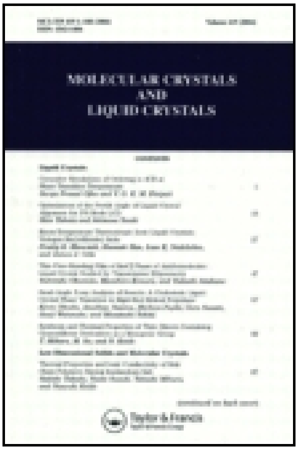

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Mesomorphic Properties of Side-Chain type Polymers Containing Hydrogen Bonding Group

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Mesomorphic Properties of Side-Chain Type Polymers Containing Hydrogen Bonding Group

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Side chain type liquid crystalline polymer(SLCP)s with a carboxylic acid or an amide group in the side chain were synthesized by radical polymerization to examine the influence of intermolecular interaction on thermal properties of the polymers. An enantiotropic smectic phase was induced for the butoxyazobenzene copolymers containing 50~60 mol% of carboxylic acid moiety, while two smectic phases were observed for amide type SLCPs with butoxy group as a mesogenic terminal group. It demonstrates that intermolecular hydrogen bonding formed between carboxylic acid groups and between each mesogenic group in the side chain plays an important role to exhibit the liquid crystalline phase by thermally controlled FT-IR measurements.

Keywords: side chain type liquid crystalline polymer; hydrogen bonding; thermally controlled FT-IR

INTRODUCTION

Mesomorphic properties of liquid crystalline compounds were influenced by forming the specific molecular-molecular interactions, such as electron donor and electron acceptor interaction, ionic bonding, or hydrogen bonding between either the mesogenic cores or terminal moieties [1–6]. A smectic phase was induced for mixtures of nematic liquid crystals having an electron acceptor group like CN and/or NO_2 group with ones containing an electron donor group such as an alkyl and/or alkoxy group. Ionic liquid crystalline compounds similar to surfactants tended to exhibit the thermotropic bilayer smectic phase.

For the rigid core structures of calamitic liquid crystals, at least two benzene rings are required to enable the generation of liquid crystalline phases, however, p-alkoxy benzoic acid exhibits a nematic phase. The molecular structure of p-alkoxy benzoic acid is not rigid and long enough to exhibit a liquid crystalline phase. The exhibition of a liquid crystalline phase for p-alkoxy benzoic acid is attributable to the formation of the dimer structure through the hydrogen bonding of carboxylic acid groups. The intermolecular hydrogen bonding is responsible for giving an elongated unit with a rigid central core and two flexible terminal chains. Similar results were reported in the main chain type liquid crystalline polymers [7].

On the other hand, mesomorphic properties of SLCPs depend upon the chemical structure of the polymer backbone, a flexible spacer and the rigid mesogenic unit. In addition, it was reported that the thermal properties of SLCPs were also influenced by the specific molecular-molecular interaction groups in the polymer backbone or in the side chains [8–9]. Vibrational spectroscopy (IR, Raman spectroscopy) measurements were useful tools for observing the specific molecular-molecular interactions.

In this report, side chain type polymers were synthesized. One was acrylic type copolymers composed of different amounts of the carboxylic acid monomer to investigate the influence of inter- or intra-molecular hydrogen bonding of carboxylic acid group on thermal properties for the polymers [9]. Further amide type homopolymers were exploited for the investigation of lateral hydrogen bonding between the mesogenic groups.

