

STUDY ON CHIRAL LIQUID CRYSTALLINE POLYMERS WITH BIPHENYLENE AND AZO-BENZENE AS THE MESOGENS

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ABSTRACT

Chiral liquid crystalline polymers containing biphenylene and azobenzene as the mesogens and S(-)-2-methyl-1-butanol as the chiral end group were synthesized and characterized by DSC, POM and X-ray diffraction. These polymers show crystalline or glassy liquid crystalline phase at room temperature. Most polymers show smectic A or highly ordered smectic phases above melting temperature.

INTRODUCTION

Chiral liquid crystalline phases have gained great attention in recent years. The chiral smectic Sc* phase are interesting due to their ferroelectric properties and fast switching time (in the order of microsecond in an electric fields)^[1,2].

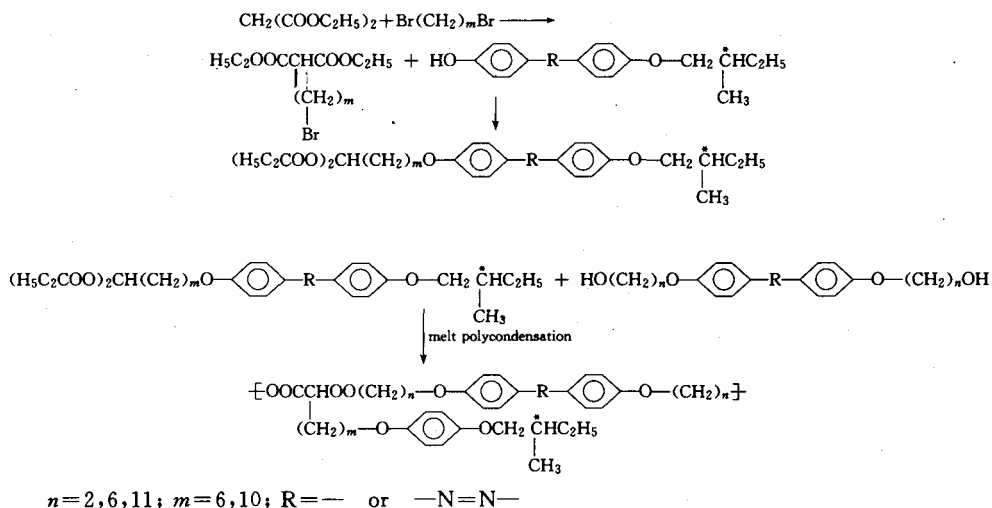
Liquid crystalline polymers exhibit Sc* phases have been studied recently and a few of them have shown ferroelectric properties^[3-5]. In this case, a ferroelectric liquid crystalline polymers can be obtained which can combine the properties of polymers (a glassy state in which ferroelectric structure may be frozen, the capacity of making films, specific mechanical properties, etc) with the properties of ferroelectric liquid crystalline in the Sc* phase. Study of such polymers seems promising. The combined liquid crystalline polymer, i. e. polymers containing the mesogenic groups in the main chain as well as in the side chain are especially interesting. The combined main/side chain liquid crystalline polymers often form liquid crystalline polymorphism and are easy to be modified chemically^[6]. On the other hand, the introduction of additional functional groups such as

photochromic moiety will further enlarge the scope of combining new properties.

In this work, synthesis and characterization of chiral main/side group combined liquid crystalline polymers containing dissimilar mesogens and different spacer lengths in the main chain and side groups or containing trans-azobenzene units as both mesogenic and photochromic groups were investigated. It is expected that the study of these polymers will provide information about the liquid crystalline behaviour of the polymers containing different mesogens and dissimilar spacer lengths.

EXPERIMENTAL

Scheme 1 represents the reaction pathway used to prepare the mesogenic diols, malonates and combined chiral liquid crystalline polymers. Table 1 and Table 2 show the elemental analysis and ¹H-NMR of mesogenic diols and malonates.



Scheme 1 Synthesis of combined main/side chain polymalonates

The melt polycondensation of the polymers was carried out as described in ref. [5], but the time and the maximum temperature were reduced. The mesogenic diols and malonates (mole 1:1) were mixed in the reaction flask. To the molten mixture, 3 drops of a mixture of tetraisopropyl orthotitanate and diethylene glycol dimethyl ether (vol 1:9) were added under nitrogen. With a slow nitrogen flow the melt temperature was raised to 150°C in 2 hr. After the addition of another 3 drops of the catalyst solution, the reaction mixture was heated to 170°C, then evacuated and reduced the pressure to

10mmHg within 2h. The polycondensation was completed by stirring the melt for 3 hr at 170°C. The polymers were purified by dissolving in CHCl₃ and precipitated from methanol at least twice. Yield 80—90%. The polymers were confirmed by ¹H-NMR.

