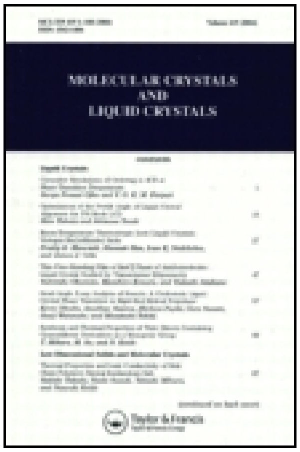

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Thermal Properties and FT-IR Investigation of Side Chain Type Liquid Crystalline Copolymers

Takashi Mihara [a] , Kazunari Mori [a] & Naoyuki Koide [a]
[a] Department of Chemistry, Faculty of Science, Science University of Tokyo, 1-3 Kagurazaka, Shinjuku-ku, Tokyo, 162, Japan

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Thermal Properties and FT-IR Investigation of Side Chain Type Liquid Crystalline Copolymers

TAKASHI MIHARA, KAZUNARI MORI, and NAOYUKI KOIDE*
Department of Chemistry, Faculty of Science, Science University of Tokyo,
1-3 Kagurazaka, Shinjuku-ku, Tokyo 162, Japan

In order to investigate the effect of hydrogen bonding formed between carboxylic acid groups on thermal properties of the side chain type liquid crystalline polymers, we synthesized the side chain type copolymers composed of a mesogenic monomer and a non-mesogenic monomer with carboxylic acid group. Hydrogen bonding was examined by thermally controlled FT-IR measurements. A mesophase was exhibited for the copolymers containing the mesogenic monomer above 40~65 mol%. The mesomorphic temperature range(MR) of the copolymers increased in the order of the copolymer with methacrylic acid monomer, with benzoic acid monomer containing a flexible spacer and with benzoic acid monomer. This difference in the MR of the copolymers was demonstrated by FT-IR quantitative analysis of the area of the peak assigned to the dimer structure of the carboxylic acid group.

Keywords: side chain type liquid crystalline copolymer, hydrogen bonding, thermally controlled FT-IR, carboxylic acid dimer

INTRODUCTION

Thermal properties of side chain type liquid crystalline polymer(SLCP)s depended upon the chemical structures of mesogenic groups, flexible spacers and polymer backbones. Mesogenic groups which have the chemical structure like low molar mass liquid crystals were attached via a flexible spacer or directly into the side chain of SLCPs. As a flexible spacer, alkyl chain, oligoethyleneoxide, oligosiloxane, etc. were used for SLCPs. It is well-known that these flexible spacers would decouple the mesogenic group from the polymer backbone of SLCPs. A smectic phase tends to be exhibited with

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* To whom correspondence should be addressed

increasing flexible spacer length of SLCPs. Polyacrylate, polymethacrylate, polysiloxane, etc., which have a relative flexible chemical structure were employed as a polymer backbone of SLCPs. Moreover thermal properties of SLCPs were influenced by intermolecular interaction like hydrogen bonding. We already reported that hydrogen bonding among urethane moieties in the polymer backbones of side chain type polyurethane plays an important role to exhibit mesomorphic properties.[1] The hydrogen bonding between the urethane bonds among the polymer backbones would act like a crosslinking agent.

Further we paid attention to the hydrogen bonding formed among side chains compared with that among polymer backbones. In the case of low molecular liquid crystals, it is well-known that the carboxylic acid dimer structure of alkoxy benzoic acid compounds was formed through the hydrogen bonding of carboxylic acid groups.[2,3,4] Mesomorphic properties of alkoxy benzoic acid compounds were exhibited when the dimer structure of carboxylic acid groups was formed through the hydrogen bonding. We think that the hydrogen bonding formed among carboxylic acid groups would act like a crosslinking agent for the side chain type polymers when the carboxylic acid groups were introduced into the polymer side chain. Therefore we were interested in what kinds of carboxylic acid dimer affected deeply the thermal properties of the SLCPs. In order to examine the influence of the hydrogen bonding of carboxylic acid groups on thermal properties of side chain type copolymers, we tried to synthesize copolymers containing different carboxylic acid monomers.

