BUTTERWORTH
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*Polymer* Vol. 36 No. 14, pp. 2819–2825, 1995

0032-3861/95/$10.00+0.00

# Synthesis of polyesters containing an aromatic Triad mesogen

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*(Received 6 June 1994; revised 20 November 1994)*

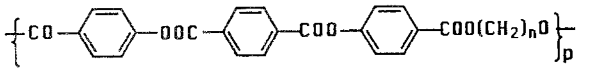
Thermotropic liquid crystalline polymers containing bis(*p*-oxybenzoyl terephthalate) (Triad) mesogen units linked by flexible polymethylene units were prepared by melt and solution polymerization reactions. Analogous Triad polymers based on a central isophthalate group were also prepared, but these polymers, which contained non-linear rigid segments, did not exhibit liquid crystalline behaviour. Copolymers composed of a mixture of linear and non-linear Triad units were also evaluated. In addition, a series of random Triad copolymers that contained butylene terephthalate (BT) units were also synthesized in solution. The liquid crystalline behaviour of these copolymers depended on the relative number of BT moieties present.

**(Keywords: solution polymerization; melt polymerization; copolymers)**

## INTRODUCTION

There is a growing interest in polymer blends containing thermotropic liquid crystalline polymers (TLCPs)[1,2]. These blends are reported to match or even exceed the performance of fibre-reinforced composites which have a fibre–matrix interface that affects the mechanical performance of the composites. Use of TLCPs in the polymer blends can eliminate such an interface, and hence minimize the problems associated with control of the interface. TLCPs can form fibres *in situ* during the melt processing of polymer blends and thus simulate the behaviour of fibre-reinforced composites. Additional beneficial property changes associated with the use of these TLCP blends include lower melt viscosity and lower thermal shrinkage.

The goal of the present research was to design and prepare TLCPs that were compatible with thermoplastic polyesters, especially with poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT). The TLCPs evaluated were based on semirigid, rod-like, main-chain thermotropic polyesters, which consisted of stiff aromatic ester Triad hard segments connected by flexible polymethylene spacer units, i.e.



Triad-*n* polymers **A** ($n = 4$), **B** ($n = 6$) and **C** (50 mol% of each, $n = 4$ and $n = 6$)

These aromatic Triad polyesters were first prepared in our laboratory[3]. Recently, Shin and Chung[4] have explored blends of a Triad polymer containing a decamethylene spacer ($n = 10$) with PET. Their results indicated some improvement in the strength and modulus of polymer blends they studied.

In the present work, Triad polymers were synthesized by acidolysis melt polycondensation, and the polymers obtained were compared to those prepared in solution. Triad polymers containing a central isophthalate moiety were also synthesized in solution, as were random copolymers containing varying numbers of butylene terephthalate (BT) units, and all these polyesters were examined for liquid crystalline properties.

## EXPERIMENTAL

### *Materials*

The chemicals used in this study were purchased from Aldrich and used without further purification, except as indicated below. Terephthaloyl chloride and isophthaloyl chloride were purified by sublimation under vacuum, and 1-chloronaphthalene (1-CN) was vacuum distilled over anhydrous calcium hydride. Other solvents were obtained anhydrous or dried over molecular sieves. Purified terephthalic acid was obtained from Amoco.

### *Monomer and polymer characterization*

Polymer melting temperatures were measured on a Fisher–Johns melting point apparatus and are uncorrected. Elemental analyses were performed by the Microanalytical Laboratory at the University of Massachusetts. Thermal transitions were studied on a Perkin–Elmer DSC-7 at a heating/cooling rate of 20°C min$^{-1}$ under an $N_2$ atmosphere. The thermal stabilities of the polymers were measured using a Perkin–Elmer TGA-7 instrument under an $N_2$ atmosphere at a heating rate of 20°C min$^{-1}$. N.m.r. spectra were obtained on a Bruker AC-200 or MSL-300

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spectrometer, using tetramethylsilane as an internal standard. Polarizing optical microscopy (POM) studies were carried out on a Zeiss microscope in combination with a Mettler FP2 hot stage. Inherent viscosities were measured at 45°C using *p*-chlorophenol or a 60/40 mixture of *p*-chlorophenol and tetrachloroethane as the solvent, at a concentration of $0.5\,g\,dl^{-1}$.

