

THERMOTROPIC LIQUID CRYSTALLINE POLYMERS. AROMATIC COPOLYESTERS CONTAINING SUBSTITUTED BENZENE RINGS AND KINKING COMPONENTS*

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ABSTRACT

A series of copolyesters were prepared from chloro-hydroquinone or methyl-hydroquinone, terephthalic acid, and two kinds of comonomers, such as oxy-4,4'-diphenol and isophthalic acid, which could provide kinking and bending in chain.

The four-components copolyesters in certain range of compositions have low melting point, steady mesophase in a broad temperature range and fiber-forming tendency.

This report focuses on the relations of their molecular composition-transitions-liquid crystallinity and fiber-forming tendency, and the morphologic characterizations of mesophase.

Thermotropic liquid crystalline polymer is a new interesting field in recent years. This type of polymers offers a great potential in combination of ease of processability with superior mechanical properties.

The basic structure of liquid crystalline polyesters consists of para-substituted benzene ring, but the homopolyesters derived from the rigid monomers: p-hydroxy-benzoic acid or hydroquinone and terephthalic acid are much too intractable for melting processing. Other monomers must be introduced that would increase tractability enough so that melting processing is possible. Several approaches could be used: introducing flexible spacer units, introducing substituted units or/and nonlinear aromatic comonomer units which could provide kink in the chain.

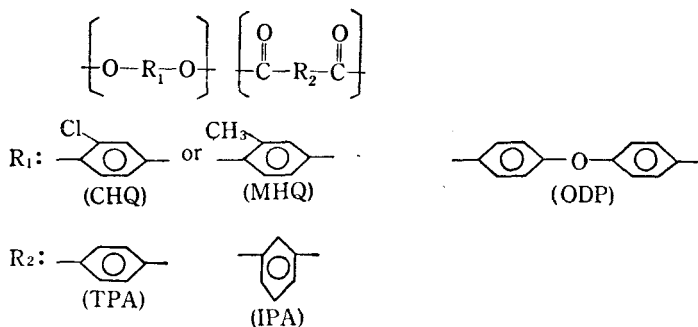
In the previous paper^[1], the aromatic copolyesters of p-acetoxybenzoic acid containing naphthalene rings were reported. This series of polymers in certain range of compositions displayed apparent liquid crystallinity and fiber-forming tendency.

The liquid crystalline copolyesters having side-substituted benzene rings were reported in earlier literatures^[2,3]. Most of these are three-components copolyesters. They have rather narrow mesophase range.

In this report, a series of copolyesters were prepared from chloro-/ or methylhydroquinone, terephthalic acid and two types of kinking components: oxy-4,4'-diphenol (semirigid kinking) and isophthalic acid (rigid bending). By selecting the ratio of compositions, we have prepared the polymers, which display the following characteristics: low melting point, strong stir-opalescence in a broad temperature range and fiber-forming tendency.

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This polymers have the structures as follows:



This paper focuses on the relations of composition-transitions-liquid crystallinity and fiber-forming tendency; and the morphologic features of mesophase of these copolyesters were characterized by polarized microscope, small-angle light scattering, X-ray diffraction.

EXPERIMENTAL

Preparation of copolyesters

All of the copolyesters were prepared by melting polycondensation from diphenol (chloro- or methyl-hydroquinone, oxy-4,4'-diphenol) diacetate and dicarboxylic acid (terephthalic acid, isophthalic acid). Detailed procedures were described previously^[1].

These copolyesters are insoluble or part-soluble in common solvents of polyesters such as o-chlorophenol, phenol/tetrachloroethane etc.

Test of spinnability

To dip one end of a long steel knife into the thick melt of polymer and then draw the melt out into a fiber.

Polymer characterizations

The thermal properties were measured under a nitrogen atmosphere on the Du Pont Type 1090 Thermal Analyzer coupled to the DSC modul with a heating rate of 20°C/min.

For microscopy and small-angle light scattering studies, a small amount of the polymer sample was placed between two microscope cover glasses on an oven, which had been preheated to a temperature of 40–50°C above the polymer melting point. After the sample melted completely, the melt was rapidly quenched and stored at room temperature. The optical texture of the samples was studied by using a microscope equipped with a pair of crossed polarizers. The small-angle light scattering characteristics of the sample were examined by a He-Ne (6328 Å) laser fitted with a red filter on an optical bench with a pair of crossed polarizers.

X-ray diffraction spectra were obtained using diffractometer with CuK_α -radiation. The quenched and annealed samples were reserved for X-ray analysis.