Recently Shibaev et al. reported that the *intramolecular* hydrogen bonding was formed between hydroxy group in acrylic acid moiety and carbonyl group in a mesogenic moiety or between acrylic acid groups for the acrylate SLCPs composed of a mesogenic monomer and acrylic acid monomer.[5] A smectic phase was induced for the side chain type copolymers containing 40~50 mol% of the acrylic acid monomers.

In this report, we investigated thermal properties of methacrylate side chain type copolymers composed of a mesogenic monomer and a non-mesogenic monomer containing carboxylic acid group by using of polarizing optical microscopy, differential scanning calorimetry(DSC) and X-ray diffraction spectroscopy measurements. Further in order to clarify what kinds of hydrogen bonding is formed, inter- or intramolecular hydrogen bonding, various kinds of carboxylic acid groups was attached to the polymer backbone as one component of the side chain type copolymers and hydrogen bonding formed among the carboxylic acid groups was examined by thermally controlled FT-IR measurements.

RESULTS AND DISCUSSION

The chemical structures of the side chain type copolymers were shown in Fig.1. Two kinds of non-mesogenic monomers containing carboxylic acid group and the mesogenic monomer were employed for the synthesis of the side chain type copolymers in order to investigate the influence of the chemical structure of the non-mesogenic monomers containing carboxylic acid group on the thermal properties of the side chain type copolymers. The side chain type copolymers were synthesized by radical copolymerization of a mesogenic monomer and a non-mesogenic monomer with a different feed ratio.

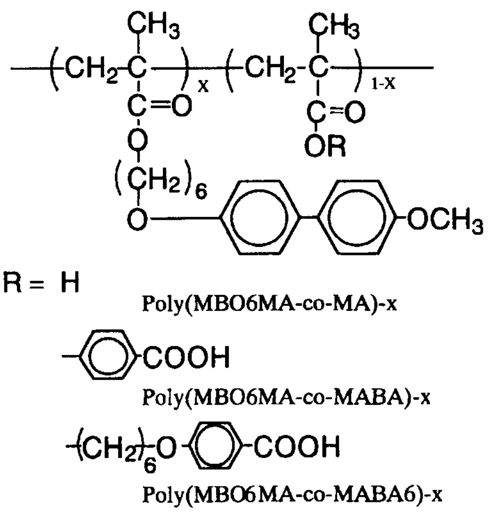

FIGURE 1. Structures of side chain type copolymers.

Thermal properties of the side chain type copolymers containing methacrylic acid monomers[poly(MBO6MA-co-MA)-x, x indicates the mesogenic monomer fraction] are summarized in Table I. A smectic phase was exhibited for the mesogenic homopolymer and the poly(MBO6MA-co-MA)-x above 65.4 mol% of mesogenic monomers. In the DSC curves of the mesomorphic poly (MBO6MA-co-MA)-x, two peaks were detected on both heating and cooling runs. A batonnet texture was mainly observed between the two transition temperatures.

The isotropization temperature increased with increasing fraction of the methacrylic acid monomer in the copolymer. On the other hand, the melting points for the copolymers decreased with increasing fraction of the methacrylic acid monomer. Owing to the increase in the isotropization temperature and the decrease in the melting point, the mesomorphic temperature range (MR) increased with increasing fraction of the methacrylic acid monomer in the copolymer.

TABLE I. Phase transition temperatures and molecular weights of poly(MBO6MA-co-MA)-x

Mesogenic monomer fraction(x) /mol%		Phase transition temp. /°C	$\mathrm{MR}^{b)}$	$\overline{M_n}/10^3$	$\overline{M_w}/\overline{M_n}$
Feed	Calcd[a)]				
100	100.0	$\mathrm{K} \underset{115.1}{\overset{122.5}{\rightleftharpoons}} \mathrm{S} \underset{127.8}{\overset{128.1}{\rightleftharpoons}} \mathrm{I}$	5.6	6.9	1.91
80	86.1	$\mathrm{K} \underset{110.4}{\overset{120.0}{\rightleftharpoons}} \mathrm{S} \underset{133.0}{\overset{134.3}{\rightleftharpoons}} \mathrm{I}$	14.3	7.0	2.00
60	65.4	$\mathrm{K} \underset{99.4}{\overset{107.1}{\rightleftharpoons}} \mathrm{S} \underset{138.0}{\overset{141.7}{\rightleftharpoons}} \mathrm{I}$	34.6	6.8	1.19
50	—	$\mathrm{K} \underset{134.9}{\overset{142.0}{\rightleftharpoons}} \mathrm{I}$	—	4.6	1.49
40	—	$\mathrm{K} \underset{132.7}{\overset{138.7}{\rightleftharpoons}} \mathrm{I}$	—	5.3	1.52

