Cholesteric–Isotropic Biphasic Morphology in Liquid Crystalline Polyesters with Chiral Substituents as Pendant Groups

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ABSTRACT: A series of copolyesters based on 2-[(S)-(+)-methyl-1-butoxy]hydroquinone, **I**, as the chiral monomer with non-chiral hydroquinone monomers was investigated for formation of a biphasic morphology in which a cholesteric and isotropic phases coexisted close to an isotropic transition temperature. For the copolyesters with hydroquinone, the biphasic formation occurred for the lower molecular weight copolyester over a wider temperature range presumably because of both molecular weight and the chemical heterogeneity effects on the isotropization transition. The temperature range of the biphasic morphology was influenced by a substituent of the copolymerized non-chiral hydroquinone monomer.

KEY WORDS   Cholesteric Liquid Crystal / Isotropization Transition / Biphasic Morphology / Copolymerization / Molecular Weight Distribution / Chemical Heterogeneity /

This report concerns the continuation of our study on a new family of main chain cholesteric liquid crystalline polyesters, ChLCPs, which are based upon mesogenic units that have chiral substituents.[1,2] The chiral mesogenic units, which consist of a triad ester containing the residue of 2-[(S)-(+)-2-methyl-1-butoxy]hydroquinone, **I**, and two *p*-hydroxybenzoic acid residues, are connected by flexible polymethylene spacers as shown below;
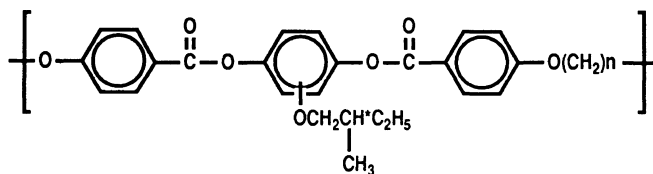
In contrast, the other main chain ChLCPs have the chiral centers in the backbones. For the preparation of these polymers, only a limited number of difunctional chiral monomers, such as (R)-3-methyladipic acid, have been available, and the synthesis of such monomers can be quite difficult.[3–6] In this type of polymers, monofunctional chiral compounds, such as (S)-(−)-2-methyl-1-butanol, can be used for preparation of new monomers having a chiral substituent.

Copolyesters containing non-chiral hydroquinone units were also prepared as described in our previous report,[2] and these formed cholesteric phases, which exhibited several different types of textures depending on the composition of the copolyesters. Morphology control in the polymers is important for the

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application that the ChLCPs exhibit their own performance which cause the helical structure, therefore, the present report is concerned with the LC domains control and biphasic mor-phology containing both a cholesteric and iso-tropic phases in two series of copolyesters, **II** and **III**, having the structures shown below;
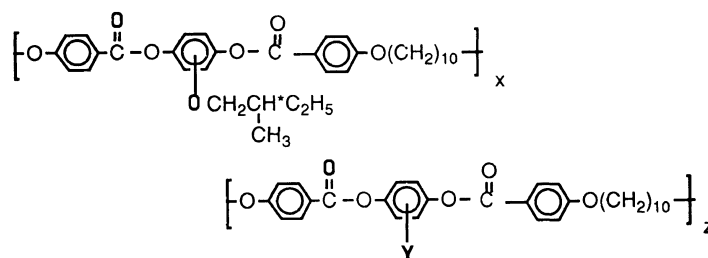
in which Y is H for Series **II** and Y is $-O(C_2H_5O)_2C_2H_5$ for Series **III**.

