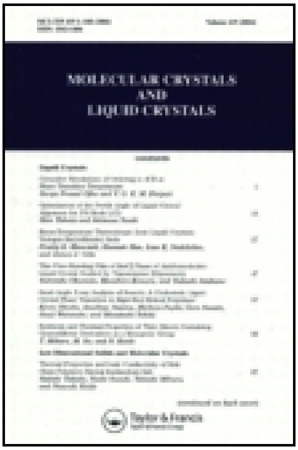

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Synthesis and Thermal Properties of Side Chain Type Liquid Crystalline Polymers With Chiral Unit in the Flexible Moiety

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SYNTHESIS AND THERMAL PROPERTIES OF SIDE CHAIN TYPE LIQUID CRYSTALLINE POLYMERS WITH CHIRAL UNIT IN THE FLEXIBLE MOIETY

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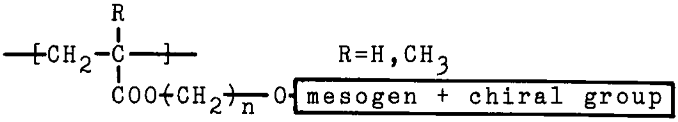
Abstract This paper is concerned with the synthesis and thermal properties for five families of side-chain type liquid crystalline polymers. All these side-chain type polymers showed an enantiotropic mesomorphic nature. A sharp reflection was observed in the small angle region, whereas a broad halo or a relatively sharp peak was also detected in the wide angle region for all the polymers. The experimental values of the thickness of the smectic layer which can be easily assigned by the polarizing microscopic measurements were smaller than that of the calculated ones. This difference would be caused from the tilted arrangement in the smectic layer or smectic A like structure in which the side chains would be overlapped.

INTRODUCTION

Liquid crystalline side-chain polymers have been investigated tremendously in recent years because their scientific and technological potentials. The mesophases of the smectic, nematic and cholesteric types can be realized in the liquid crystalline side-chain polymers. A considerable research effort has been made in electro-optic display using nematic,[1] smectic[2] or cholesteric[3] side-chain polymers. However, owing to the high viscosity of the polymers their response times in the electric field are much larger than the response times of the low molecular mass liquid crystals.[4] Therefore, interest in the synthesis of optically active smectic liquid crystalline polymers has increased considerably since the event of a fast switching based on their ferroelectric properties of the low molecular mass liquid crystal materials.[5] Despite a number of the synthesized homopolymers containing chiral unit in the mesogenic group, there are a few reports on the polymers exhibiting a clear chiral smectic C phase.[6-8]

This paper reports on the thermal properties for five families of side-chain polymers with the following general formula:



$$-\!\left(CH_2-\underset{COO(CH_2)_n-O-\boxed{\text{mesogen + chiral group}}}{\overset{R}{C}}\right)\!- \qquad R=H,CH_3$$

2-Methylbutoxy or 2-chloropropyloxy moiety was used as a chiral component in the pendant group. The spacer length which can play the decoupling between the polymer backbone and mesogenic group was used with six and eleven methylene number tending to the smectic arrangement for low molecular mass liquid crystal compounds.

EXPERIMENTALS Preparation of the monomers.
The monomers were synthesized by standard methods. A typical reaction scheme of monomer II is shown in Figure 1.