a)calculated by IR b)Ti-Tk-s(on heating scan)

K, solid; S, smectic; I, isotropic.

Thermal properties of the copolymers containing benzoic acid moieties [poly(MBO6MA-co-MABA)-x, x indicates the mesogenic monomer fraction] are shown in Table II. A mesophase was exhibited for the copolymer containing the mesogenic monomers above 53.9 mol%. In the DSC curves of the mesomorphic poly(MBO6MA-co-MABA)-x, a shift of the baseline and a transition peak were observed. The shift of the baseline was assigned to glass transition temperature, while the peak was attributed to the mesophase-isotropic transition. The transition entropy change of the isotropization for the mesomorphic poly(MBO6MA-co-MABA)-x was larger than that of the conventional nematic SLCPs. By using of polarizing optical microscopy measurements, a batonnet like texture was observed between the two transition temperatures. A broad peak was observed in the wide angle region by X-ray diffraction measurements of poly(MBO6MA-co-MABA)-75.0 and 53.9.

TABLE II. Phase transition temperatures and molecular weights of poly(MBO6MA-co-MABA)-x

Mesogenic monomer fraction(x)/mol%		Phase transition temp. /°C	MR[b)]	$\overline{M_n}/10^3$	$\overline{M_w}/\overline{M_n}$
Feed	Calcd[a)]				
100	100	$K \underset{115.1}{\overset{122.5}{\rightleftharpoons}} S \underset{127.8}{\overset{128.1}{\rightleftharpoons}} I$	5.6	6.9	1.91
80	75.0	$g \underset{?}{\overset{100.0}{\rightleftharpoons}} N \underset{145.9}{\overset{151.9}{\rightleftharpoons}} I$	51.9	8.3	2.12
60	53.9	$g \underset{?}{\overset{90.0}{\rightleftharpoons}} N \underset{164.2}{\overset{167.0}{\rightleftharpoons}} I$	77.0	—[c)]	—[c)]
50	43.1	$K \underset{174.7}{\overset{176.7}{\rightleftharpoons}} I$	—	—[c)]	—[c)]
40	30.5	$K \underset{192.3}{\overset{192.8}{\rightleftharpoons}} I$	—	—[c)]	—[c)]
0	0	$K \xrightarrow{295.6} \text{Decom}$	—	—[c)]	—[c)]

a) calculated by NMR b) $T_i - T_{K\text{-}S \text{ or } g\text{-}N}$ (on heating scan)

c) A peak can not be detected in the elution curve of GPC measurements.

g, glassy; K, solid; S, smectic; N, nematic; I, isotropic.

As these results, a nematic phase was exhibited for poly(MBO6MA-co-MABA)-75.0 and 53.9. The side chain type copolymers containing benzoic acid monomers exhibited a nematic phase instead of the smectic phase for mesogenic homopolymer. An appearance of the nematic phase can be considered that a steric hindrance of the benzoic acid moieties would be larger than that of methacrylic acid moieties. Consequently the benzoic acid monomers in the side chain type copolymers would be disturbed the lateral orientation of mesogenic groups itself.

The isotropization temperature of poly(MBO6MA-co-MABA)-x increased with increasing fraction of the benzoic acid monomers, while glass transition temperature of poly(MBO6MA-co-MABA)-x decreased with increasing the fraction of benzoic acid monomers. As a result, the MR of poly(MBO6MA-co-MABA)-x also increased with increasing the fraction of the benzoic acid monomers.