EXPERIMENTAL

All monomers including 2-[(S)-(+)-methyl-1-butoxy]hydroquinone, **I**, and the copolymers were prepared as previously described.[1,2] To obtain a series of copolyesters of different molecular weights, an appropriate excess of the 4,4'-dichloroformyl-α,ω-diphenoxyalkane monomer was used in the copolymerization reactions, and shorter reaction times at the reflux temperature of the dichloromethane solvent were also used than in the previous study. In addition, some of the copolyesters were fractionated by extraction with acetone after precipitation in methanol. All of the copolyesters prepared were characterized for molecular weights, thermal transitions and crystalline and liquid crystalline structures as previously described.[1,2] The molar fraction of the chiral monomer, **I**, in the copolyesters, Z_m, was estimated by ^{1}H NMR spectroscopy based on the integrated value of the methyl protons of 2-methyl-1-butoxy group at 0.7—0.9 ppm, S_m, and the 3,3'-aryl protons at 8.14 ppm, S_a, for solutions of the copolyesters in deutrated trifluoroacetic acid according to the following equation:

$$Z_m = 4S_m/6S_a \qquad (1)$$

RESULTS AND DISCUSSION

Observations of copolyesters, Series **II** (Y = H, $x = z = 50$), on a hot stage of a polarized light microscope revealed the formation of several different textures depending on the thermal treatment in the cholesteric phase. In the cooling cycle from the isotropic phase, fine droplets appeared in the isotropic phase as shown in Figure 1a, and these droplets filled the appearance as seen in Figure 1b. The domain sizes in these textures were strongly influenced by the cooling rate and by annealing conditions during the cooling cycle. That is, to form a planar texture containing large domains, the polymers had to be annealed at a temperature close to T_i until the fine droplets coalesced, then the sample was cooled very slowly. During this annealing process, the phase separation was observed to form a biphasic morphology in which the cholesteric and isotropic phases coexist, and on the further cooling, the isotropic region was continuously converted to the cholesteric phase as seen in Figure 1c.

The formation of a biphasic morphology is believed to depend partly on the molecular weight distribution of the copolyesters, and the isotropic phase probably contains the relatively lower molecular weight fraction. In addition to this molecular weight effect, the normal chemical heterogeneity of the members of this
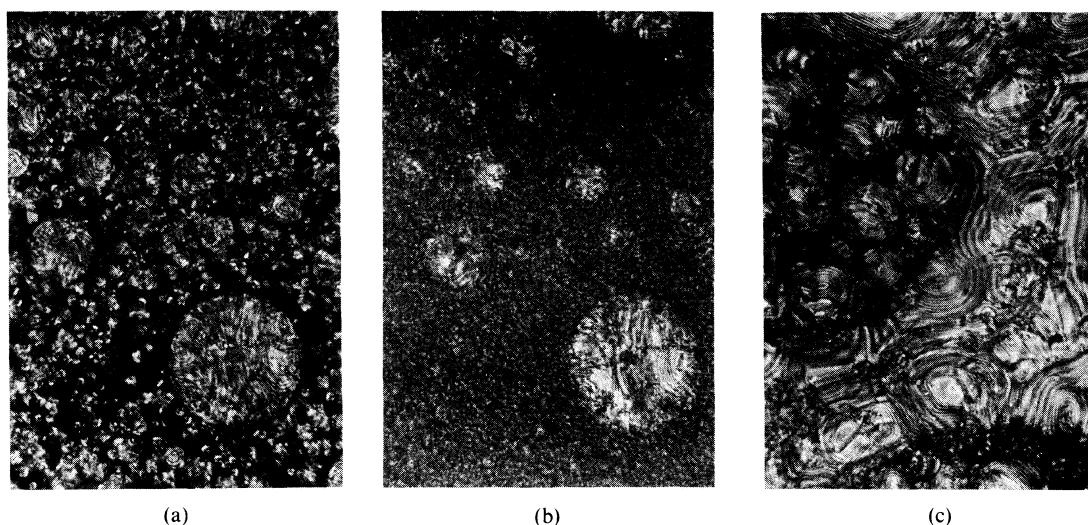
Figure 1. Microphotographs for polymer II-2 on cooling cycle: (a) at 250°C; (b) at 228°C; (c) annealed at 226°C for 6 hours.

Table I. Yields and properties of copolyesters of series II[a]

Polymer	Yield %	Molecular weights[b]			$[\eta_{inh}]^c$ dl g^{-1}	Thermal transitions °C			$Z_m{}^d$
		$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$		T_m	T^*	T_i	
II-1	90	62000	130000	2.1	0.93	154	190	249	0.50
II-2	88	15000	66000	4.5	0.59	142	188	240	0.49
II-3	80	4100	21000	5.1	0.26	128	191	228	0.49

[a] $Y = H$, $x = z = 50$.
[b] Based on polystyrene standards.
[c] Inherent viscosities in p-chlorophenol at 45°C.
[d] Mole fraction of I in the copolyesters according to eq 1.

series of copolyesters should also contribute to their biphasic behavior as previously reported for other types of nematic liquid crystalline copolymers.[7–10]

As predicted theoretically[11] the molecular weight dependence of the isotropization transitions is observed to be quite strong at low molecular weights. We expect low molecular weight copolyesters to be biphasic morphology over a wide temperature range, therefore, a series of copolyesters having relatively lower molecular weights were prepared, their properties are collected in Table I,

and DSC thermograms of the second heating cycles are shown in Figure 2. The isotropization transition temperature, T_i, and the melting transition temperature, T_m, decreased slightly, while the transition temperature from a smectic C phase to a cholesteric phase, T^*, did not change with decreasing molecular weight. In addition, the lower molecular weight copolyester had the broader molecular weight distribution and the broader isotropization transition peak. By the polarized light microscope, the wider temperature range of the biphasic morphology was observed for the

lower molecular weight copolyesters.

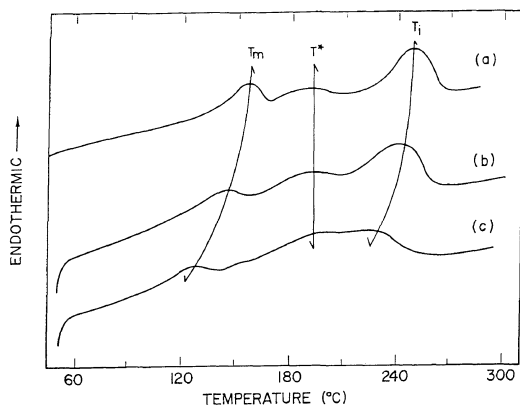Furthermore, this series of copolyesters were fractionated by extraction with acetone.

Figure 2. DSC thermograms for copolyesters series **II** having different molecular weight on the second heating: (a) **II**-1; (b) **II**-2; (c) **II**-3. T_m, crystalline-to-smectic phases transition; T^*, smectic-to-cholesteric phases transition; T_i, isotropization transition.

Polymer **II**-1 and **II**-2 yielded less than 1 and 2% of acetone-soluble fractions, respectively, while Polymer **II**-3 yielded 10% of an acetone-soluble fraction, so Fractions 3a and 3b were characterized by a GPC, DSC, polarized light microscopy and ^{1}H NMR, with the results collected in Table II. The acetone-soluble fraction, Fraction 3b, exhibited an identifiable cholesteric texture between T_m and T_i in both the heating and cooling cycles, and it had a lower T_i with a lower molecular weight and a higher content of monomer I, Z_m, than the original copolyester, **II**-3. The acetone-insoluble fraction, Fraction 3a, had a higher T_i by 5°C and a lower content of monomer **I**. As these results, Series **II** copolyesters demonstrate a molecular weight distribution and chemical heterogeneity existed within the copolyesters and that the relatively lower molecular weight fraction with the higher

Table II. Yields and properties for fractionated copolymers

Copolymer[a]	Yield[b] %	Molecular weights			Thermal transitions[c] °C			Z_m[d]
		$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	T_m	T^*	T_i	
II-3	—	4100	21000	5.1	128	193	228	0.49
Fraction **3a**	90	4700	22500	4.8	128	193	232	0.47
Fraction **3b**	10	1600	2800	1.8	66	—	144	0.62

[a] Fraction **3a**, acetone-insoluble fraction; Fraction **3b**, acetone-soluble fraction.
[b] Yields were determined based on the initial amount of Copolymer **II**-3.
[c] T_m, crystalline-to-smectic phases transition; T^*, smectic-to-cholesteric phases transition; T_i, isotropization transition.
[d] Mole fraction of **I** in the copolyesters according to eq 1.