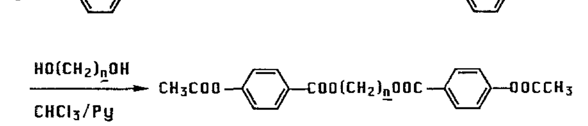
### *Monomer syntheses*

Bis($\omega$-hydroxybutyl)terephthalate (BHBT) was prepared according to the procedure reported in the literature[5] and purified by extraction with water in a Soxhlet apparatus for two days. The aqueous solution was cooled to precipitate BHBT, which was filtered and recrystallized from ethyl acetate. The purity was determined by high performance liquid chromatography.

1,2-Bis(4-hydroxybenzoyloxy)ethane **I-2**, 1,4-bis(4-hydroxybenzoyloxy)butane **I-4** and 1,6-bis(4-hydroxybenzoyloxy)hexane **I-6** were synthesized from 4-hydroxybenzoic acid according to a reaction scheme previously reported[3].

1,4-Bis(4-acetoxybenzoyloxy)butane **II-4** was synthesized from 4-acetoxybenzoic acid according to *Scheme 1*. 4-Acetoxybenzoic acid (93.5 g) was mixed with 150 ml of thionyl chloride and was stirred at 50°C for 4 h. Excess thionyl chloride was removed under reduced pressure and the remaining oil was vacuum distilled. The product obtained was recrystallized from hexane to give pure 4-acetoxybenzoyl chloride in 75% yield (melting point 28°C). 4-Acetoxybenzoyl chloride (40 g, 0.2 mol) was dissolved in 125 ml of dry chloroform and warmed with stirring. A solution of 7.86 g (0.087 mol) of 1,4-butanediol in 25 ml chloroform and 45 ml pyridine was added dropwise to this solution. After the addition was complete, the reaction mixture was heated to reflux with stirring for 24 h. The reaction mixture was then cooled and washed with water. The organic layer was separated and washed successively with dilute hydrochloric acid solution, 5% sodium bicarbonate solution and water. The organic layer was dried over calcium chloride and the solvent was removed. The resulting product was recrystallized from acetonitrile to give **II-4** as a fine white powder in 56% yield (melting point 106°C). Analysis calculated for $C_{22}H_{22}O_8$: C, 63.76; H, 5.31. Found: C, 63.75; H, 5.35. $^1H$ n.m.r. ($CDCl_3$, ppm): 1.95 (m, 4H), 2.39 (s, 6H), 4.20 (m, 4H), 7.2 (d, 4H), 8.10 (d, 4H).

1,6-Bis(4-acetoxybenzoyloxy)hexane **II-6** was prepared and purified in a manner similar to compound **II-4**. Thus, 4-acetoxybenzoyl chloride (34.5 g, 0.174 mol) was reacted with hexanediol (8.92 g, 0.075 mol) to give the pure compound in 63% yield (melting point 84–85°C). Analysis calculated for $C_{24}H_{26}O_8$: C, 65.15; H, 5.88. Found: C, 65.28; H, 5.93. $^1H$ n.m.r. ($CDCl_3$, ppm): 1.50 (m, 4H), 1.80 (m, 4H), 2.35 (s, 6H), 7.15 (d, 4H), 8.08 (d, 4H).



**Scheme 1** Synthesis of monomers **II-4** ($n = 4$) and **II-6** ($n = 6$)

### *Polymer syntheses: melt polymerizations*

*Triad-4 homopolymers A.* The diacetate monomer **II-4** (4.000 g) was mixed with 1.603 g of terephthalic acid and 0.050 g of zinc acetate using a mortar and pestle. The solid mixture was placed in a reaction vessel having an argon inlet and a distillation head connected to a cold trap. The reaction vessel was flushed with a slow stream of argon and it was placed in a salt bath at 180°C. The temperature of the stirred reaction mixture was slowly raised to 285°C over a period of 5 h and then to 295°C. A high vacuum ($<0.1$ torr) was then applied for 1.5 h. The product was then cooled and ground to a powder. This powder was then heated at 250°C for 2 h under high vacuum to facilitate further polymerization. The product was extracted with methanol and dried under vacuum to give 3.4 g of Triad-4 polymer **A** (77% yield).

*Triad-6 polymer **B**.* A finely ground mixture consisting of 3.800 g of monomer **II-6**, 1.427 g of terephthalic acid and 0.050 g of zinc acetate was placed in a reaction vessel flushed with argon. The reaction vessel was then placed in a salt bath at 180°C and the temperature of the bath was slowly raised to 270°C over a period of 2 h. The temperature was further raised to 280°C and held there for 2.5 h. Finally, a high vacuum was applied and the reaction temperature was raised to 290°C for 1 h. The product was cooled, ground and kept at 215°C for 20 h under vacuum to induce further polymerization. The product was then extracted with methanol and dried in a vacuum oven to give 2.0 g of Triad-6 polymer **B** (48% yield).

