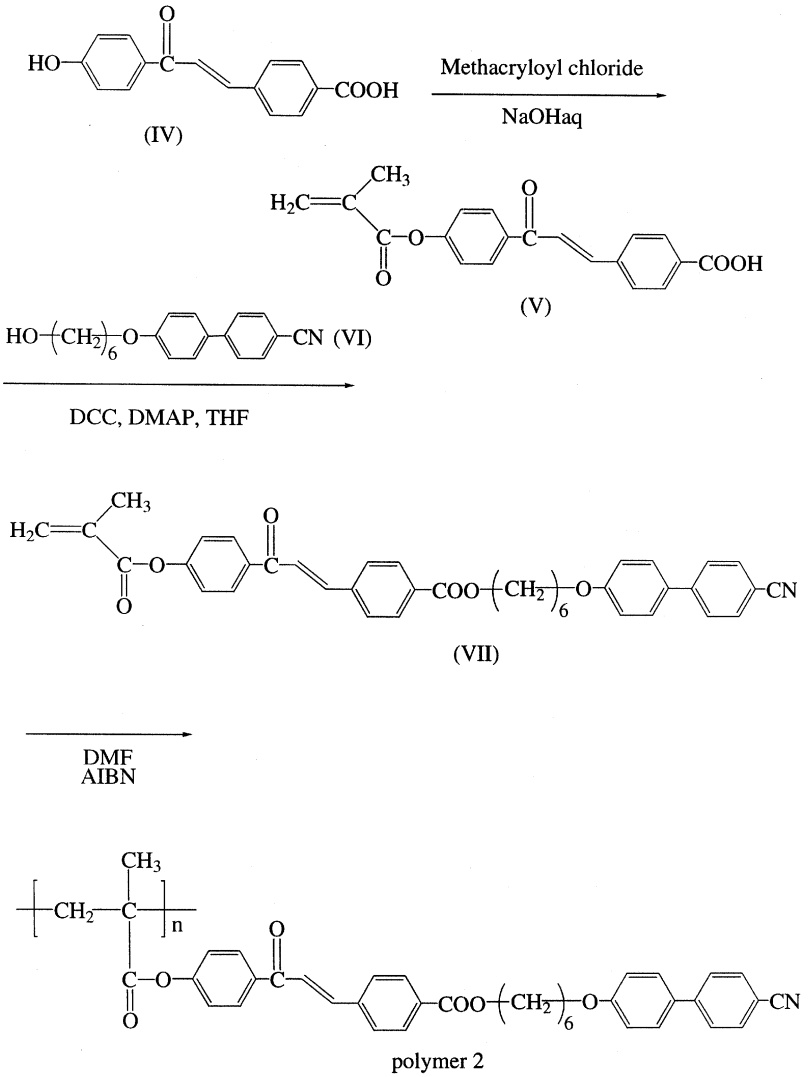
4′-(11-methacryloyloxyundecanoxy) benzene-4-chalcone carboxylate (III)

Thionyl chloride (10 ml) and a small amount of dimethylformamide were added to the intermediate (I) (3.1 g, 0.0082 mol). Then the reaction



SCHEME 1 Synthesis of polymer 1.

mixture was stirred for 4 h at room temperature. An excess of thionyl chloride was evaporated under reduced pressure, and then the residue was dissolved in tetrahydrofuran (THF) (30 ml). This THF solution was added dropwise to the THF solution of 4-hydroxychalcone (II) (2.2 g, 0.0099 mol) and pyridine (1.6 g, 0.0205 mol). The reaction mixture was stirred for 12 h at room temperature. THF was evaporated and the residue was poured into the HCl aqueous solution. The product was extracted with diethyl ether,



SCHEME 2 Synthesis of polymer 2.

and the diethyl ether solution was dried over magnesium sulfate. The diethyl ether was evaporated to dryness. The product was purified by recrystallization from a mixed solvent (THF : methanol = 1 : 2). The product was obtained in a 48.9% yield (2.1 g).

IR (nujol) $\nu\,\mathrm{cm}^{-1}$: 1716 (C=O, ester), 1657(C=O, ketone), 1637(C=C, methacryloyl group), 1604 and 1512 (aromatic group).