RESULTS AND DISCUSSION

The two series (Chloro- and Methyl-) copolyesters were synthesized. The results indicated that there are some similarities between the two series of copolyesters in the relations of

molecular composition-transitions, although these two kinds of substituents are different in their polarity. It is apparent that, in general, the steric effect is more important for L. C. polymers.

The results reported here arise from efforts to discuss the effects of kinking components.

Three-components copolyesters containing rigid bending components (IPA)

Fig. 1 is DSC thermogram of the three-components copolyesters containing different contents of rigid bending components (IPA). A number of endotherms were found. The stirr- opalescence of melt is very weak, it could not be drawn into a fiber.

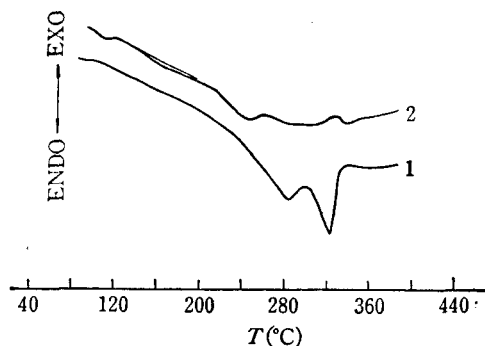


Fig. 1 Thermogram of CHQ/TPA/IPA three-components copolyesters
Composition (mole %):
Curve 1 100/80/20; 2 100/70/30

Three-components copolyesters containing bisphenol units with kinking spacer (ODP)

Fig. 2 includes a group of DSC curves of chloro-copolyesters. They indicates the effect of content of bisphenol on melting transitions. The copolymer containing less of ODP (curve 1)

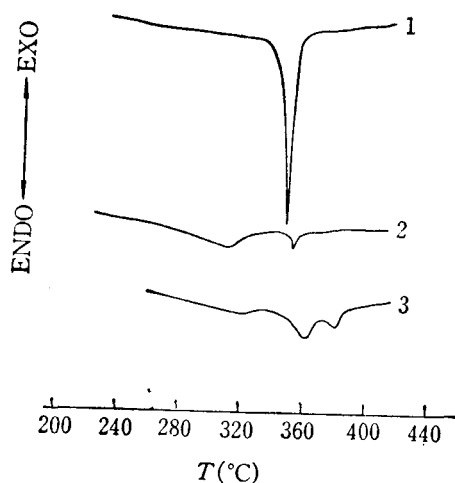


Fig. 2 DSC thermogram of CHQ/ODP/TPA copolyesters
Composition (mole %):
Curve 1 80/20/100; 2 70/30/100; 3 60/40/100

shows a sharp and well-defined melting transition. The copolymers containing 40 mole % (curve 3) or more of ODP show a number of melting peaks. The exception is the copolymer containing 30 mole % of ODP (curve 2), which exhibits somewhat of stir-opalescence, but the temperature range of mesophase is narrow.

It is interesting that, based on the above-mentioned three-components, incorporating rigid bending components such as IPA to substitute a part of TPA, the formation of a steady mesophase in a broad temperature range is resulted. It is helpful to spinning in mesomorphic state.

Comparison between three-components and four-components copolyesters

Fig. 3 shows a group of DSC curves of chloro-copolyesters containing 30 mole % of ODP. Curve 0 is the thermogram of the three-components copolyesters. It contains two endotherm peaks, one for melting point and another one at elevated temperature for the transition from the anisotropic to isotropic melt (T_i). Curve 1, 2, 3, 4 are the DSC thermograms of the four-components copolyesters with different contents of IPA. Fig. 4 shows another group of DSC

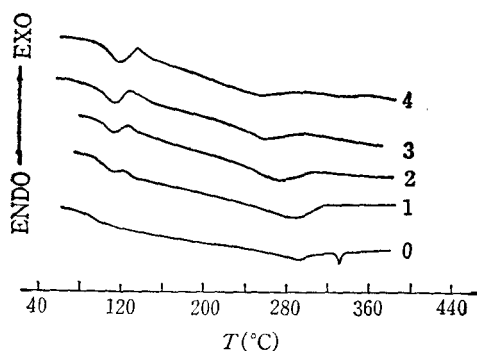


Fig. 3 Thermograms of CHQ/ODP/TPA/IPA copolyesters (containing 30 mole % of ODP)
Content of IPA (mole %):
Curve 0 (0); 1 (10); 2 (15); 3 (20); 4 (25)

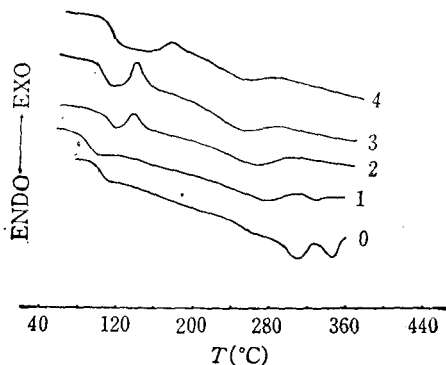


Fig. 4 Thermograms of MHQ/ODP/TPA/IPA copolyesters (containing 30 mole % of ODP)
Content of IPA (mole %):
Curve 0 (0); 1 (10); 2 (15); 3 (20); 4 (25)

curves of methyl-copolyesters containing 30 mole % of ODP, it is the same as that of Fig. 3. Fig. 5 shows a group of DSC curves of chloro-copolyesters containing 20 mole % of ODP. The lower curve is for the three-components copolyesters. It contains a sharp melting peak, the upper curves is the DSC thermogram of four-components copolyesters containing 30 mole % of IPA.

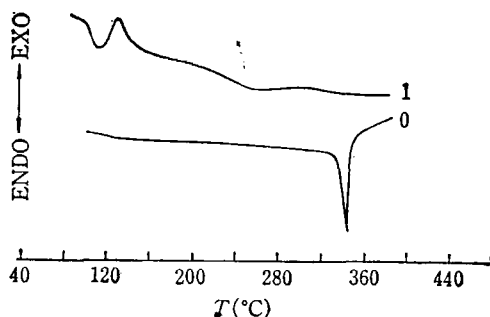


Fig. 5 Thermograms of CHQ/ODP/TPA/IPA copolyesters containing 20 mole % of ODP
Content of IPA (mole %):
Curve 0 (0); 1 (30)

In contrast to the above-mentioned three-components copolyesters, in the thermograms of the quenched four-components copolyesters (in certain range of compositions), the glass-transition (T_g), cold crystallization (T_{cc}) and melting transition (T_m) were recorded with the increase of temperature, the melting peak is broad and shallow, the isotropic transition (T_i) could not be detected till 430°C (except the methyl-copolyester containing 10 mole % of IPA) (above 430°C, the melt would be extruded out from sample cell). T.O.A (off-set polarized, thermal-optical-analysis) also demonstrated that strong birefringence was retained untill the upper test limit was reached. These four-components copolyesters exhibit pearl-like gloss and spinnability. Table 1 illustrates the differences between three-components and four-components copolyesters in melting transition, liquid crystallinity and spinnability.

It is well known, that the helical-wormlike (HW) model was proved to be useful for theoretical understanding of mesomorphic polymer system^[4,5]. HW chain is defined as an elastic wire model with both bending and torsional energies, such that when its total configurational energy becomes a minimum, its contour takes a helical form. We suppose that HW model could provide a phenomenal explanation: the concerted effect of two types of kinking components: semirigid kinking components (such as bisphenol containing kinking spacer) and rigid bending components (such as meta-substituted benzene ring) may facilitate the formation of helical wormlike conformation, so that the steady mesophase could be formed. It is a very interesting and practical result.

The effect of content of IPA on transition

As seen from Figs. 3, 4, 5, we noticed that, the cold crystallization peak (T_{cc}) shifted to right (higher temperature) with increasing content of rigid bending components (IPA), and melting peak (T_m) shifted to left (lower temperature) with increasing content of IPA (see Tab. 2). These regular experimental results might provide more evidence for above supposition.

Table 1 Comparison between three-components and four-components copolyesters

Number	Composition (mole %)					T_m (°C)	T_i (°C)	Stir- opalescence	Spinn ability
	CHQ	MHQ	ODP	IPA	TPA				
C-1	70		30	0	100	308.6	351.3	Strong	Poor
2	70		30	10	90	289.1	—	Very strong	Good
3	70		30	15	85	266.9	—	Very strong	Good
4	70		30	20	80	256.8	—	Very strong	Good
5	80		20	0	100	346.5		—	—
6	80		20	30	70	254.7	—	Very strong	Good
M-1		70	30	0	100	307.4	346.0	Strong	Poor
2		70	30	10	90	291.2	347.0	Strong	Good
3		70	30	15	85	259.4	—	Very strong	Good
4		70	30	20	80	250.9	—	Very strong	Good

Table. 2 Effect of content of rigid bending components (IPA) on transitions*

Content of IPA mole (%)	T_{cc} (°C)	T_m (°C)
10	121.2	289.1
12.5	124.5	279.7
15	127.3	266.9
20	127.7	256.8
25	133.3	251.4
30	135.0	248.5
35	139.9	235.4

* Taken from DSC thermograms of quenched sample of CHQ/ODP/TPA/IPA copolyesters

The cold crystallization taken place above the glass transition is ascribed to local ordering of segments of polymer, resulting in the formation of small imperfect metastable crystallites. In the case of stretch-oriented flexible polymer (such as PET), the cold crystallization also can be observed^[6]. In the case of the liquid crystalline polymers, by quenching the polymers from the anisotropic melts, solids with a certain disorder would be formed, which at low temperature undergo a local rearrangements towards a more highly ordered phase, the rigid core moiety or domain may be used as the "nucleus of crystal" in solid phase^{[7][8]}. With the increase of percentage of rigid bending components (IPA), the helical would become tighter, so local ordering of segment would become more difficult. On the other hand, the rigidity of chain and intermolecular interaction energy would decrease, so that the melting peak would

shift to lower temperature.

Morphologic features of mesophase

The morphologic features of these copolyesters were characterized by polarized microscope, small-angle laser light scattering, X-ray diffraction, etc.

Typical Schlieren optical texture of nematic state were observed on cross-polarizing microscope for both melt and freeze-in mesophase film. The shearing-oriented thin film has been examined using polarized microscope, and row-like or banded structure with the striations perpendicular to the shearing direction was observed. Fig. 6 a, b are the optical micrographs for the quenched films in the both cases. These structures are remarkably similar to that recorded in lyotropic polymer systems. Small-angle light scattering patterns (Hv) of quenched melt film were circular (Fig. 7 a) and patterns of shear-oriented thin film were strengthened in the shearing direction (Fig. 7 b). It could be explained in terms of grating effect of row-like structure.

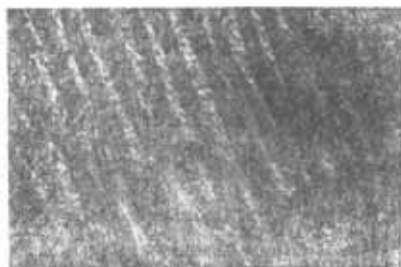


Fig. 6 Optical micrograph for the quenched film of thermotropic L.C. copolyester



Fig. 7 The patterns of small-angle scattering (Hv) of the quenched films of thermotropic L.C. copolyester

X-ray diffraction curves of the quenched and annealed sample of L. C. copolyester are shown in Fig. 8. The curve of quenched sample in ice-water is similar to that of amorphous polymers. There is a broad diffuse maxima near 20° . Using X-ray diffraction results of L. C. compounds as reference^[9], it is related to a short range order of the molecule. This is one of characteristics of freeze-in nematic phase.

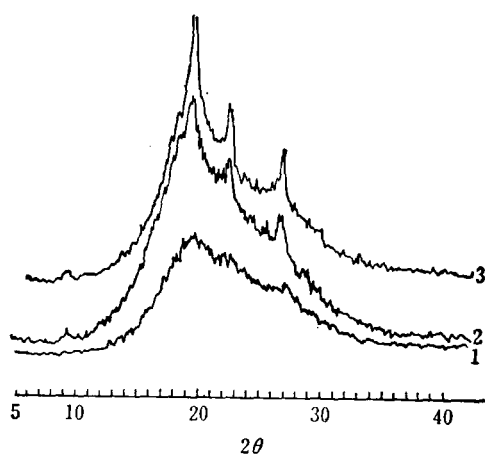


Fig. 8 X-ray diffraction curves for L.C. copolyester

REFERENCES

- [1] 谢萍、陆道惠、郑树洪、黄琦、宝净生等《全国高分子学术论文报告会论文摘要集》(杭州)1983, 247页。
- [2] Kleinschuster, J.J. and Pletcher, T. C., *U.S.P.* 4,066,620, 1978.
- [3] Lenz, R.W. and Jin J.-I. *Macromolecules*, 1981, 14, 1405—1411.
- [4] Ten Bosch A., Maissa P. and Sixou P., *Polymer. Preprints*, 1983, 24, 246.
- [5] Motoharu Fujii, Kyosuke Nagasaka, Jiroschimada and Hiromi Yamakawa, *Macromolecules*, 1983, 16, 1613—1623.
- [6] Hamidi A., Abhiraman A.S. and Asher P., *J. Appl. Polym. Sci.*, 1983, 28, 567—578.
- [7] Vittorio Frosini, Augusto Marchetti, Silvano de petris. *Makromol. Chem., Rapid Commun.* 1982, 3, 795—801.
- [8] Janusz Grebowicz and Bernhard Wunderlich. *J. Polym. Sci. Phys.*, 1983, 21, 141—150.
- [9] Bata L., "Advances in liquid crystal research and applications" (Proc. Third. Liq. Crys. Conf.), 1979, 943.