RESULTS AND DISCUSSION

The structures of the copolymers containing acrylic acid and the homopolymers containing amide group are shown in Fig.1 (a) [poly(AA-co-A6MeOAzo)-

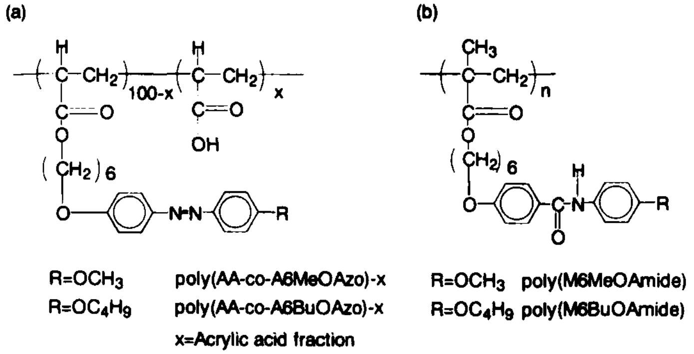

FIGURE 1 Structures of copolymers containing carboxylic acid group(a), and polymers containing amide group(b).

x and poly(AA-co-A6BuOAzo)-x, x indicates acrylic acid fraction.] and (b) [poly(M6MeOAmide) and poly(M6BuOAmide)], respectively.

Thermal properties of poly(AA-co-A6MeOAzo) -x were shown in Fig. 2. A nematic phase was exhibited for the mesogenic homopolymer and the copolymers. The isotropization temperature decreased gradually with increasing fraction of acrylic acid monomer in the copolymer. Phase transition points from solid to nematic phase were not observed for poly(AA-co-A6MeOAzo) -x above 40mol% of acrylic acid fraction. Therefore temperature range of a nematic phase for poly(AA-co-A6MeOAzo) -x with 50~60 mol% of acrylic acid moiety became wider than that for poly(AA-co-A6MeOAzo) -x below 40mol% of the acrylic acid fraction.

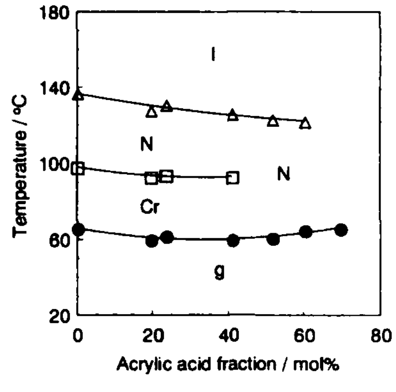

FIGURE 2 Phase transition temperatures as a function of acrylic acid fraction in poly(AA-co-A6MeOAzo)-x: g, glassy; Cr, solid; N, nematic; I, isotropic.

On the other hand, thermal properties of poly(AA-co-A6BuOAzo)-x were shown in Fig. 3 on heating run. Thermal properties of the copolymers were deeply dependent upon the fraction of the acrylic acid monomer. A nematic phase was exhibited for the mesogenic homopolymer and copolymers below 44 mol% of the acrylic acid fraction. A monotropic smectic phase was observed for the homopolymer, while an enantiotropic smectic phase was observed for the copolymers with 50~60 mol% of the acrylic acid fraction. A sharp peak in the small angle region and a broad peak in the wide angle region were observed by X-ray measurements for the copolymers with 50~60mol% of the acrylic acid fraction. The layer spacing estimated from the peak position in the small angle region was about 59.6 Å corresponding to a bilayer smectic A phase.

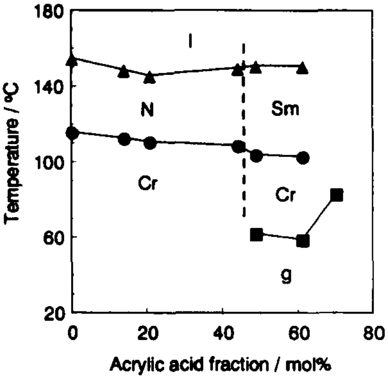

FIGURE 3 Phase transition temperatures as a function of acrylic acid fraction in poly(AA-co-A6BuOAzo)-x on heating run: g, glassy; Cr, solid; Sm, smectic; N, nematic; I, isotropic.

By comparing thermal properties of poly(AA-co-A6BuOAzo)-x(Fig. 3) with those of poly(AA-co-A6MeOAzo)-x(Fig. 2), only a nematic phase was showed for poly(AA-co-A6MeOAzo)-x, however some poly(AA-co-A6BuOAzo)-x exhibited an enantiotropic smectic phase. The exhibition of a smectic phase may arise from the chemical structure of the mesogenic group in poly(AA-co-A6BuOAzo)-x, because it is well-known that mesogens with long terminal alkyl chains exhibit a smectic phase more easily than that with short ones. In fact, the mesogenic homopolymer with butoxyazobenzene exhibited a monotropic smectic phase on cooling run.