^{1}H-NMR ($CDCl_3$) δ ppm: 1.3–1.8(m, 18H, CH_2), 2.0(s, 3*H*, CH_3), 4.0(t, 2H, OCH_2, 4.2(t, 2H, $COOCH_2$), 5.6(s, 1H, CH_2=), 6.1(s, 1H, CH_2=), 6.9(d, 2H, Ar-H), 7.3–7.8(m, 9H, chalconyl group), 8.2(m, 4H, Ar-H and chalconyl group).

4-carboxy-4′-hydroxy chalcone (IV)

Terephthalaldehydic acid (18.0 g, 0.12 mol) and 4′-hydroxyacetophenone (19.6 g, 0.144 mol) were dissolved in the mixture solution of ethanol (80 ml) with 10% of NaOHaq (180 ml). The reaction mixture was heated at 80°C for 7 h. The mixture was left at room temperature overnight. An HCl aqueous solution was added to the mixture, and then a yellow precipitate was obtained. The precipitate was washed with water until a neutral aqueous solution was obtained. The obtained yellow solid was purified by recrystallization from acetone. Then, the solid was washed with methanol and dried under vacuum at 60°C. The product was obtained in a 44% yield (14.2 g).

IR (nujol) ν cm^{-1}: 2669 and 2549 (OH, carboxylic acid), 1685 (C=O, carboxylic acid), 1662 (C=O, ketone), 1647 (C=C, chalconyl group), 1608 and 1512 (aromatic group).

4-carboxy-4′-(methacryloyloxy) chalcone (V)

4-carboxy-4′-hydroxy chalcone (IV) (11 g, 0.041 mol) was dissolved in a sodium hydroxide aqueous solution (4.1 g, 0.103 mol/250 ml). Methacryloyl chloride (8.6 g, 0.082 mol) was added dropwise to the aqueous solution of 4-carboxy-4′-hydroxy chalcone. The reaction mixture was stirred for 6 h. The precipitated white solid was washed with water until a neutral aqueous solution was obtained. The obtained white solid was stirred in methanol, and then filtered. This procedure was repeated 2 times. This product was used without further purification and was obtained in a 52% yield (7.2 g).

IR (nujol) ν cm^{-1}: 2678 and 2565 (OH, carboxylic acid), 1741 (C=O, ester), 1674 (C=O, ketone), 1637 (C=C, methacryloyl group), 1610 and 1506 (aromatic group).

4-cyano-4′-(6-hydroxyhexyloxy) biphenyl (VI)

4-cyano-4′-hydroxybiphenyl (3.1 g, 0.0159 mol) was dissolved in ethylmethylketone (200 ml). 6-chloro-1-hexanol (7.0 g, 0.051 mol), potassium carbonate (8.5 g, 0.0615 mol), and a small amount of potassium iodide were added to the ethylmethylketone solution. The reaction mixture was refluxed for 36 h. After filtration, the filtrate was evaporated to dryness under reduced pressure. The residue was extracted with chloroform. The chloroform solution was dried over magnesium sulfate and was then evaporated to dryness under reduced pressure. The crude product was stirred in hexane to remove an excess of 6-chloro-1-hexanol. The product was obtained in an 83% yield (3.9 g).

^{1}H-NMR ($CDC1_3$) δ ppm: 1.4–1.8(m, 8H, CH_2), 3.7(t, 2H, OCH_2), 4.0(t, 2H, OCH_2), 7.0–7.7(m, 8H, Ar-H).

4-cyanobiphenyl-4′-hexyloxy-(4′-methacryloyloxychalcone)carboxylate (VII)

The intermediate (V) (3.0 g, 0.0089 mol) and (VI) (3.2 g, 0.010 mol)) were dissolved in dry THF. N,N'-dicyclohexylcarbodiimide (2.4 g, 0.012 mol) and 4-dimethylaminopyridine (0.15 g, 0.0012 mol) were added to the THF solution. After the reaction mixture was stirred for 23 h at room temperature, the filtrate was evaporated to dryness under reduced pressure and the residue was purified by column chromatography (eluent chloroform). The product was obtained in a 30% yield (1.0 g).

IR (nujol) ν cm^{-1}: 2225(CN), 1735 (C=O, ester), 1712 (C=O, ester), 1664 (C=O, ketone), 1637 (C=C, methacryloyl group), 1604 and 1495 (aromatic group).