*Triad-4-*co*-Triad-6 copolymer C.* Monomer **II-4** (3.020 g) and monomer **II-6** (3.224 g) were mixed with 2.421 g of terephthalic acid and 0.050 g of zinc acetate. The mixture was finely ground and was transferred to a vessel flushed with argon. The reaction vessel was then placed in a salt bath at 180°C. The reaction temperature was slowly raised to 295°C over a period of 6 h and kept at 295°C for 1 h under vacuum. The product was cooled, ground and then heated at 180–192°C for 6 h under vacuum to induce further polymerization. The final product was extracted with methanol and dried under vacuum to give 2.8 g of polymer **C** (86% yield).

### *Polymer syntheses: solution polymerizations*

*General method.* All polymers synthesized in solution were obtained by this general procedure. The appropriate diol monomers were combined with an equivalent amount of aromatic diacid chlorides in a Schlenk flask fitted with an argon inlet/outlet, reflux condenser and a magnetic stirring bar. 1-CN was added, a slow stream of argon was passed through the flask and the flask was placed in a salt bath at 180°C. The temperature of the salt bath was increased to 200°C after 1 h. The reaction was continued until no more HCl was detected in the gas stream, and then the solution was cooled, precipitated in methanol, filtered and extracted with acetone in a Soxhlet apparatus. The polymer was dried under vacuum at 100°C for at least 24 h.

*Triad-4 polymer A.* In a typical polymerization in solution, polymer **A** was prepared from 9.720 g

(0.029 42 mol) of monomer **I-4** and 5.974 g (0.029 42 mol) of terephthaloyl chloride in 25 ml of 1-CN. The initial temperature was 185°C, and this was increased to 245°C after 2 h in order to keep the polymer in solution. The temperature was held at 245°C for a further 24 h, giving 12.17 g (90%) of polymer **A**. $^1$H n.m.r. ($CF_3COOD$, ppm): 2.0 (s, 4H), 4.50 (s, 4H), 7.35–7.40 (d, 4H), 8.17–8.21 (d, 4H), 8.40 (s, 4H).

*Triad-4 polymer* ***E***. Monomer **I-4** (1.6271 g, 4.925 mmol) and isophthaloyl chloride (1.000 g, 4.925 mmol) were dissolved in 15 ml of 1-CN. The initial temperature of the reaction was 180°C, which was raised to 200°C after 1 h. The reaction was allowed to proceed for 24 h. The polymer yield was 2 g (88%). $^1$H n.m.r. ($CF_3COOD$, ppm): 2.0 (s, 4H), 4.50 (s, 4H), 7.36–7.38 (d, 2H), 7.75–7.82 (t, 1H), 8.18–8.22 (d, 2H), 8.58–8.61 (d, 2H), 9.1 (s, 1H).

*Triad-4-*co*-PBT random copolymer* ***J***. Polymer **J** was prepared using the general method described above. Thus, 1.000 g (3.0272 mmol, 50%) of monomer **I-4** was combined with 0.9404 g (3.0301 mmol, 50%) of BHBT and 1.2291 g (6.054 mmol) of terephthaloyl chloride in 15 ml of 1-CN. The temperature was raised to 200°C and held there for 24 h. The polymer yield was 2.4 g (88%).

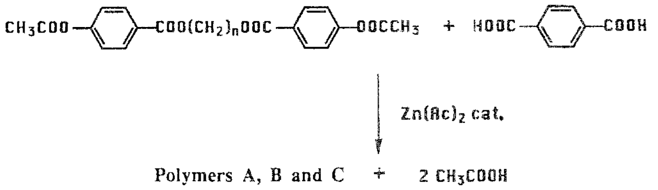
## RESULTS AND DISCUSSION

### *Comparison of Triad polymers prepared by melt and solution polymerizations*

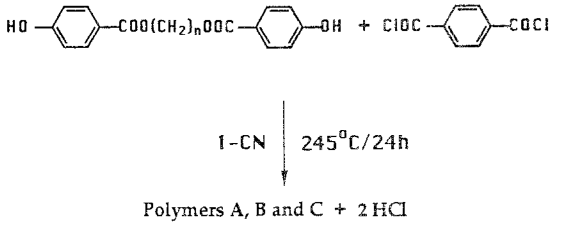
The synthesis of Triad-*n* polymers has been carried out in solution using either a 'premesogenic' monomer like **I-4** or with terephthaloyl bis(4-oxybenzoyl chloride) (TOBC) monomer[3]. In both cases the inherent viscosities of the polymers obtained were low because the polymer precipitated from tetrachloroethane (TCE), which was the reaction solvent. Bilibin *et al.*[6] modified the TOBC scheme by using a high-boiling solvent, such as 1-CN, as the reaction medium and by carrying out the reaction at elevated temperatures. Under these conditions, the polymers remained in solution, yielding high molecular weight products.