On the other hand, the exhibition of a smectic phase depends upon the fraction of the acrylic acid monomer. It would be considered that the exhibition of a smectic phase for the copolymers was originated from the hydrogen bonding formed between the acrylic acid monomers, because an enantiotropic smectic phase was observed for only the copolymers. Therefore, in order to clarify the influence of the hydrogen bonding formed between the acrylic acid monomers on the thermal properties for the copolymers, thermally controlled FT-IR measurements were performed.

In the carbonyl region for the copolymers, two peaks namely overlapping peak of free (non-hydrogen bonding) acrylic acid monomer and ester bond in the mesogenic monomer, and hydrogen bonding (dimer structure) acrylic acid monomer were observed. A typical peak assigned to the dimer structure for the acrylic acid monomer in the copolymers was observed near 1706 cm^{-1}. The intermolecular hydrogen bonding would be formed between carboxylic acid groups due to the wavenumber of the peak attributed to the dimer structure of the carboxylic acid moieties. Further the intermolecular hydrogen bonding was also supported by the formation of the bilayer structure detected by X-ray measurements.

We tried the quantitative analysis of the peak attributed to the dimer structure of the acrylic acid monomers by FT-IR measurements. The carbonyl region in FT-IR spectrum of the copolymers was divided into two peaks according to the literature [10].

We estimated the quantity of the dimer structure from the peak area ratio (AR) of hydrogen bonding formed between the acrylic acid monomers and all peaks in carbonyl group region. Temperature dependence of AR for poly(AA-co-A6BuOAzo)-49.0 and poly(AA-co-A6MeOAzo)-51.8 were shown in Fig. 4. AR for

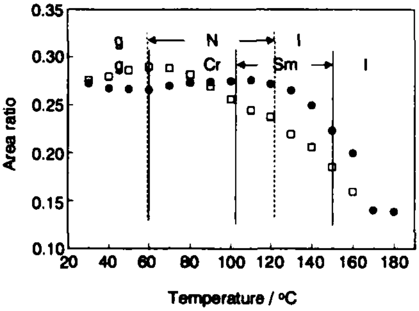

FIGURE 4 Temperature dependence of area ratio for hydrogen bonding carboxylic acid group and all peaks in carbonyl group region: poly(AA-co-A6BuOAzo)-49.0(●) and polyAA-co-A6MeOAzo)-51.8(□); broken line, transition temperatures for poly(AA-co-A6MeOAzo)-51.8; solid line, transition temperatures for poly(AA-co-A6BuOAzo)-49.0.

nematic poly(AA-co-A6MeOAzo)-51.8 decreased linearly with increasing temperature, however that for smectic poly(AA-co-A6BuOAzo)-49.0 did not decrease linearly with increasing temperature. This result for poly(AA-co-A6MeOAzo)-51.8 means that the strength of hydrogen bonding formed between the acrylic acid monomers decreased linearly with increasing temperature, while this result for poly(AA-co-A6BuOAzo)-49.0 indicates the same strength of hydrogen bonding as a solid phase was still preserved until the middle range in the smectic phase, followed by a decrease in the strength of hydrogen bonding. Therefore it was considered that the difference in the mesophase structure for the copolymers depended upon the strength of hydrogen bonding formed between the acrylic acid monomers.

We also investigated that the influence of hydrogen bonding formed between the mesogens (amide groups) on the thermal properties for poly(M6MeOAmide) and poly(M6BuOAmide). Thermal properties of poly(M6BuOAmide) and poly(M6MeOAmide) were summarized in Table I.

TABLE I Phase transition temperatures and molecular weights of poly(M6MeOAmide) and poly(M6BuOAmide).