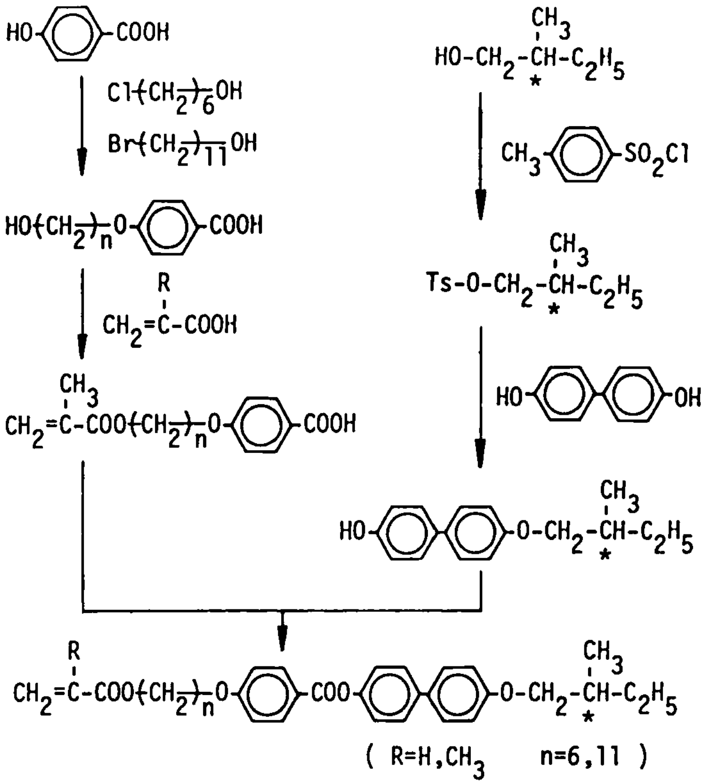


FIGURE 1. Reaction scheme of monomer-II

4(ω-Hydroxy alkoxy)benzoic acid (HABA-n): 0.36mol of 4-hydroxybenzoic acid was dissolved in a mixture of 128 ml of ethanol, 55g of KOH in 55 ml of water and a small amounts of KI. 0.28 ml of ω-bromoalkane-1-ol was then added to the mixture and the mixture was refluxed for 24 hours. After the reaction the solvent was removed with a evaporator. The product was dissolved in 400 ml of water and acidified with HCl. The precipitate was filtered off and washed by cold water, and recrystallized from the mixed solvent (ethanol:H_2O=1:1).

4(ω-Methacryloyloxy or acryloyloxy)benzoic acid: 0.03 mol of HABA-n was esterified during 12 hours in a Dean Stark apparatus with 100ml of methacrylic or acrylic acid in 200ml of chloroform, with adding 11.4g of p-toluenesulfonic acid as a dehydration agent and 9.6g of hydroquinone for preventing a polymerization. After removing the solvent, the product was washed several times with hot water and dissolved in ether. The ether layer was dried with magnesium sulfate. After evaporating the solvent, the solid was recrystallized from a mixed solvent of chloroform and methanol.

2-Methylbutyl-p-toluenesulfonate: 0.25 mol of S(-)-2-methyl-1-butanol was dissolved in pyridine. After cooling the solution, 0.5 mol of toluene sulfonic chloride was added dropwise and the mixture was stirring for 2 hours at room temperature. Then the solution was stored in a refrigerator for 12 hours. The solution was diluted with 100ml of water and added 2N HCl and ether to the solution. The ether layer was washed several times with water and dried with sodium sulfate. The product was obtained by removing ether.

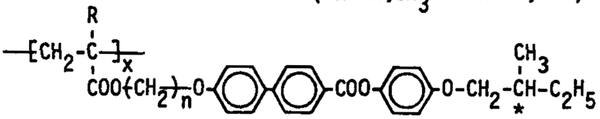
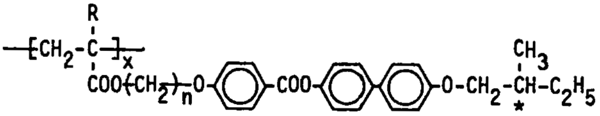
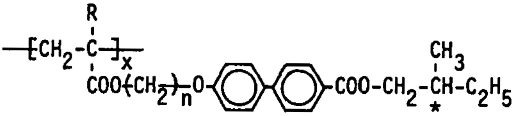
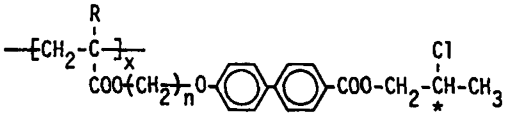
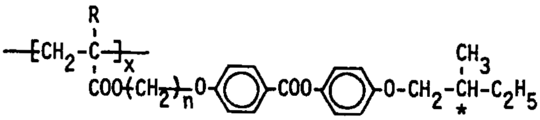
p(2-Methylbutyloxy)-phenol (MBP), p(2-methylbutyloxy)biphenol(MBB): 0.2 mol of hydroquinone was dissolved in a mixture of 36 ml of ethanol and 300ml of water dissolving of 12g of KOH. 0.1 mol of 2-methylbutyl-p-toluenesulphonate was added dropwise to the solution and the mixture was then refluxed for 24 hours. After evaporating the solvent, 500 ml of toluene was added, and the solution was washed several times with warm water. After evaporating toluene, the solid was recrystallized from the hexane solution. p (2-methylbutoxy)biphenyl was synthesized by the same methods of MBP.