The thermal properties of the poly(MBO6MA-co-MABA6)-x were summarized in Table III. A nematic phase was observed for the copolymers containing the mesogenic moiety above 40 mol%. No typical texture was observed for the mesomorphic poly(MBO6MA-co-MABA6)-x. In DSC curves for the mesomorphic poly(MBO6MA-co-MABA6)-x, a shift of the base-line and a transition peak were observed. These were assigned to a glass transition temperature and clearing temperature, respectively. The transition entropy change of the isotropization for the mesomorphic poly (MBO6MA-co-MABA6)-x was also larger than that of the conventional nematic SLCPs. From the results of the transition entropy change for the mesomorphic poly(MBO6MA-co-MABA)-x and poly(MBO6MA-co-MABA6)-x, it seemed that the transition entropy change of the isotropization for the copolymers with benzoic acid groups in the side chain was larger than that of the conventional nematic SLCPs owing to the formation of the hydrogen bonding.

TABLE III. Phase transition temperatures and molecular weights of poly(MBO6MA-co-MABA6)-x.

Mesogenic monomer fraction(x)/mol%		Phase transition temp./ °C	MR[b)]	$\overline{M}_n/10^3$	$\overline{M}_w/\overline{M}_n$
Feed	Calcd[a)]				
100	100	$K \underset{115.1}{\overset{122.5}{\rightleftharpoons}} S \underset{127.8}{\overset{128.1}{\rightleftharpoons}} I$	5.6	6.9	1.91
80	79.2	$K \underset{69.7}{\overset{75.1}{\rightleftharpoons}} N \underset{116.0}{\overset{119.2}{\rightleftharpoons}} I$	44.1	15.8	1.75
60	65.8	$g \underset{?}{\overset{83.1}{\rightleftharpoons}} N \underset{129.7}{\overset{131.5}{\rightleftharpoons}} I$	48.4	—c)	—c)
50	50.2	$g \underset{?}{\overset{95.0}{\rightleftharpoons}} N \underset{133.7}{\overset{135.6}{\rightleftharpoons}} I$	40.6	—c)	—c)
40	40.8	$g \underset{?}{\overset{93.0}{\rightleftharpoons}} N \underset{135.1}{\overset{137.5}{\rightleftharpoons}} I$	44.5	—c)	—c)
20	18.5	$K \underset{143.2}{\overset{144.2}{\rightleftharpoons}} I$	—	—c)	—c)
0	0	$K \underset{139.7}{\overset{151.0}{\rightleftharpoons}} I$	—	—c)	—c)

a) calculated by NMR b) Ti-TK-S (N) or g-N (on heating scan)

c) A peak can not be detected in the elution curve of GPC measurements.

g, glassy; K, solid; S, smectic; N, nematic; I, isotropic

A broad peak in the wide angle region was observed for the mesomorphic poly(MBO6MA-co-MABA6)-x by X-ray diffraction spectroscopy measurements. This result showed that the mesomorphic phase structure was a nematic phase. A nematic phase was exhibited for poly(MBO6MA-co-MABA6)-x with the wider range of mesogenic group fraction compared with that of the poly(MBO6MA-co-MABA)-x. Owing to the introduction of a flexible spacer into the non-mesogenic monomer, the formation of dimer structure of benzoic acid groups would occurred easily. The dimer structure of benzoic acid groups would function as a mesogenic core. As a consequence, a nematic phase was observed for poly (MBO6MA-co-MABA6)-x with the wide range of mesogenic moiety fraction.

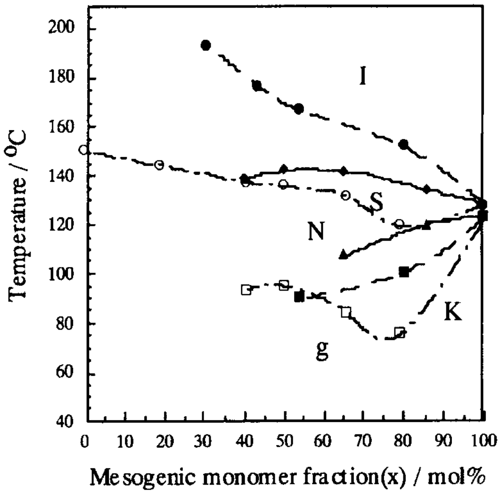

FIGURE 2. Phase transition temperatures as a function of the mesogenic monomer fraction in the copolymers [poly(MBO6MA-co-MA)-x (▲,◆), poly(MBO6MA-co-MABA)-x (■,●) and poly (MBO6MA-co-MABA6)-x (□,○)]: g, glassy; K, solid; S, smectic; N, nematic; I, isotropic.