In the present study, the synthesis of Triad-*n* polymers was carried out by a melt polymerization technique. The polymers obtained were compared to those prepared in solution, starting from the premesogenic monomer **I-4** or **I-6**. Melt polymerization reactions usually involve either the condensation of dicarboxylic acids (or alkyl esters) with diols or the acidolysis of diol diacetates with dicarboxylic acids in the presence of a catalyst. The melt acidolysis method generally works best by using the reaction of aromatic acids with phenol acetates. The diacetate monomers **II-4** and **II-6** were prepared from 4-acetoxybenzoic acid as shown in *Scheme 1* from the corresponding acid chloride and diol. Each monomer was subsequently reacted with terephthalic acid in the presence of a catalytic amount of zinc acetate under an inert atmosphere at high temperature, as illustrated in *Scheme 2*.

The by-product acetic acid was removed throughout the polymerization reaction. Polymers **A** and **B** and the new copolymer **C**, formed from a 50/50 mixture of monomers **II-4** and **II-6**, were prepared by this method.



**Scheme 2** Synthesis of Triad-*n* polymers by melt polycondensation



**Scheme 3** Synthesis of Triad-*n* polymers in solution

These polymers were also prepared in solution starting from the premesogenic monomers **I-4** and **I-6** and terephthaloyl chloride, as shown in *Scheme 3*.

The properties of the three polymers **A**, **B** and **C**, synthesized either in the melt or in solution, are summarized in *Table 1*. The inherent viscosities of the polymers prepared in 1-CN were higher than those reported earlier[3], where the polymerization reactions were carried out in TCE. The polymers prepared in the melt had somewhat lower inherent viscosities.

The thermal properties of the polymers were different according to whether the polymers were prepared by melt or solution methods. The greatest difference in the transition temperatures was shown by polymer **A**, for which the crystal to nematic transition of the sample prepared from the melt was 37°C lower than that of the product prepared from solution. The elemental analyses of polymers **A**, **B** and **C** were in agreement for samples made by the two preparative methods, and the inherent viscosities of the polymers were in the same range, although a substantial difference in the decomposition temperatures was evident for the polymers prepared by the two methods. The melt polymerization method produced polymers that decomposed at least 60°C lower than those made in solution. Generally, all of the polymers prepared from solution had decomposition temperatures ($T_{dec}$, for a 5% weight loss) of approximately 390–400°C. The lower $T_{dec}$ for melt-polymerized samples could be caused by residual amounts of the reaction catalyst, which could facilitate thermal degradation. The differences in the thermal transitions could have resulted from some degree of transesterification with the aliphatic ester functionality in the Triad polymer, which could have occurred under the conditions of the melt polymerization process.

All three polymers **A**, **B** and **C**, regardless of the method of preparation, exhibited a nematic liquid crystalline behaviour. Complete isotropization took place near or above 340°C in each case (340°C was the maximum temperature of the hot stage used). The new Triad copolymer **C** had a broad mesophase temperature range because its crystal to nematic transition temperature was significantly lower than that of the homopolymers **A** and **B**, while the isotropization took place around 340°C.

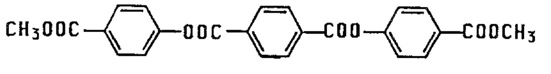
Another method of preparing polymer **B** was also attempted. Bis(4-methoxycarbonylphenyl) terephthalate

**Table 1** Comparison of properties of Triad polymers prepared by melt and solution polymerization

| Polymer | Scheme | $n$[a] | $\eta_{inh}$[b] (dl g$^{-1}$) | $T_{k-n}$[c] (°C) | $T_{n-i}$[d] (°C) | $T_{dec}$[e] (°C) | Empirical formula | Elemental analyses | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | C (%) | H (%) |
| | | | | | | | | Calculated | 67.82 | 4.38 |
| **A** | 2 | 4 | 0.52 | 243 | > 340 | 340 | $C_{26}H_{20}O_8$ | