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Synthesis and mesomorphic behaviour of some aromatic polyesters

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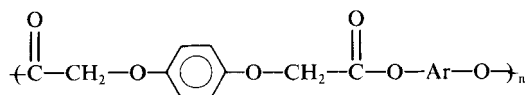
(Received 4 May 1987; accepted 17 December 1987)

Six new aromatic polyesters were synthesized by the phase-transfer catalytic polycondensation. The polymers obtained were characterized by infra-red, X-ray diffraction, D.S.C., depolarized light intensity and polarizing microscope. Poly(*p,p'*-hydroquinone-1,4-phenylene dioxyacetate) and poly(*p,p'*-hydroquinone-1,4,7-trioxaheptamethylene dibenzoate) were found to be thermotropic liquid crystals but related polyesters are not. The results are discussed on the basis of the thermodynamic data obtained.

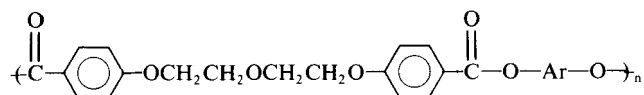
1. Introduction

In recent years there has been increased interest in the liquid crystal polymer consisting of the mesogenic units and the flexible spacers in the main chain [1-5]. These polymers were first reported by Roviello and Sirigu in 1975 [1]. In the same year de Gennes predicated theoretically that these polymers would be nematic [2]. Recently Lenz *et al.* reported their preliminary findings on the thermotropic liquid crystal behaviour of several series of new polyesters in relation to the chemical structure [3, 4]. In order to study the effect of structural variations on thermodynamic properties of aromatic polyesters mesophases, we have attempted to synthesize two series of new polyesters with the following structures:

- (1) Polyesters prepared from 1,4-phenylene dioxyacetyl chloride and aromatic diols (hydroquinone, bisphenol A, phenolphthalein)



- (2) Polyesters prepared from 1,4,7-trioxaheptamethylene dibenzoyl chloride and aromatic diols

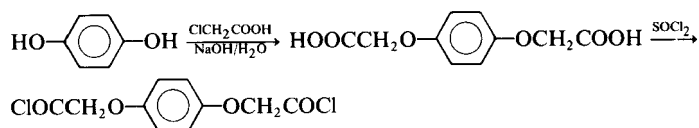


2. Experimental

2.1. Preparation of monomers

All reagents were obtained commercially and purified either by recrystallization or distillation under reduced pressure. 1,4-phenyldioxyacetyl chloride was synthesized

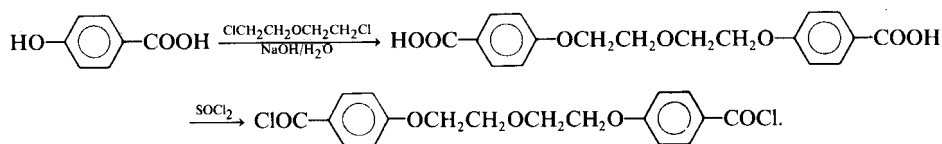
by the method [6] shown in the following scheme:



First, hydroquinone was condensed with chloroacetic acid under alkaline conditions. The crude product was recrystallized from acetic acid; m.p. of the product obtained is 251–252°C (yield 74 per cent).

Second, the above product was reacted with thionyl chloride. The crude product was recrystallized from *n*-hexane to give the 1,4-phenyldioxyacetyl chloride, m.p. 83.5–84°C yield 60 per cent.

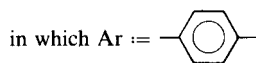
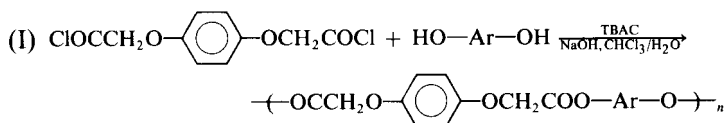
1,4,7-Trioxaheptamethylene dibenzoyl chloride was prepared by the standard procedure [7] shown in the following scheme:



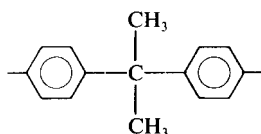
The first crude product was washed several times with distilled water and dried (m.p. 298–299°C yield 70.5 per cent). Then 1,4,7-trioxaheptamethylene dibenzoic acid was reacted with thionyl chloride. The crude product was recrystallized from *n*-hexane to give the 1,4,7-trioxaheptamethylene dibenzoyl chloride, yield 61 per cent m.p. 146–147°C.