Abbriviation	Phase transition temperatures/°C	$\overline{Mn}/10^4$	$\overline{Mw}/\overline{Mn}$
Poly(M6MeOAmide)	$\mathrm{g} \underset{?}{\overset{67}{\rightleftharpoons}} \mathrm{SmE} \xrightarrow{117} \mathrm{SmX} \xrightarrow{129} \mathrm{I}$ $\mathrm{SmE} \xleftarrow[116]{} \mathrm{I}$	6.0	1.98
Poly(M6BuOAmide)	$\mathrm{Cr} \underset{100}{\overset{128}{\rightleftharpoons}} \mathrm{SmC} \underset{150}{\overset{152}{\rightleftharpoons}} \mathrm{SmA} \underset{161}{\overset{165}{\rightleftharpoons}} \mathrm{I}$	5.6	2.80

g,glassy; Cr,solid; SmA, smectic A; SmC, smectic C; SmE, smectic E; SmX. highly ordered smectic; I, isotropic

Both poly (M6MeOAmide) and poly(M6BuOAmide) exhibited two smectic phases. The order of smectic phases for poly(M6MeOAmide) was higher than that of smectic phase for poly(M6BuOAmide) due to the result of X-ray measurements. A X-ray pattern similar to a smectic E phase was observed for poly(M6MeOAmide).

A sharp peak in the small angle region and a broad peak in the wide angle region were observed by X-ray measurements for the poly(M6BuOAmide). The layer spacing (*d*) was shorter than the estimated all-trans molecular length of the mesogenic side chain. Therefore we considered that the phase structure of the poly(M6BuOAmide) in the lower mesomorphic temperature range was a smectic C phase (d = 24.8 Å, tilt angle 17° at 120°C on cooling). On the other hand, a smectic A phase (d = 27.4 Å) was exhibited in the higher mesomorphic temperature range for the poly(M6BuOAmide). A focal conic texture was observed in the smectic A phase for poly(M6BuOAmide) by optical microscopy measurements.

We estimated the influence of hydrogen bonding formed between the mesogens on the mesomorphic properties for the polymers by the quantitative analysis in FT-IR measurements according to the literature [11]. The quantitative analysis of the peak assigned to the amide bond in FT-IR measurements was employed to investigate the hydrogen bonding formed between amide bonds in the polyamide. The method was applied to our research of the hydrogen bonding formed between amide bond in the mesogens. A schematic model of hydrogen bonding for carbonyl groups was shown in Fig.5. In the case of poly(M6BuOAmide), the strength of hydrogen bonding formed between the amide groups in the mesogens decreased remarkably in the smectic phases, however, with regard to peak area of the ordered hydrogen bonding carbonyl group, the peak area in a smectic C phase was larger than that in a smectic A phase. It can be considered that ordered hydrogen bonding would influence the formation of the smectic C layer. A tilt of the mesogenic side chain in the smectic layer would originate from the formation of ordered hydrogen bonding between the

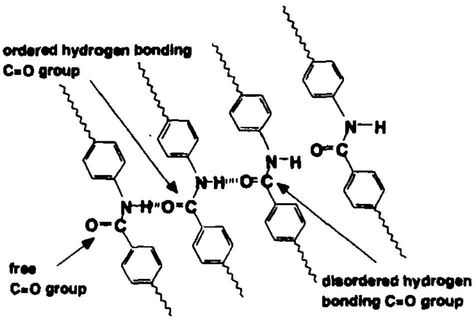

FIGURE 5 A schematic model of intermolecular interactions formed between amide groups.

amide groups in the mesogens.

The strength of hydrogen bonding formed between the amide groups for poly(M6MeOAmide) did not change in the solid and smectic E phases, while in smectic X phase, the strength of hydrogen bonding formed between the amide groups increased regardless of increasing temperature and the endothermic phase transition from a smectic E phase to a smectic X phase on DSC measurements. The reason for the increase in the strength of hydrogen bonding is not clear.

Acknowledgments

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