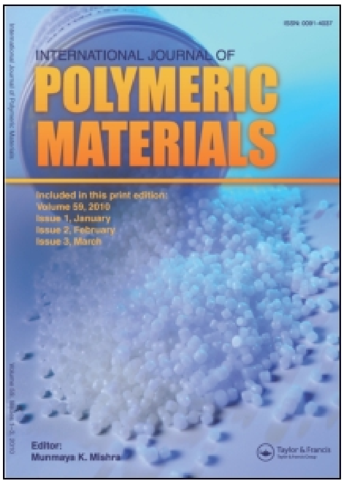

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Synthesis and Characterization of Thermotropic Liquid Crystalline Copolyester

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The thermotropic liquid crystalline copolyesters were prepared by direct polycondensation reaction of terephthalic acid, isophthalic acid, *p*-acetoxy benzoic acid with various diacetylated diols. All these copolyesters were characterized by their elemental analysis and spectroscopic techniques. The transition temperatures of all compounds are confirmed by DSC technique and optical texture of the copolyesters in liquid crystalline state were observed on polarizing microscope. Most of the polymers exhibit a typical nematic mesophase. All polymers have very good thermal stability.

Keywords: Thermotropic liquid crystalline copolyesters; nematic mesophase; thermal stability

INTRODUCTION

Thermotropic liquid crystal behaviour of polymeric system has been intensively investigated in recent years. Aromatic polyesters having main chain mesogenic units are among the most promising materials, however, it is recognized that it is necessary to disrupt the perfect regularity of sample para-linked aromatic polymers in order to lower the melting range to manageable levels.

In general, copolymers obtained are random or statistical in composition. Furthermore, the acidolysis reaction has been successfully

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applied to preparation of random copolyesters by interchanging monomers and high molecular weight polymers, most notably in the preparation of poly(ethylene terephthalate-co-oxybenzoate) by the insertion reaction of *p*-acetoxy benzoic acid with performed poly(ethylene terephthalate) [1, 2].

The problem of polymer solubility is particularly important, and can be a limiting factor, in the preparation of high molecular weight aromatic polyesters because such rigid polymers have, in general, both very high melting points and very low solubility in all presently available reaction solvents. As a results of these characteristics, and in order to achieve very high molecular weight, aromatic polyesters must be prepared by a two step sequence involving first either a homogeneous solution polymerization reaction or melt polymerization reaction to form a polymer of intermediate molecular weight, followed by a final reaction of the polymer in the solid state. This later reaction, often referred to as 'solid stating', occurs presumably in the non-crystalline phase of the semi-crystalline polymer at a temperature slightly below its melting point and, if carried out under high vacuum, is capable of generating very high molecular weight polymer [2].

EXPERIMENTAL

Materials

Terephthalic acid, isophthalic acid (Aldrich) and all other chemicals were of high purity and were further purified by standard methods [3]. A general procedure for acetylation was applied for all diols [4, 5]. Acetylated diols were recrystallized from alcochol or acetic acid-water.

Synthesis of Copolyesters

The reactor was a three necked round bottomed flask (100 or 250 ml) equipped with mechanical glass stirrer and a condenser. A salt bath with an adjustable temperature from 20 to 400°C was used. The system was purged with nitrogen for 5 min before use.

A general polymerization procedure was used for all experiments; A mixture of 4,4′-diacetoxy diols (0.08 mol), *p*-acetoxy benzoic acid