2.2. Synthesis of polymers

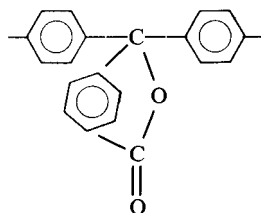
Polyesters were synthesized by the phase-transfer catalytic polycondensation as shown in the following two schemes:



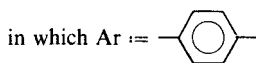
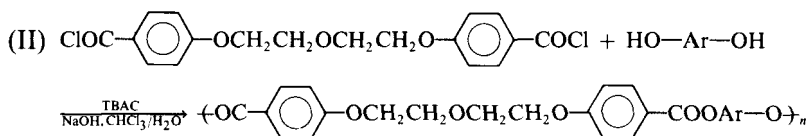
(APH polymer)



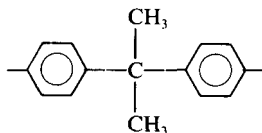
(APB polymer)



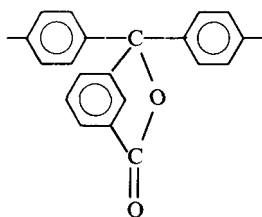
(APP polymer)



(BPH polymer)



(BPB polymer)



(BPP polymer)

Procedure. A chloroform solution of 1,4-phenyldioxyacetyl chloride or 1,4,7-trioxaheptamethylene dibenzoyl chloride was added to the water solution of aromatic diol, sodium hydroxide and tetrabutylammonium chloride (TBAC), at 0°C, in a blender. After rapid stirring for 15 min, *n*-hexane was added. The precipitate was filtered and washed with distilled water to eliminate Cl⁻.

2.3. Physical properties of polymers

Inherent viscosity measurements were performed in an Ubbelohde viscometer, using tetrachloroethane-phenol (40/60 w/w) as a solvent, at 30 ± 0.1°C. Polymers were characterized by infra-red, thermogravimetric analysis, and solubility in several solvents. X-ray powder spectra of polymers were taken on the DC-10X diffraction apparatus (CuK α radiation).

2.4. Mesomorphic behaviour of polymers

The thermal behaviour was determined with a Perkin-Elmer DSC-II instrument. All the runs were made under a nitrogen atmosphere with a heating or cooling rate of 20°C/min. The phase transition temperatures refer to the endotherm maximum point. For the evaluation of the transition enthalpies an indium sample has been used as a reference. The microscopic analysis employed a Leitz-Ortholux II Pol-BK polarizing microscope equipped with heating stage and a photographic camera was used. Depolarized light intensity analysis was taken and recorded on a DLI instrument made in our laboratory.

3. Results and discussion

The molecular weight of polyesters prepared by PTC polycondensation is relatively high. The properties of the polymers are presented in table 1. The characteristic infra-red absorption bands of these polymers are tabulated in table 2.

Table 1. Properties of polymers obtained.

Polymer	Yield (wt%)	η_{inh}^\dagger	m.p. (°C)	The quantitative elemental analysis			
				Calculated		Found	
				C (per cent)	H (per cent)	C (per cent)	H (per cent)
APH	91.3	0.319	217	64.00	4.03	65.70	3.65
APB	98.5	0.685	128	71.76	5.30	71.36	5.57
APP	96.2	0.419	Noncrystal	70.86	3.97	70.35	3.84
BPH	89.5	0.386	192	68.57	4.80	68.07	4.70
BPB	95.2	0.710	Noncrystal	73.58	5.63	71.62	5.10
BPP	94.8	0.492	Noncrystal	72.60	4.50	72.55	4.06

$^\dagger \eta_{inh}$ measurements were performed in an Ubbelohde viscometer using tetrachloroethane/phenol (40/60 w/w) mixture solvents, at $30 \pm 0.1^\circ\text{C}$.

Solubility. All polymers obtained are insoluble in the following solvents: acetone, cyclohexanone, *n*-hexane, carbon tetrachloride, methanol, acetic acid. There is good solubility in *m*-cresol, concentrated sulphuric acid and the 1,1,2,2-tetrachloroethane/phenol mixture, APB, APP, BPB, BPP polymers consisting of bisphenol *A* or phenolphthalein groups are also soluble in tetrahydrofuran and nitrobenzene.

Crystalline and liquid crystalline behaviour. The X-ray diffraction diagrams of the polymers are shown in figure 1. APH, APB and BPH polymers showed diffraction patterns typical of semicrystalline polymers, whereas APP, BPB, BPP polymers were noncrystalline polymers. Thermogravimetric analysis indicated that the decomposition temperature of these polymers were all over 330°C . APH, BPH polymers