The MR of poly(MBO6MA-co-MABA6)-x was wider than that of the mesogenic homopolymer. The phase transition temperatures of the copolymers were plotted as a function of the mesogenic content in the copolymers in Fig. 2. With regard to the MR of the copolymers, the MR of the copolymers increased in the order of poly(MBO6MA-co-MA)-x, poly(MBO6MA-co-MABA6)-x and poly(MBO6MA-co-MABA)-x. The MR of benzoic acid type copolymers [poly(MBO6MA-co-MABA6)-x and poly(MBO6MA-co-MABA)-x] was wider than that of the methacrylic acid type copolymer [poly(MBO6MA-co-MA)-x]. We thought that the difference in the MR for the copolymers would occur from the strength of the hydrogen bonding formed between carboxylic acid groups, because it is well-known that the hydrogen bonding among benzoic acid groups is easily formed.

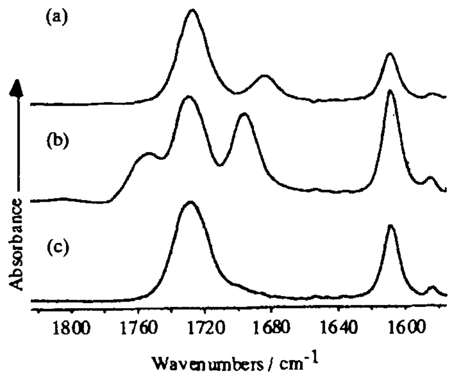

FIGURE 3. IR spectra, in the range of 1820~1580cm^{-1}, for poly(MBO6MA-co-MABA6)-x(a), poly(MBO6MA-co-MABA)-x(b) and poly(MBO6MA-co-MA)-x(c).

In order to clarify the relationship between the hydrogen bonding among carboxylic acid groups of non-mesogenic monomers and the thermal properties for the copolymers, thermally controlled FT-IR measurements were performed. Typical FT-IR spectra of carbonyl group region for the copolymers were shown in Fig. 3. In the carbonyl region for poly(MBO6MA-co-MABA6)-x, two peaks were observed. One peak was assigned to an overlapping peak of carbonyl groups of free benzoic acid group and ester bond in the mesogenic and non-mesogenic monomers (1730 cm^{-1}), and another one is assigned to hydrogen bonding formed between carbonyl and hydroxy groups in the dimer structure of benzoic acid groups(1683cm^{-1}).

On the other hand, three peaks were detected in the carbonyl region for poly(MBO6MA-co-MABA)-x. These three peaks were assigned to carbonyl group of ester bond in the non-mesogenic monomer(1755cm^{-1}), an overlapping peak of carbonyl groups of free benzoic acid group and ester bond in the mesogenic monomer (1730cm^{-1}), and hydrogen bonding formed between carbonyl and hydroxy groups in the dimer structure of benzoic acid groups(1700cm^{-1}), respectively.

In the carbonyl region for poly(MBO6MA-co-MA)-x, two peaks namely an overlapping peak of carbonyl groups of free methacrylic acid group and ester bond in the mesogenic monomer (1730cm^{-1}), and hydrogen bonding formed between carbonyl and hydroxy groups in the dimer structure of methacrylic acid groups(1700cm^{-1}) were detected.

In the case of poly(MBO6MA-co-MA)-x and poly(MBO6MA-co-MABA)-x, a typical peak for the dimer structure of the carboxylic acid moieties through the hydrogen bonding was observed near 1700 cm^{-1}.[2,3] The wavenumber of the peak attributed to the dimer structure of the carboxylic acid moieties indicated that the intermolecular hydrogen bonding was formed among carboxylic acid groups.[6] While the peak attributed to the dimer structure of benzoic acid groups for poly (MBO6MA-co-MABA6)-x was observed near 1683cm^{-1}. The strength of hydrogen bonding which formed the dimer structure of carboxylic acid groups for poly(MBO6MA-co-MABA6)-x was stronger than that of poly(MBO6MA-co-MABA)-x, because the peak assigned to the dimer structure of the carboxylic acid groups for poly(MBO6MA-co-MABA6)-x was observed at the lower wavenumber compared with that of poly(MBO6MA-co-MABA)-x.

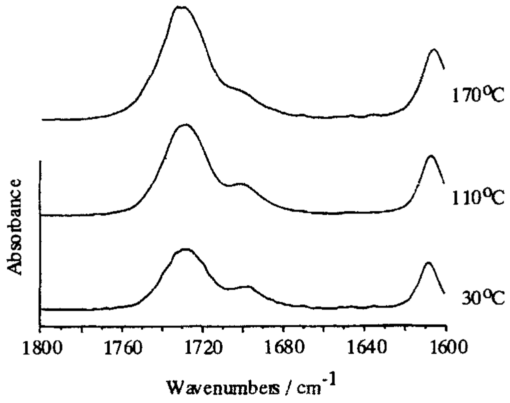

FIGURE 4. Temperature dependence of IR spectra of the copolymer [poly(MBO6MA-co-MA)-65.4].

The peak assigned to the dimer structure of the carboxylic acid groups for the copolymers was slightly shifted to higher wavenumber with increasing temperature as shown in Fig 4. These results showed that the strength of the hydrogen bonding which formed the dimer structure of the carboxylic acid group decreased with increasing temperature, however the exhibition of the mesophase needed a stronger dimer structure formed through the hydrogen bonding compared with that of the isotropic phase. We can not clarify the difference of the MR for the copolymers by the shift tendency of the peak assigned to the dimer structure of carboxylic acid groups. In other words, we can not explain the difference in MR of the copolymers by temperature dependence of the strength in hydrogen bonding of carboxylic acid groups.

So we carried out the quantitative FT-IR analysis of the peak attributed to the dimer structure of the carboxylic acid groups for poly(MBO6MA-co-MA)-x and poly (MBO6MA-co-MABA)-x. The peaks assigned to the carboxylic acid dimer structure for poly(MBO6MA-co-MA)-x and poly(MBO6MA-co-MABA)-x were observed at same wavenumber. This result showed that the strength in the hydrogen bonding of the carboxylic acid groups for poly(MBO6MA-co-MA)-x and poly(MBO6MA-co-MABA)-x was almost same. Therefore we investigated temperature dependence of the amount of carboxylic acid dimer structure for these copolymers by the quantitative FT-IR analysis.

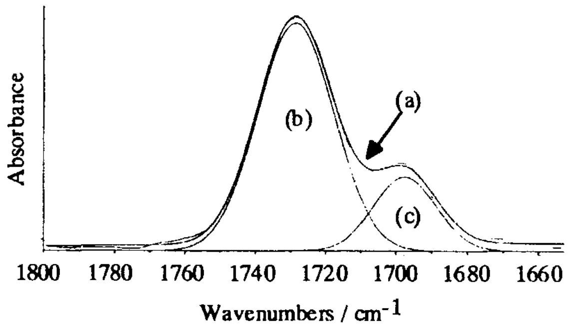

FIGURE 5. Least squares deconvolution of carbonyl group of poly(MBO6MA-co-MA)-65.4 at 110°C: (a) original peak of carbonyl group, (b) overlapping peak of carbonyl groups of free carboxylic acid group and ester bond in the mesogenic monomer , (c) hydrogen bonding formed between carbonyl and hydroxy groups in the dimer structure of carboxylic acid groups.

The carbonyl region in FT-IR spectrum was divided into two or three components as shown in Fig 5. One example of the curve fitting results of the carbonyl region was summarized in Table IV. In particular, our attention was focused to the peak attributed to the dimer structure of the carboxylic acid groups. We estimated the amount of the dimer structure from the area ratio of the hydrogen bonding formed between carbonyl and hydroxy groups in the dimer structure of carboxylic acid groups and all peaks in the carbonyl group region.