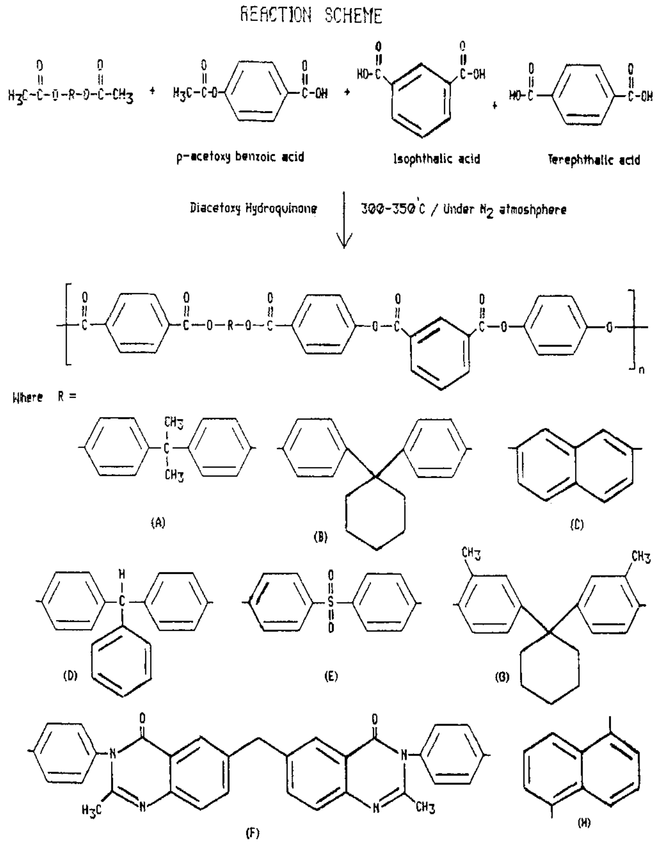
(0.287 mol), terephthalic acid (0.083 mol), isophthalic acid (0.028 mol) and acetylated hydroquinone (3.11 g) were placed in a polymerization reactor. The monomer mixture was heated to melt (220–280°C) and then raised to 300°C over a period of 60 min. During that time maximum percentage of acetic acid was evolved. After that time removal of acetic acid was nearly nil, the nitrogen flow was halted and low vacuum was employed. The pressure was slowly reduced to < 1 mm for 30 min. at 350°C. Subsequently, the vacuum was released, and the reactor was cooled to room temperature in cold water, the product was recovered and powdered using a mortar and pestle.

Measurements

Microanalysis of the compounds was performed on Heraeus Elemental analyzer CHN-O-RAPID instrument. IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer using the KBr pellet technique. Liquid crystalline properties were studied on Leitz-Labrolux II polarizing microscope providing with heating stage. DSC thermograms were investigated on a Du Pont 9900 thermal analyzer conducted to a Du pont 910 differential scanning calorimeter module at a heating rate of 10°C min^{-1} in a nitrogen atmosphere. Thermogravimetric analysis of all copolyesters were performed on Du Pont 951 thermal analyzer coupled with plug in module model 990 thermal analyzer at heating rate of 10°C min^{-1} in a N_2 atmosphere.

RESULTS AND DISCUSSION

All copolyester were characterized by elemental analysis, their results were found satisfactory in accordance with calculated values. The copolyesters are almost insoluble in all common organic solvents and solvent combinations as chloroform, xylene, cresols, phenol, *p*-chlorophenol, phenol/1,1,2,2-tetrachloro ethane (60/40), phenol/chloroform (60/40) etc. However polymer B, C, D (reaction scheme) were found to be sparingly soluble in a mixture of phenol/*p*-chlorophenol/tetrachloroethane (25/40/35).



Examination of the IR spectra of all the copolyesters revealed that many of the characteristics due to structural features are common. Some selected IR spectra of the copolyesters are shown in Figure 1. All the spectra showed common characteristic bands in the region 1740–1745 cm^{-1}, due to the carbonyl ($C = O$) group of ester linkage of polyester. Medium bands at 1600 cm^{-1} and 1500 cm^{-1} confirms the presence of ($C = C$) and broad absorption band between 1220–1250 cm^{-1} confirms the presence of C—O—C of ester linkage. Other characteristic bands are; the weak bands at 2930–2850 cm^{-1} due to CH_3 stretching vibrations and at 1190 cm^{-1} are due to gem dimethyl group of bisphenol-A in polymer G and A respectively. Three bands at 1160, 1070 and 585 are due to —SO_2, — ($S = O$)— and C —S stretching for