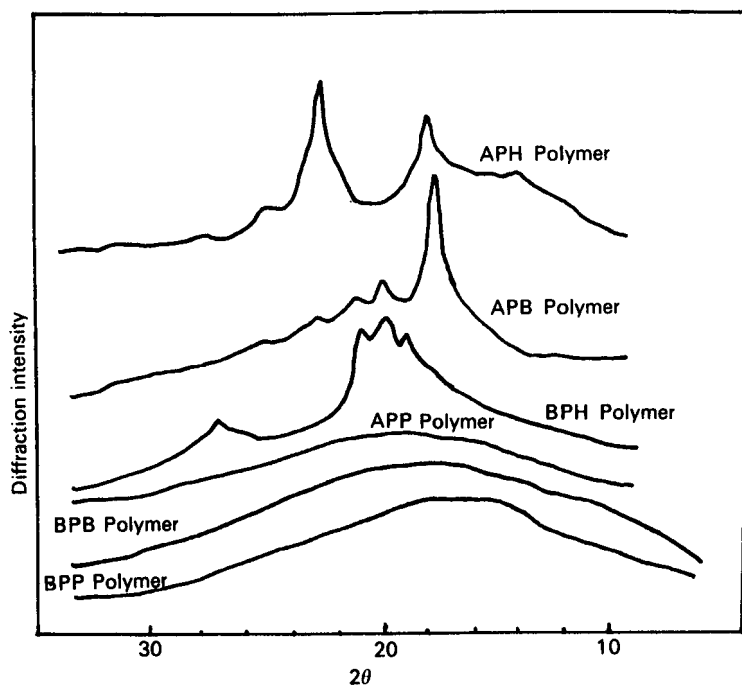


Figure 1. X-ray spectra of polymers.

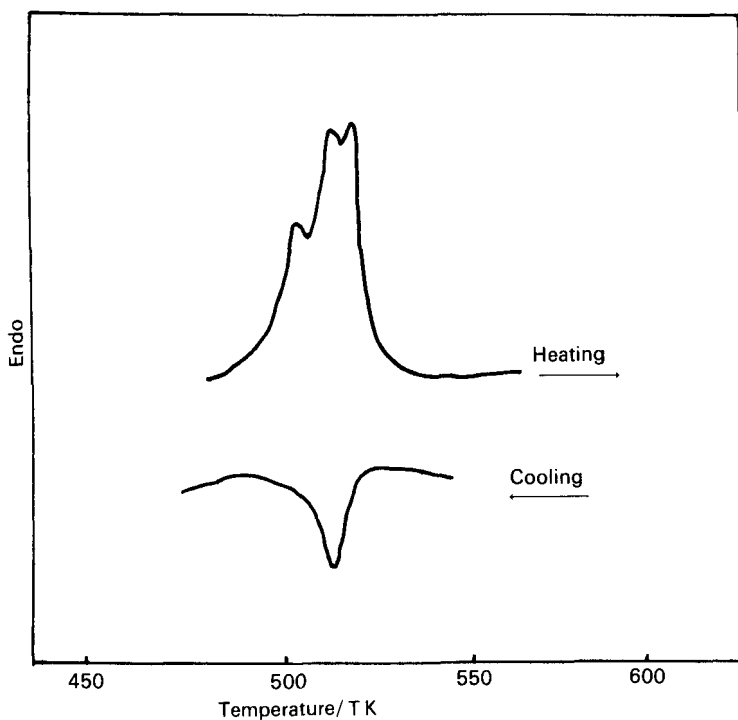


Figure 2. D.S.C. thermogram of APH polymer, the top curve is for heating, the bottom for cooling.

were found to be thermotropic liquid crystals by polarizing microscopy. Such polymers, consisting of mesogenic units and flexible spacers, coincide with de Gennes's predication [2]. APB, APP, BPB, BPP polymers in which chain backbones have unsymmetrical or large substituents did not exhibit liquid crystalline behaviour.

APH, BPH polymers formed turbid melts that show strong stir opalescence up to the transition temperature (i.e. the clearing point T_i) for the formation of an isotropic phase. Typical nematic threaded-schlieren optical textures were observed on a hot stage cross polarizing microscope. The transitions from the mesophase to the isotropic phase are reversible by visual observations on the microscope.

By slowly cooling ($2^\circ\text{C}/\text{min.}$) the anisotropic liquid, traces of the nematic thread texture were preserved down to room temperature in the solid phase, this is similar to the report of Roviello *et al.* [1]. It seems as if the linear singularities of the liquid crystal phase may act as nucleation lines for crystallization in such a way that the microcrystals ordering in the solid phase keeps some memory of the original semi-ordered liquid texture.

The D.S.C. thermograms of polymers shown in figures 2–3 contain broad endothermic peaks at elevated temperatures. They are believed to correspond to the transition from the liquid crystalline to the isotropic phase. The thermal behaviour depends upon the thermal history as shown in figure 3. The peak positions of the endotherm in the D.S.C. diagrams are slightly changed according to the thermal history.

The thermodynamic properties are summarized in table 3. The values of ΔH_i and ΔS_i for the BPH polymer are higher than those of the APH polymer, which implies that the mesophase of BPH polymer has a higher degree of molecular order. It also

Table 2. I.R. spectrum data of polymers obtained.