p-[4-(ω-Methacryloyloxyalkoxy)benzoyloxy]-p'-(2-methylbutyloxy)biphenyl: 0.013 mol of 4(ω-methacryoyloxyalkoxy)benzoic acid was stirred during 30 min with 50ml thionylchloride in the presence of a small amounts of 2,6-Di-tert-butyl-p-cresol and N,N-dimethylformamide during 30 minutes at room temperature. After the reaction excess thionyl chloride was removed in vacuo, and the precipitated white solid was dissolved in THF. 0.02mol of (2-methylbutyl)biphenol and 2.2ml of triethylamine were dissolved in 100ml THF. The acid chloride solution was added to this solution at -10°C. The mixture was stirred during 12 hours at room temperature. After evaporating the solvent the solid product was dissolved in 500ml of chloroform, and the solution was washed several times with water and dried with calcium chloride. After evaporating the solvent, the white solid was recrystallized from a mixed solvent of chloroform and methanol.

2-Chloropropylalcohol: The mixture of 11.8g of ethyllactate and 7.2g of pyridine was added dropwise to the cooled 22g of phosphorus pentachloride. After the reaction unreacted phosphorus pentachloride was slowly decomposed with water. The product was extracted several times by ether, The organic layer was dried with sodium sulphate. After evaporating the solvent the product, chloroethyllactate, was distilled. 1.79g of lithium aluminium hydride was stirred during 3 hours with 63ml of dry ether. 8g of chloroethyllactate was added dropwise to the above mixture with vigorous stirring. After the mixture was stirring during 15 minutes,the excess of lithium aluminium hydride was decomposed with adding of water, and then the mixture was diluted with 10% sulfuric acid. The organic layer was separated, dried with magnesium sulfate. The ether was evaporated and the residual solution was purified by distillation($[\alpha]_{25}^{D}=-15.1$, c=9.928g 100cm^{-3} in chloroform).

POLYMERIZATION Radical polymerization of monomers with 1mol% of 2,2'-azoisobutyronitrile in N,N-dimethylformamide was carried out in a sealed glass tube under nitrogen atmosphere for 48 hours at 60°C. The polymer was precipitated with an addition of methanol to the reaction mixture. The polymer was purified by reprecipitated several times by chloroform.

TABLE I Structures of polymers

Poly-a-b-n*	structures
	(R= H,CH_3 n= 6,11)
Poly-a-I-n	
Poly-a-II-n	
Poly-a-III-n	
Poly-a-IV-n	
Poly-a-V-n	

* a:acrylic(A) or methacrylic(M), b:mesogen, n:spacer length

RESULTS AND DISCUSSION

The structure of the polymers is shown in Table I. Biphenylcarbonyloxyphenyl(I), phenylcarbonyloxybiphenyl(II), biphenyl(III and IV) and phenyl benzoate(V) were chosen as the mesogenic group. Polymers I and polymers II in Table I have the same mesogen length but different chemical bonding order of the biphenyl and phenyl group.

The thermal properties of the monomers and polymers are summarized in Tables II and III.

TABLE II. Characteristic of monomers

No.	Monomer	Transition temp.(°C)
1	M-I-6	K 111 I
3	M-II-6	K 69.5 I
4	M-II-11	K 65.4 S 77.1 I
5	A-II-6	K 84.9 S 139.4 I
6	A-II-11	K 80.2 S 135.7 I
7	M-III-6	K 105 I
8	A-III-11	K 80 S 130 I
9	A-IV-11	K 90 Meso.