Table1 The mesogenic diols

Monomers	Structures		Elemental analysis(%)				¹ H-NMR
	n	R	Found		Calc.		
			C	H	C	H	
M-2	2	-	69.90	6.25	70.02	6.62	3.6(t;4H,-OCH ₂) 3.9(t;4H,-OCH ₂ OH) 6.9-7.4(m;8H,-C ₆ H ₄ C ₆ H ₄ -)
M-6	6	-	74.55	8.82	74.61	8.81	3.6-3.8(m;8H,-OCH ₂). 6.7-7.2(m;8H,-C ₆ H ₄ C ₆ H ₄ -)
M-11	11	-	77.97	10.48	77.50	10.34	1.2(m;36H,-CH ₂), 2.9-3.8(m;10H,OCH ₂), 6.7-7.3(m;8H,-C ₆ H ₄ C ₆ H ₄ -)
M-2N	2	-N=N-	63.32	6.26	63.58	5.98	3.7-4.1(m;8H,-CH ₂ O-)
				N=9.32		N=9.32	7.1-7.8(m;8H,-C ₆ H ₄ C ₆ H ₄ -)
M-11N	11	-N=N-	73.33	9.78	73.64	9.75	1.4(m;36H,-CH ₂), 3.3-4.0(m;8H,-OCH ₂), 7.1-7.8(m;8H,-C ₆ H ₄ C ₆ H ₄ -)
			N=5.05		N=5.02		

Table 2 The mesogenic malonates

Monomers	Structures		Elemental analysis(%)			¹ H-NMR
	n	R	Found	Calc.	mp(°C)	
S-6	6	-	C 72.29 H 8.45	72.23 7.89	53.0	1.0-1.8(m;19H,(CH ₂) ₅ -CHC ₂ H ₅), 1.3(t;6H,-CH ₃) CH ₃ 3.9(m;8H,-OCH ₂ -) 6.7-7.4(m;8H,-C ₆ H ₄ C ₆ H ₄)
S-10	10	-	C 73.61 H 9.08	73.47 9.21	58.0	1.0-1.8(m;27H,CH(CH ₃ -C ₂ H ₅ ,-(CH ₂) ₉ -), 6.7-7.4(m;8H,-C ₆ H ₄ C ₆ H ₄)
S-6N	6	-N=N-	C 68.40 H 8.04 N 5.32	68.19 7.79 5.16	62.0	7.0-7.9(m;8H,-C ₆ H ₄ C ₆ H ₄)

The liquid crystalline phase of the monomers and polymers was studied by a Dupont 1090 thermoanalyzer with DSC 910 at a heating rate of 10°C/min or 20°C/min. The microphotographs were taken on polarizing microscope. An Olympus model BH-2 microscope equipped with Fp-5 hot

stage was used to observe the thermal transition and to analyse the mesophase textures. The X-ray experiments were performed using a Siemens D-500 with FeK α radiation source. U. V. absorption spectra of combined chiral polymers were determined on a model HP-8451 UV-visible spectrum.

RESULTS AND DISCUSSION

Mesogenic diols M-2, M-6 and M-11 exhibited a wide mesophase. M-2N and M-11N whose mesogens possess azobenzene ring show a narrow mesophase temperature range. Both the crystalline to smectic and smectic to isotropic phase transition temperatures are decreased with increasing the length of methylene of mesogenic diols. Thermal transition behaviour and observation of liquid crystal phases of the mesogenic diols are listed in Table 3.

Table 3 Characterization of mesogenic diols

Diols	Structure	Transition By DSC	Temperature(°C) By microscopy
M-2	$\text{HO}(\text{CH}_2)_2\text{O}-\text{C}_6\text{H}_4\text{C}_6\text{H}_4-\text{O}(\text{CH}_2)_2\text{OH}$	K145. 8S211I	K148S212I
M-6	$\text{HO}(\text{CH}_2)_2\text{O}-\text{C}_6\text{H}_4\text{C}_6\text{H}_4-\text{O}(\text{CH}_2)_6\text{OH}$	K93. 1S173. 7I	K98S174I
M-11	$\text{HO}(\text{CH}_2)_{11}\text{O}-\text{C}_6\text{H}_4\text{C}_6\text{H}_4-\text{O}(\text{CH}_2)_{11}\text{OH}$	K112. 9S156I	K130S158I
M-2N	$\text{HO}(\text{CH}_2)_2\text{O}-\text{C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{O}(\text{CH}_2)_2-\text{OH}$	K181. 7S204. 2I	K188S202I
M-11N	$\text{HO}(\text{CH}_2)_{11}-\text{O}-\text{C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_4\text{O}(\text{CH}_2)_{11}-\text{OH}$	K143. 3I	K143. 3I