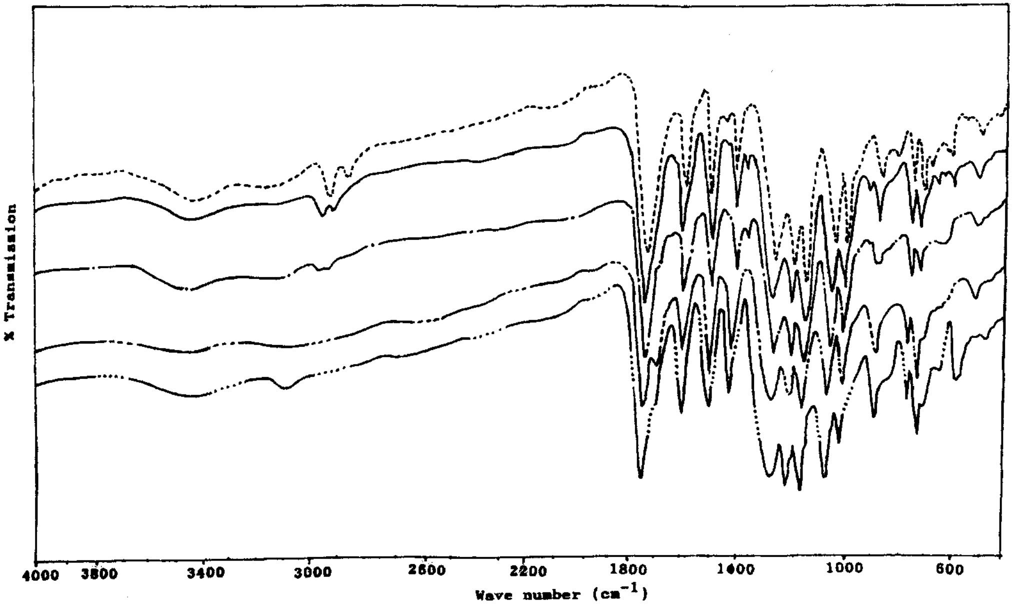


FIGURE 1 IR spectra of copolyesters (1) A (– – –), (2) B (— · —), (3) C (———), (4) D (— · · · —) and (5) E (— ···· —).

polymer E. A strong band at 1300 cm^{-1} and medium band at 1320 cm^{-1} are due to N—Ph stretching vibration bands and broad band in the region between 3100 – 3450 cm^{-1} is due to N —H stretching vibration in polymer E.

Differential scanning calorimetric analysis was performed on all the samples between 30 – 550°C under nitrogen atmosphere. Dispite the fact that the recorded DSC thermograms were difficult to interpret, except for glass transition temperature (T_g) (Tab. I). Most of the polymers exhibited the multiple melting endotherms on DSC analysis. DSC thermogram of polymer A, B, D and G shows that the melting temperature of polymer A and D are lower than that of polymer B and G. This can be attributed to the flexible alkyl group of bisphenols. An introduction of substituted methyl group (polymer G) on polymer B, slightly decreases the endotherm peak and transition temperature because linearity is disturbed with increase in molecular breadth.

The optical textures of the polymers in liquid crystalline state were observed on a hot stage attached with polarizing microscope, most of

TABLE I % Yield, elemental analysis, transition temperature, glass transition temperature and melting temperature of copolyesters

Polymer No.	*Transition Temperature* $^{@}$	*Elemental analysis* %*C* *Found* (*cal*)	%*H* *Found*(*cal*)	% *Yield*	T_g (°*C*)	T_m (°*C*)
A	$K \xrightarrow{302^\circ C} N$	73.2 (73.5)	4.4 (4.2)	90.1	173	320
B	$K \xrightarrow{308^\circ C} N$	74.6 (74.4)	4.3 (4.4)	88.3	184	373
C	$K \xrightarrow{250^\circ C} N$	71.8 (72.0)	3.1 (3.2)	89.4	–	–
D	$K \xrightarrow{305^\circ C} N$	74.9 (75.6)	4.1 (4.3)	92.5	119	350
E	$K \xrightarrow{303^\circ C} N$	85.1 (84.9)	3.9 (4.1)	91.2	170	325
F	$K \xrightarrow{270^\circ C} PM \xrightarrow{300^\circ C} U$	84.5 (84.9)	4.4 (4.6)	87.5	125	375
G	$K \xrightarrow{303^\circ C} N$	74.9 (74.6)	4.9 (5.1)	88.2	169	300
H	$K \xrightarrow{303^\circ C} N$	71.8 (72.0)	3.2 (3.3)	89.8	–	390

Where, K = Crystalline solid, N = Nematic, I = Istotropic, PM = Partially melt,
U = Remain unchanged,
@ = Transition temperature observed under hot-stage polarizing microscope,
T_g and T_m were observed from DSC measurements.