TABLE IV. Deconvolution results for carbonyl group region of the copolymers.

(a) poly(MBO6MA-co-MA)-65.4

	$Co^{a)}$				$Cd^{b)}$			
Temp. (°C)	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	Area	Area ratio $^{d)}$	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	Area	Area ratio $^{d)}$
30	1728.3	25.5	16.7	0.789	1697.5	20.6	4.47	0.211
110	1728.6	26.0	25.1	0.810	1697.8	21.2	5.90	0.190
170	1729.5	27.7	33.4	0.880	1698.1	20.4	4.57	0.120

(b) poly(MBO6MA-co-MABA)-53.9

	$Ce^{c)}$				$Co^{a)}$				$Cd^{b)}$			
Temp. (°C)	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	Area	Area ratio $^{d)}$	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	Area	Area ratio $^{d)}$	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	Area	Area ratio $^{d)}$
30	1756.0	22.3	8.45	0.241	1727.8	22.7	11.2	0.325	1695.9	23.3	15.2	0.434
120	1754.9	22.8	7.17	0.252	1728.4	21.6	8.62	0.303	1697.5	25.2	12.7	0.445
170	1754.5	22.8	6.74	0.251	1729.7	22.5	9.12	0.339	1699.2	27.9	11.0	0.410

a) overlapping peak of carbonyl groups of free carboxylic acid group and ester bond in the mesogenic monomer

b) peak of hydrogen bonding formed between carbonyl and hydroxy groups in the dimer structure of carboxylic acid groups

c) peak of carbonyl group of ester bond in the non-mesogenic monomer

d) Area (Ce, Co or Cd) / Total area (Ce + Co + Cd)

In the case of poly(MBO6MA-co-MABA)-x, the peak area ratio of the hydrogen bonding formed between carbonyl and hydroxy groups in the dimer structure of benzoic acid groups and total area of the carbonyl region did not change in the glassy state and the mesophase, however it decreased in the isotropic phase. In contrast, the peak ratio of poly(MBO6MA-co-MA)-x decreased gradually with increasing temperature. With no decrease in the peak area ratio of the hydrogen bonding formed between carbonyl and hydroxy groups in the dimer structure of carboxylic acid groups and total area of the carbonyl region for poly(MBO6MA-co-MABA)-x, it was shown that the amount of the dimer structure formed through the hydrogen bonding of benzoic acid groups below a glass transition temperature was preserved in the mesophase.

On the other hand, with the gradual decrease in the peak area ratio for poly(MBO6MA-co-MA)-x, it was demonstrated that the amount of the dimer structure of carboxylic acid groups decreased with increasing temperature. Temperature dependence of the hydrogen bonding for poly(MBO6MA-co-MABA)-x was smaller than that of poly(MBO6MA-co-MA)-x. We concluded that the MR of the copolymers would be influenced by the remained amount of dimer structure of the carboxylic acid groups.

CONCLUSION

The exhibition of the mesophase depended upon the mesogenic monomer content in the copolymers. The mesomorphic temperature range(MR) of the copolymers increased in the order of the copolymers with methacrylic acid monomers, with benzoic acid monomers containing a flexible spacer and with benzoic acid monomers. Hydrogen bonding of benzoic acid groups was stable compared with that of the methacrylic acid groups because temperature dependence of the hydrogen bonding of benzoic acid groups was smaller than that of the methacrylic acid groups. The MR of the copolymers would be influenced by the amount of the dimer structure of carboxylic acid groups for the copolymers in the mesophase.

EXPERIMENTAL

Materials

Mesogenic monomer and non-mesogenic comonomers containing carboxylic acid group were synthesized according to the literature[7,8].