^{1}H-NMR ($CDC1_3$)δ ppm: 1.5–2.0(m, 8H, CH_2), 2.1(s, 3H, CH_3), 4.0(t, 2H, OCH_2), 4.4(t, 2H, $COOCH_2$), 5.7(s, 1H, CH_2=), 6.4(s, 1H, CH_2=), 6.9(d, 2H, Ar-H), 7.3–7.8(m, 12H, chalconyl group and Ar-H), 8.2(m, 4H, chalconyl group)

Polymerization

The polymers were prepared by radical polymerization in sealed ampoules with 1.0 mol% of α,α'-azobisisobutyronitrile in anhydrous N,N'-dimethylformamide at 60°C for 48 ~ 55 h. The polymers were obtained by reprecipitation with methanol and were dissolved in THF and reprecipitated with methanol 3 times. They were dried at 40°C under vacuum.

Characterization

^{1}H-NMR was carried out with a JEOL JNM-LA 400 spectrometer using $CDCl_3$ as the solvent. Infrared spectra were recorded on a JEOL JIR 7000 spectrometer. Spectra were collected at 4 cm^{-1} resolution. DSC measurements were conducted with a Mettler DSC821^e. Optical microscopy was performed on a Nikon polarizing optical microscope, OPTIPHOTO-POL, equipped with a Mettler FP80 controller and a FP82 hot stage. Phase transition temperatures were determined by DSC and optical microscopic measurements. Phase structures of polymers were assigned by X-ray diffraction measurements.

Gel permeation chromatography (GPC) was carried out with a Tosoh HLC-8020 instrument using chloroform as the eluent, equipped with 4 columns (TSK gel G4000H_{HR}, G3000H_{HR}, G2000H_{HR}, and G2000H_{HR}). The instrument was calibrated with a polystyrene standard. X-ray diffraction patterns were recorded with a RIGAKU RINT2500 series with Ni-filtered

CuKα radiation. The sample in quartz capillary(diameter 1 mm) was held in a temperature-controlled cell (RIGAKU LC high-temperature controller).

RESULTS AND DISCUSSION

Polymer Synthesis

We synthesized two types of polymers containing chalconyl moieties. One (polymer 1) is a polymer having the chalconyl moiety directly connected to the benzoate component, and the other (polymer 2) is a polymer with a spacer group introduced between the cyanobiphenyl and the chalconyl moiety.

Polymer 1 was obtained in a 61% yield. The number-average molecular weight of polymer 1 was 27,300 and its dispersion was 3.7. Polymer 2 was obtained in an 84% yield. The number-average molecular weight of polymer 2 was 3300 and the dispersion was 1.2. The molecular weight of polymer 2 was very small even if polymerization was carried out by the same method as the polymer 1. A steric hindrance of the phenyl group and methacryl group for polymer 2 would be larger compared to that of polymer 1 which had a flexible spacer between the methacryl group and phenyl group. The steric hindrance between the phenyl group and methacryl group would lead to the small molecular weight of polymer 2.

Thermal Properties of Monomers and Polymers

The thermal properties of these monomers were summarized in Table 1. Monomer III showed two mesophases on the cooling run. Monomer VII did not exhibit any mesophases.

The thermal properties of the polymers were summarized in Table 2. Polymer 1 had chalcone derivatives as a mesogenic group, as shown in Scheme 1, while polymer 2 had a mesogenic group connected with a chalcone derivative via the flexible spacer in the side chain, as shown in

TABLE 1 Thermal Properties of Monomers

Monomers	Phase Transition Temperatures/°C
Monomer III	$\mathrm{Cr}\ \overset{\xrightarrow{\hspace{5em}76\hspace{5em}}}{\underset{54}{\longleftarrow}\ \mathrm{M}\ \underset{71}{\longleftarrow}\ \mathrm{N}\ \underset{75}{\longleftarrow}}\ \mathrm{I}$
Monomer VII	$\mathrm{Cr}\ \underset{96}{\overset{133}{\rightleftarrows}}\ \mathrm{I}$

Cr, crystal; N, nematic phase; M, mesophase; I, isotropic melt.

TABLE 2 Thermal Properties of Side-chain Polymers Containing Chalcone Derivative

Polymers	Phase Transition Temperatures/°C
Polymer 1	$\mathrm{g} \underset{31}{\overset{34}{\rightleftarrows}} \mathrm{SmA_1} \underset{188}{\overset{196}{\rightleftarrows}} \mathrm{I}$
Polymer 2	$\mathrm{g} \underset{78}{\overset{87}{\rightleftarrows}} \mathrm{SmA_1} \underset{162}{\overset{165}{\rightleftarrows}} \mathrm{I}$

g, glassy; $\mathrm{SmA_1}$, smectic $\mathrm{A_1}$ phase; I, isotropic melt.