Table 4 Characterization of combined polymalonates with biphenylene as mesogens

Polymers	Structure		Phase transition(°C)	η_{inh}	$[\alpha]_D^{20}$
	<i>n</i>	<i>m</i>			
P-1	2	6	K168. 8S172. 8I	0. 49	+ 4. 2
P-2	6	6	K139I	0. 61	
P-3	11	6	K75. 6S116. 8I	0. 63	+ 2. 7
P-4	2	10	K115. 1S164. 2I	0. 63	+ 1. 9
P-5	6	10	K110. 3S ₁ 128S ₂ 143I	0. 46	+ 3. 4
P-6	11	10	K123. 8II	0. 36	+ 3. 6

a) *n* and *m* indicated according to Scheme 1 , b) $[\alpha]_D^{20}$ determined in CHCl_3

The characterization of polymalonates with biphenylene or azobenzene as mesogens are summarized in Table 4. and Table 5, respectively. The heating curves of polymers P-4, P-5, P-8 and P-10 show a first order transition at the clearing point and a second phase change from the S_A to highly ordered smectic phase transition. For all polymers no glass transition temperature could be determined due to the crystalline or the restricted

mobility in highly ordered smectic phase of polymers. Most of polymers exhibit smectic phase above melting transition. The mesophase temperature range of polymers depended on spacer length. If azobenzene replaced biphenylene as mesogen, the crystallinity of polymers was suppressed, but it did not strongly affect the clearing temperature. So the temperature range of phase transition of polymers are broad as compared with that of polymer with the biphenylene as mesogens.

Table 5 Characterization of combined polymalonates with trans-azobenzene as mesogens

Polymers	Structure			Phase transition(°C)	η_{inh}	$[\alpha]_D^{20}$
	<i>n</i>	<i>m</i>	mesogens			
P-7	11	6	Ar Ar'	93. 9S106. 2I	0. 70	-2. 1
P-8	11	6	Ar' Ar	K53S ₁ 94S ₂ 104. 2I	0. 33	-3. 1
P-9	2	10	Ar' Ar	K130. 3S163. 4I	0. 24	+2. 5
P-10	2	6	Ar' Ar'	K59S ₁ 129S ₂ 142I	0. 31	+4. 7

a) *n, m* according to Scheme 1; Ar = $-\text{C}_6\text{H}_4\text{C}_6\text{H}_4-$; Ar' = $-\text{C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4-$

From the polarizing microscopy observation, most of polymers exhibit the liquid crystalline polymorphism. Upon heating polymers for the first time, the polymers displayed high viscosity, and no typical texture could be induced up to a temperature about 5–10°C below the clearing point. On cooling from the isotropic phase, the polymers P-4 and P-5 formed focal conic defects texture on annealing for 5hr at just below the clearing temperature, the texture was typical of a smectic A phase. Further cooling produced a transition to high ordered helical phase which was characterized by the formation of disclination lines in the focal conic texture. Measurements of the spacing between the lines by a graticule give a value of

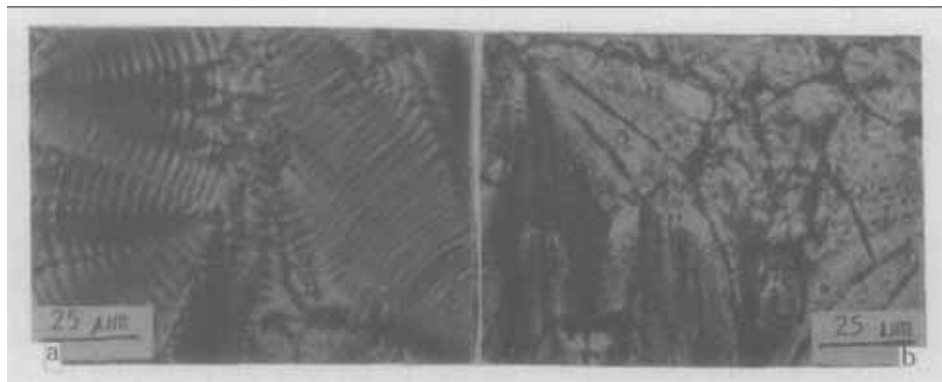


Fig. 1 Optical texture of polymers

(a) P-4 at 154°C annealed for 10hr; (b) P-5 at 127°C annealed for 5hr

the pitch length between 2.5—5 μ m. (see Fig. 1). The polymer P-3 forms completely different defect textures compared with polymer P-4. On cooling the isotropic phase, initially the polymer forms a sanded texture, on annealing at below the clearing temperature for 48hr the texture has no evident change. (see Fig. 2)