K:solid, S:smectic, I:isotropic fluid
The number of monomers corresponds to that of polymers.

The monomers show the mesomorphic nature except No. 1,3 and 7.

All these side-chain polymers show an enantiotropic mesomorphic nature.

All polymers except for No.5 polymer exhibit a fan-shaped texture which is indicative of a smectic phase, whereas a oily-streak texture characteristic of cholesteric phase is observed for

TABLE III. Characteristic of polymers

No.	Polymer a-b-n	Transition temp. (°C)					ΔT	$\overline{\text{Mn}}$
1	M-I-6	g	110	S	217	I	107	19000
2	M-I-11	K	102	Meso	226	I	124	35000
3	M-II-6	K	150	Meso	202	I	52	77000
4	M-II-11	K	99	S	200	I	101	36000
5	A-II-6	K	78	Ch	192	I	114	12000
6	A-II-11	K	122	S	210	I	88	23000
7	M-III-11	K	140	S	191	I	51	22000
8	A-III-11	K	90	Meso	?	I		5000
9	A-IV-11	K	100	Meso	?	I		6500
10	A-V-11	K	50	S	100	I	50	18000

g:glass transition, K:solid, S:smectic, Ch: cholesteric, I:isotropic fluid, ΔT:mesomorphic temperature range, $\overline{\text{Mn}}$:molecular weight, a:acrylic(A),methacrylic(M), n:spacer length. b:mesogen(see Table I)

No.5 polymer. However, textures observed in liquid crystalline polymers can be misleading and a more extensive investigation of this point by X-ray diffraction analysis, as discussed below,is needed to determine a definite assignment of the liquid crystalline phase.

Figure 2 shows the DSC traces of the No.1 (full line) and No. 2 (dotted line) polymers. Most of the polymers exhibit the similar DSC curves to the No.2 polymer, whereas the appearance of the glass transition temperature is only observed for No.1 polymer because of their amorphous nature. The phase transitions of the polymers determined by DSC and polarized microscopy are tabulated in

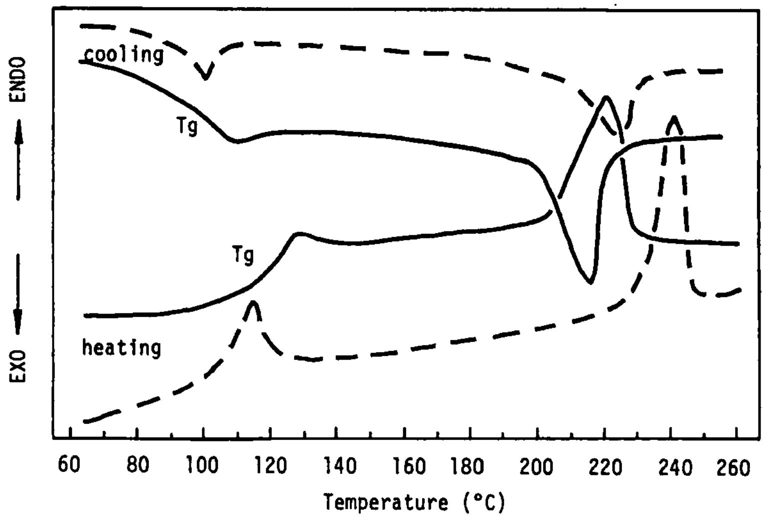


FIGURE 3. DSC curves of polymer 1(——) and polymer 2(---).