Scheme 2. The typical optical texture was not observed for either type of polymer by polarized optical microscopy measurements; however, a birefringence was shown for these polymers. DSC curves of polymer 1 are shown in Figure 1. A shift of the baseline and a peak were observed on both heating and cooling scans. The shift of the baseline was attributed to glass transition, while the peak was assigned to the transition from the mesophase to the isotropic melt.

This assignment of the phase transition temperature of polymer 1 was supported by optical microscopic observation. A birefringence of polymer 1 was observed below the transition temperature from the mesophase to the isotropic melt, while no birefringence of polymer 1 was detected by optical microscopic observation above this temperature. Therefore the phase structure of polymer 1 above 196°C was the isotropic melt.

X-ray patterns of polymer 1 are shown in Figure 2. Two sharp peaks in the small-angle region and a broad peak in the wide-angle region were observed in the X-ray pattern of polymer 1 at 80°C. We obtained 40 Å of d-spacing due to the first sharp peak in the small-angle region for polymer 1. The calculated length for the side chain with an extended conformation of polymer 1 was 37 Å. We concluded that polymer 1 exhibited a smectic $\mathrm{A_1}$ phase in the temperature range between the glass transition and the clearing temperature detected by DSC measurement of polymer 1. Above the clearing temperature (196°C) detected by DSC measurements of polymer 1, sharp peaks in the small angle region of X-ray pattern for polymer 1 disappeared and a broad peak was observed in the small- and wide angle regions, respectively. This result indicates that the layer structure attributed to the smectic phase disappeared above the clearing temperature. Therefore we determined that the phase structure of polymer 1 above 196°C was the isotropic melt based on the optical microscopic, DSC, and X-ray measurements.

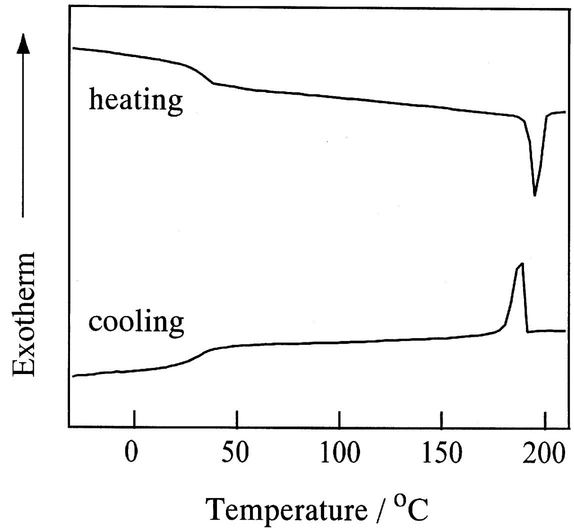


FIGURE 1 DSC curves of polymer 1.

X-ray pattern of polymer 1 below glass transition temperature was also shown in Figure 2. A similar X-ray pattern to that of the smectic phase was observed for polymer 1 below glass transition temperature. We obtained

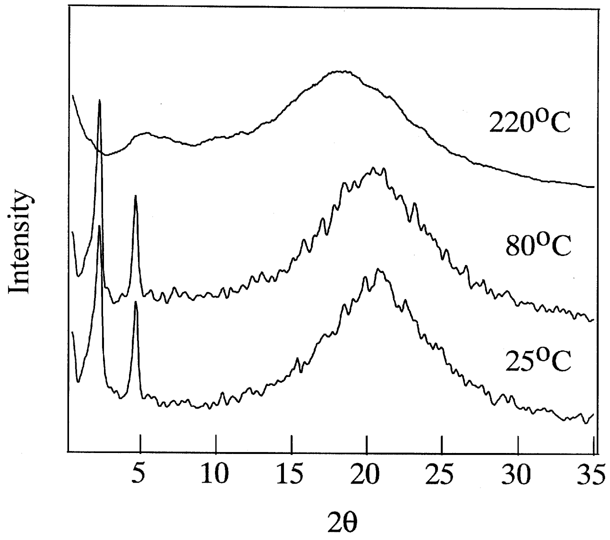


FIGURE 2 X-ray patterns of polymer 1.