Table III. Molecular weight data of polymer series **III**

Copolymer	Composition		Molecular weight[a]			$[\eta_{inh}]$[b] dl g^{-1}
	x	y	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	
III-1	20	80	72000	202000	2.8	0.91
III-2	50	50	47000	160000	3.4	1.01
III-3	80	20	14000	48000	3.4	0.42

[a] Based on polystyrene standards.
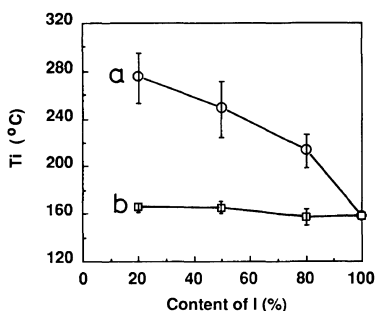[b] Inherent viscosities in *p*-chlorophenol at 45°C.

Figure 3. Isotropization transition temperatures for copolyesters, series **II** and **III**, with different compositions: (a) Series **II**; (b) Series **III**. (The peak maxima was plotted, and the temperature range of the peak was shown as a bar.)

content of **I** in the copolyesters undoubtedly contributed to formation of the unique biphasic morphology.

On the other hand, for the copolyesters Series **III**, the biphasic morphology could not be clearly observed even though the sample was annealed close to the isotropization transition. Molecular weight data and phase transition behaviors of Series **III** having different compositions are shown in Table III and Figure 3, comparing with that of a series of polymer **II**, respectively. In Series **III**, the isotropic transition temperatures changed within only 10°C over the different compositions, and the isotropic transition peaks were very sharp, whose widths were less than 15°C even though their molecular weight distributions were broader than three. Because the isotropic transition temperature was not influenced by the composition of the copolyester, the chemical heterogeneity did not presumably contribute to formation of the biphasic morphology. In contrast, copolyesters Series **II** were shown that an increase in the content of monomer **I** greatly depressed T_i, so the biphasic morphology which caused the chemical heterogeneity was apparently observed. The chemical heterogeneity usually occurs in copolymerization of several monomers having different reactivities to yield macromolecular chains with different chemical compositions. That miscibility between these chains may be different depending on the chemical composition and on the molecular weight also presumably causes formation of the biphasic morphology.

In conclusion, for this series of cholesteric main chain copolyesters exhibit a cholesteric–isotropic biphase close to the isotropization transitions, which is influenced by a substituent of the copolymerized non-chiral hydroquinone monomer. The biphasic formation occurred for the copolyesters with hydroquinone over a wider temperature range presumably because of both molecular weight and the chemical heterogeneity effects on the isotropization transition.

REFERENCES

1. K. Fujishiro and R. W. Lenz, *Macromolecules*, **25**, 81 (1992).
2. K. Fujishiro and R. W. Lenz, *Macromolecules*, **25**, 88 (1992).
3. E. Chiellini, G. Galli, S. Carrozzino, and B. Gallot, *Macromolecules*, **23**, 2106 (1990).
4. H. J. Park, J. Jin, and R. W. Lenz, *Polymer*, **26**, 1301 (1985).
5. C. Malanga, N. Spassky, R. Menicagli, and E. Chiellini, *Polym. Bull.*, **9**, 328 (1983).
6. E. Chiellini, G. Galli, C. Malanga, and N. Spassky, *Polym. Bull.*, **9**, 336 (1983).
7. P. G. Martin and S. I. Stupp, *Macromolecules*, **21**, 1222 (1988).
8. S. I. Stupp, J. S. Moore, and P. G. Martin, *Macromolecules*, **21**, 1228 (1988).
9. J. F. d'Allest, P. P. Wu, A. Blumstein, A. B. Blumstein, *Mol. Cryst. Liq. Cryst. Lett.*, **3**, 103 (1986).
10. C. K. Ober, S. MacNamee, A. Delvin, and R. H. Colby, *Polym. Prepr.*, **30** 2, 485 (1989).
11. A. Keller, G. Unger, and V. Percec, in "Liquid-Crystalline Polymers," R. A. Weiss and C. K. Ober, Ed., American Chemical Society, Washington D.C., 1990, Chapter 23.