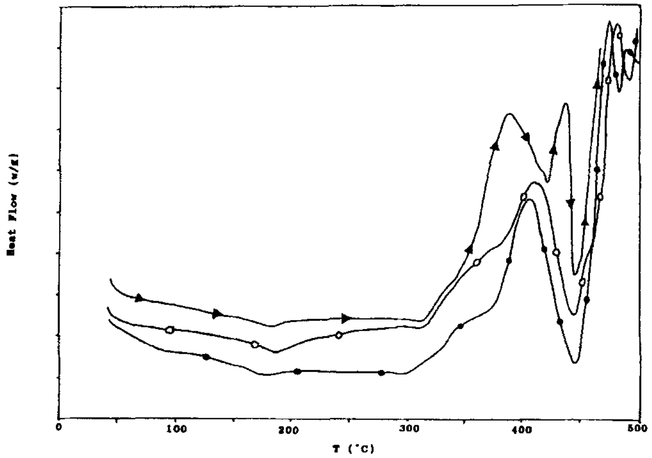


FIGURE 2 Dynamic DSC scans at 10°C min^{-1} for the copolyesters (1) A (—▶—), (2) (—o—) (3) (—•—).

the polymers exhibit a typical nematic phase (Tab. I). The liquid crystalline properties of copolyester of 1,5- and 2,7-naphthalene diol based in this series was checked based on optical textures observed for the polymer melt on a polarizing microscope, polymer H(1,5-napthalene diol based) was found to be mesomorphic, they showed the so called schlieren texture typical of nematogen while polymer C (2,7-napthalene diol based) did not show any melting, suggest that it is intrinsically amorphous or extremely slow in crystallization [6]. In case of polymer F (quinazoline-4-one based) which must be liquid crystalline, because of the higher melting point, its birefringence in a melt could not observed. The isotropization temperature, T_i of these copolymers are not indicated by polarized light microscopy because of the temperature limit of the hot stage.

The thermal behaviour of polymers was evaluated by thermogravimetric analysis. The thermogram of some selected copolyesters are represented in Figure 3.

Data of thermal degradation are listed in Table II. The initial decomposition temperature (IDT) is the point where the trace begins to display evidence of weight change and was calculated from the original TGA curve. All polymers are stable upto 275°C in nitrogen atmosphere. IDT and T_{10} (temperature for 10% weight loss) are two

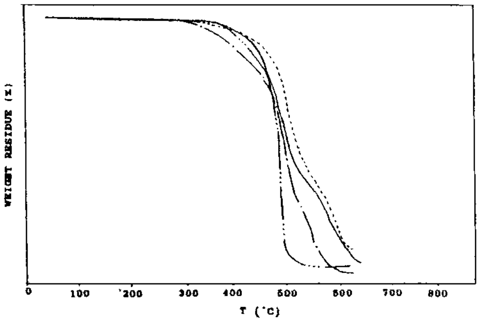


FIGURE 3 To thermogram at 10°C min^{-1} for the copolyester (1) A (– – –), (2) B (— · —) (3) D (——) (4) E(— ··· —).

TABLE II Thermal properties thermotropic copolyesters

Polymer No.	*IDT (°C)*	T_{max} *(°C)*	*IPDT (°C)*	*E kJ/mol*	*Temperature (°C) for various % decomposition*				
					10	20	30	40	50
A	287	475	513.6	42.4	430	465	480	490	515
B	287	480	559.4	44.8	425	445	480	495	540
C	300	512	559.8	50.0	430	465	490	510	525
D	300	513	525.2	46.4	438	475	495	513	525
E	263	513	543.8	36.4	415	463	475	487	510
F	275	587	576.5	31.3	425	515	555	580	605
G	263	550	514.4	37.2	420	455	485	505	512
H	300	510	540.1	45.6	425	450	490	520	525

of the main criteria used to indicate the heat stability of polymers. The higher the value of IDT and T_{10} the higher the thermal stability of the system [7]. The overall activation energy, E_A, of the degradation process were calculated by Broido's method [8]. To obtain the quantitative picture of the relative thermal stability, IPDT (integral procedural decomposition temperature) values can be regarded of significant importance, since they represent the overall nature of TGA curves [9].

CONCLUSIONS

Thermotropic liquid crystalline copolyesters prepared from melt polymerization of *p*-acetoxy benzoic acid, terephthalic acid, isophthalic acid and the appropriate diacetoxy diols exhibited typical nematic mesophase. Activation energy, E, ranged from $31-50 \pm 2\,\mathrm{kJ{\cdot}mol^{-1}}$ and IPDT values ranged from $513-576 \pm 2°\mathrm{C}$, which indicate that all copolyesters have good thermal stability.

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