Table III. The isotropization temperatures(Ti) of the polymer having longer spacer length listed in Table III are higher than that having shorter of the spacer chains. The mesomorphic transition temperature range (ΔT) of polymer containing a longer flexible spacer chain is wider than that of a shorter flexible one. A comparison of transition temperature for the polymers having a same length of mesogenic group but having a opposite chemical bonding order between the biphenyl and phenyl group, it is found that the thermal stability of No.1 and No.2 polymers is higher than that of No. 3 and No.4 polymers even if the latter polymers have a higher molecular weight. It has been reported that the thermal transition temperature for the liquid crystalline polymers increases with increasing molecular weight and reaches almost to constant temperature above a molecular weight of approximately 10000.[9] The transition temperature and thermal stability are also influenced by the structure of mesogenic moiety. From Table III, the isotropization temperatures of the polymers having longer mesogenic groups are higher than that of the polymers having shorter ones. The thermal stability of the main-chain type liquid crystal polymers also increases with increasing length of mesogenic group.[10]

Comparing with an influence of the structural unit of the polymer backbone on the transition temperature, the transition temperature of polyacrylic polymer is higher than that of polymethacrylic polymer as shown in Table III.

The polymer containing 2-chloropropyloxy chain at the end of the mesogenic moiety exhibits a mesomorphic nature, but it could not show any typical liquid crystal optical texture.

X-ray diffractograms recorded at room temperature for No.1 polymer with n=6, and No.2 polymer with n=11 are shown in Figure 3. The samples were heated up to the mesophase and kept this state for about one hour and then quenched rapidly in liquid nitrogen in order to preserve the mesophase orientation. A sharp reflection is observed in the small angle region, whereas a broad halo or a relatively sharp peak is also detected in the wide angle regions. The spacing between the layers increases from 33.7 Å for n=6 to 45.0 Å for n=11 as the spacer length increases. The lateral spacing between these two polymers is the same, whereas a wide angle x-ray diffraction region for No.2 polymer with n=11 shows a sharp diffraction

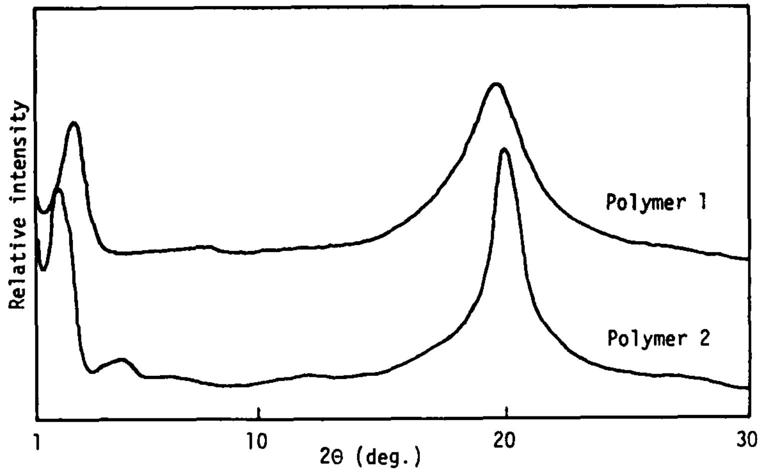


FIGURE 3. X-ray scattering curves for polymers.

TABLE IV. Spacings for polymers

polymers	observed(Å)						calculated(Å)
1	33.7						36.3
2	45.0		19.7				43.0
3	58.1	26.0	16.3	4.5			36.3
4	40.1		17.8	4.4			43.0
5	64.0	27.9	17.4	4.4			36.3
6	42.4		18.6	4.3			43.0
7	28.3	13.3	8.5	4.4	4.0	3.2	30.9
10	39.0	18.0		4.4			37.6

pattern than that for No.1 polymers with n=6. These experimental findings would be suggested that the polymer having a longer flexible spacer polymer forms a highly ordered layer of the smectic liquid crystalline phase. The X-ray results and the calculated value of the spacing based on the dreiding model are tabulated in Table IV. As seen in Table IV, All polymers exhibit a sharp peak in the small angle scattering region. The experimental values for the thickness of the smectic layer exhibit a typical fan type texture by the polarized microscopic observations are found to be shorter than the calculated ones except for No.10 polymer. This difference may be caused from the tilted arrangement in the smectic layer, that is to say, smectic C(Sc) orientation or smectic A like structure in which the side chains would be overlapped. However, the most convincing assignment for the existence of Sc phase is necessary to measure the oriented samples from the X-ray diffraction measurements. A more detail investigation of these mesophases is in progress.

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