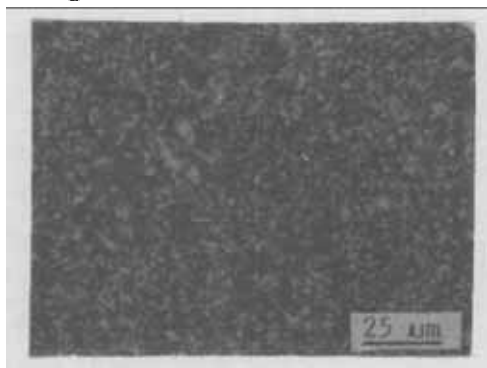


Fig. 2 Optical photograph of polymer P-3 at 115 °C for 48hr

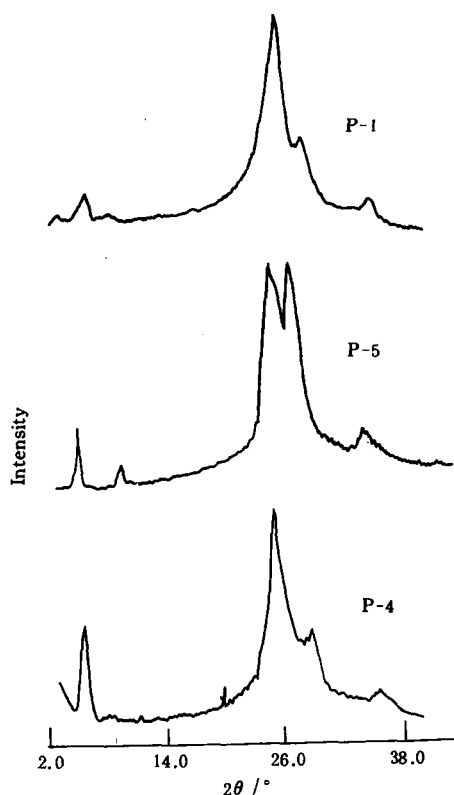


Fig. 3 X-ray diffraction patterns for quenched samples from liquid crystalline phase of polymers at room temperature

X-ray diffraction patterns for quenched samples from liquid crystalline phase of polymers were determined at room temperature. The results are presented in Fig. 3. All the polymers are in a crystalline or highly ordered smectic phase. The X-ray diffraction patterns are dominated by a sharp small angle reflection ($2\theta = 2 - 8^\circ$) and two sharp wide angle reflections ($2\theta = 20 - 23^\circ$). In addition, all polymers show a weak and broad wide angle reflection corresponding to a Bragg spacing of about 0.32nm. The layer spacings calculated from the small

angle reflection are summarized in Table 6.

Table 6 Layer spacing derived from the powder diffraction patterns of polymers

Polymers		Layer Spacing/nm			
P _c -1	3.81 ^a	2.5	0.42	0.4	0.32
P _c -4	2.47	1.27	0.4	0.41	0.33
P _c -5	2.31	0.45	0.39	0.32	

a) Very weak

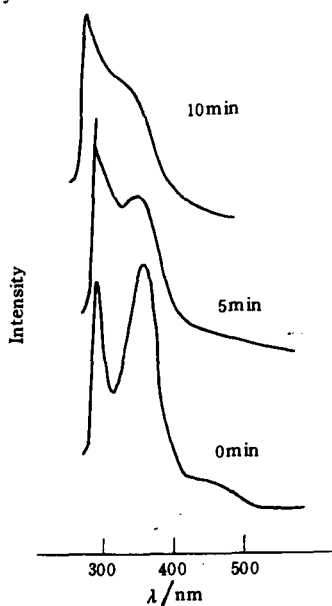


Fig. 4 The UV absorption spectra of polymer P-7 with various irradiation time

Besides, the photochromic behaviour of polymers P-7 and P-8 containing azobenzene as mesogens has been investigated in CHCl_3 solution (see Fig. 4). In the dark or at $\lambda > 245 \text{ nm}$, the azobenzene groups in the trans planar configuration characterized by a strong absorption intensity decreased with increasing irradiation time on photoinduced trans to cis isomerization.

In conclusion, the experimental results have demonstrated that the phase behaviour of main/side chain combined liquid crystalline polymers influenced by the different spacer

length and dissimilar mesogen units. The polymers form liquid crystalline polymorphism and exhibit smectic A or highly ordered smectic C* phases.

Keywords:

Chiral liquid crystalline polymers; Smectic phase.

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