4-(6-Hydroxyhexyloxy)-4'-methoxybiphenyl

6-Chloro-1-hexanol(15.0g, 0.110mol), an aqueous solution of potassium hydroxide(5.7g, 0.12mol), tetra-n-butylammonium bromide(1.0g, 0.003mol) and a small amount of potassium iodide were added to an ethanol solution of 4-methoxybiphenol(16.0g, 0.08mol). The reaction mixture was refluxed for 30 hours. Ethanol was evaporated from the reaction mixture. And then a white precipitate was obtained by filtration. The white precipitate was washed with water until neutral water was obtained. Next the precipitate was washed with methanol. The product was obtained in a 87.9% yield.
IR(Nujol) ν (cm^{-1}) 3309(OH), 1606, 1500(Ar)

4-(6-Methacryloyloxyhexyloxy)-4'-methoxybiphenyl(MBO6MA)

A tetrahydrofuran solution of methacryloyl chloride(4.2g, 0.04mol) was added dropwise to a tetrahydrofuran solution of 4-(6-hydroxyhexyloxy)-4'-methoxybiphenyl(8.0g, 0.027mol) and triethylamine(6.8g, 0.0675mol) in a chilled reaction vessel. Following stirring at room temperature for 15 hours, tetrahydrofuran solution was evaporated to dryness. The residue was poured into HCl acidic water and a precipitate was washed with water. The precipitate was washed with methanol. The product was obtained in a 41% yield.
NMR($CDCl_3$) δ 1.3~1.8(m, 8H), 1.9(s, 3H), 3.8(s, 3H), 3.8~4.3(m, 4H), 5.6, 6.2(s, 2H), 7.0, 7.5(d, 8H)
IR(Nujol) ν (cm^{-1}) 1720(COO), 1639(C=C), 1606, 1500(Ar)

4-Methacryloyloxybenzoic acid(MABA)

p-Hydroxybenzoic acid(33g, 0.24mol) was dissolved in a 10% aqueous solution of sodium hydroxide(240ml). And then methacryloyl chloride(25g, 0.24mol) was added dropwise to the solution at room temperature. Following

stirring at room temperature, 2N aqueous solution of hydrochloride was added to the reaction mixture. An obtained white precipitate was washed with water. The crude product was purified by recrystalization from acetone. The product was obtained in a 34.3%. m.p. 181.9°C
IR(Nujol) ν (cm^{-1}) 2678, 2561(OH, carboxylic acid), 1731(C=O, ester group), 1681(C=O, carboxylic acid), 1637(C=C), 1606, 1508(Ar)

Polymerization

The copolymers were synthesized by copolymerization of the mesogenic monomer with non-mesogenic monomer in sealed ampoules with 1.0 mol% α,α-azobisisobutyronitrile in anhydrous tetrahydrofuran at 60°C for 15 hours. The copolymers were obtained by reprecipitation from methanol. The copolymers obtained were purified by reprecipitation from acetone and methanol. The copolymers obtained were dried at 40°C under vacuum.

Characterization

^{1}H-NMR was carried out with a JEOL JNM-PMX60 NMR spectrometer using $CDCl_3$ as the solvent. ^{1}H-NMR for the determination of the mesogenic monomer fraction in the copolymer was carried out with a BRUKER DPX 300 spectrometer using DMSO-d_6 as the solvent. DSC measurements were conducted with a Mettler 3000 series. WAXS patterns were recorded on a Rigaku RAD-B system. Polarizing optical microscopy measurements were performed on a Nikon polarizing optical microscopy equipped with a Mettler FP80 controller and a FP82 hot stage. Gel permeation chromatography(GPC) was carried out with a Tosoh HLC-8020 instrument using tetrahydrofuran as the eluent. The instrument was calibrated with a polystyrene standard.

Infrared spectroscopy data was recorded on a JEOL JIR-7000 spectrometer. Spectra were collected at 2cm^{-1} resolution. A minimum of 100 scans were signal averaged. Elevated temperature spectra of FT-IR were obtained by placing the cells made from silicone wafer coated with rubbed polyimide in a temperature-controlled cell(Mettler FP-80 temperature controller with a FP-82 hot stage). Copolymer films were placed on silicone wafer. Before each spectral acquisition the temperature was kept constant for 5 min. to ensure complete temperature equilibration along the sample cell. At the end of the first heating run, the sample was cooled slowly to room temperature, followed by the second heating run in a similar fashion. The detailed procedure of the curve-fitting was described elsewhere.[9]

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