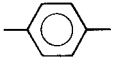
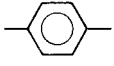
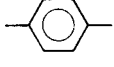

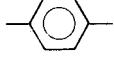
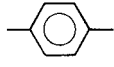
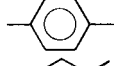

Polymer	Wavenumber (cm^{-1})	Probable assignment
APH	1778	$-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{Ar}$ 
APB	1776	$-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{Ar}-$
	817	
	1375	$-\text{CH}_3-$
APP	1760	$-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{Ar}-$
	827	
	756	
BPH	1730	$-\text{Ar}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Ar}-$
	815	
BPB	1730	$-\text{Ar}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{Ar}-$
	810	
	1390	$-\text{CH}_3$
BPP	1730	$-\text{Ar}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{Ar}-$
	815	
	750	

Table 3. Thermodynamic properties of polymers.

Polymer	T_i ($^{\circ}\text{C}$)	ΔT ($^{\circ}\text{C}$)	ΔH_i (kcal/mol.)	ΔS_i (cal/mol. K)
APH	250	33	0.74	1.41
BPH	237	45	1.19	2.33

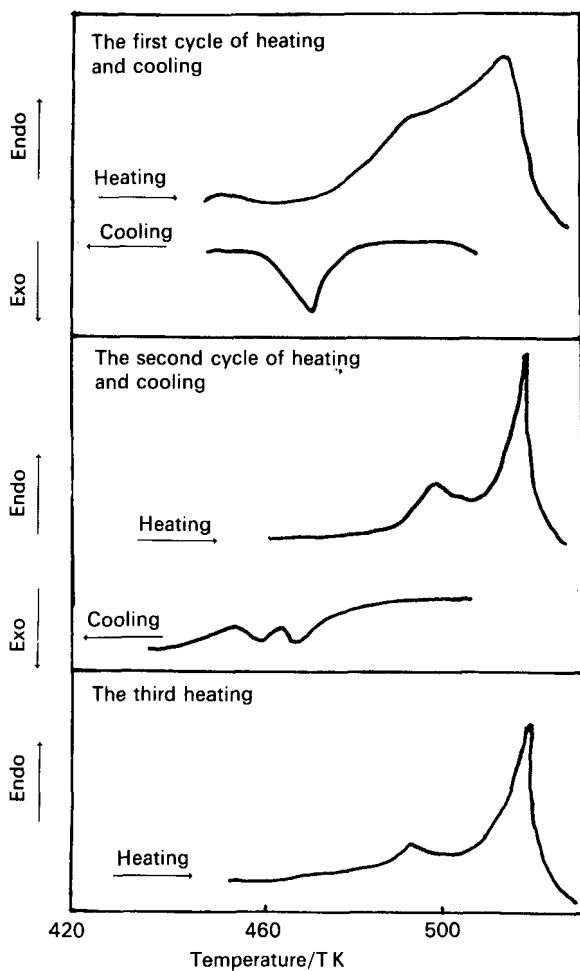


Figure 3. D.S.C. thermogram of BPH polymer.

indicates that the different structures of the liquid crystal polymers yield different thermotropic behaviour.

The depolarized light intensity (DLI) experiment of APH and PBH polymers indicate that APH, BPH polymers were liquid crystalline and their melts are strongly birefringent.

4. Conclusion

From this work, the following conclusions may be drawn. (1) Two series six new aromatic polyesters were synthesized and characterized. (2) APH and BPH polymers were found to be thermotropic liquid crystal polymers, while APB, APP, BPB and BPP polymers do not exhibit liquid-crystalline behaviour. (3) The liquid crystal polymers APH and BPH all appear to be nematic in nature. (4) The thermal behaviour of liquid crystal polymers may be affected by their structures and thermal history.

References

- [1] ROVIELLO, A., and SIRIGU, A., 1975, *Polym. Lett. Ed.*, **13**, 455.
- [2] DE GENNES, P. G., 1975, *C. r. Acad. Sci., Paris B*, **281**, 101.
- [3] JO, B. W., and LENZ, R. W., 1982, *Makromol. Chem. rap. Commun.*, **3**, 23.
- [4] JIN, J. I., ANTOUN, S., OBER, C., and LENZ, R. W., 1980, *Br. Polym. J.*, p. 132.
- [5] BLUMSTEIN, A., 1978, *Liquid Crystalline Order in Polymers* (Academic Press), p. 3.
- [6] BEILLSTEIN, *Handbuch der organische Chemie*, Vol. 1, p. 847.
- [7] HIDEO SAWADA, and AWASHI YASUE, 1964, *Kogyo Kagaku Zasshi*, No. 9, p. 1444.