39 Å of d-spacing due to the first sharp peak in the small-angle region for polymer 1. Therefore the smectic A_1 phase structure of polymer 1 was preserved below glass transition temperature.

Similar DSC curves to that of polymer 1 were detected by DSC measurements of polymer 2. A birefringence of polymer 2 was observed by optical microscopic observation below the clearing temperature (165°C), while the birefringence of polymer 2 disappeared above the clearing temperature.

A peak in the small-angle region and a broad peak in the wide-angle region were also observed for polymer 2, as shown in Figure 3. The d-spacing was 28 Å based on the peak in the small-angle region of X-ray pattern for polymer 2 at 130°C, and then the calculated length of the side chain with all *trans* conformations was 25 Å for polymer 2. Therefore, we considered that tha mesophase structure for polymer 2 was also a smectic A_1 phase. On the other hand, the d-spacing for polymer 2 was 29 Å based on the peak in the small-angle region at room temperature. The phase structure was preserved below glass transition temperature. The peak in the small-angle region of polymer 2 was weak and broad compared to that of polymer 1. This result indicated that the smectic layer of polymer 2 would be formed more loosely than that of polymer 1. Above the clearing temperature (190°C), a broad peak in the wide-angle region was observed in the X-ray pattern of polymer 2. We concluded that the phase structure

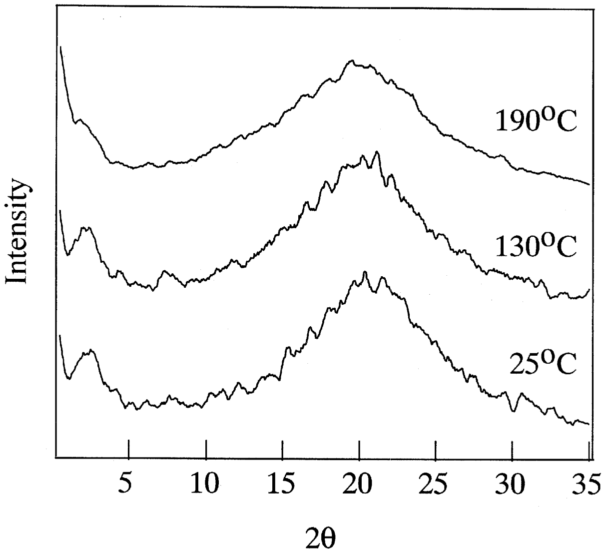


FIGURE 3 X-ray patterns of polymer 2.

above the clearing temperature was the isotropic melt based on the X-ray and microscopic observations.

Chudgar et al. reported that 4-n-alkoxy-4′-hydroxy chalcones did not exhibit any mesophases; however 4-n-alkoxy-4′-(4″-n-alkoxybenzoyl)-chalcones showed a nematic phase [27]. The chemical structure of these chalcone derivatives is similar to that of our mesogenic group in polymer 1. Many researchers reported synthesis and properties of polymers with the chalconyl group in the side chain [21–25]. However no mesophase was exhibited for these polymers. These results indicate that the chalconyl group can not be regarded as a mesogenic group. Only a melting point (solid-isotropic phase transition) was detected by the optical microscopic observation and DSC measurements of the polymer obtained by radical polymerization of the compound (I) in Scheme 1. No mesophase was exhibited for the polymer. Therefore the benzoate moiety in our chalconyl derivative of polymer 1 plays an important role for the exhibition of the mesophase for the polymer.

Polymer 2 had a mesogenic group connected with a chalcone derivative via the flexible spacer in the side chain, as shown in Scheme 2. Polymer 2 exhibited a smectic phase. A smectic phase was exhibited in the temperature range between 55 and 100°C for the methacrylate polymer with the cyanobiphenyl group via the six methylene spacer in the side chain [28]. Polymer 2 also exhibited a smectic phase in the temperature range between 87 and 165°C. Phase transition temperatures of polymer 2 were higher than those of the polymer with the cyanobiphenyl group in the side chain. The cyanobiphenyl group would act as a mesogenic group because the polymer with the chalconyl group did not show any mesophases [21–25]. The chalconyl moiety in the side chain of polymer 2 would enhance the rigidity of the side chain. Therefore we concluded that the chalcone moiety in the side chain of polymer 2 would not hinder the appearance of the smectic phase.

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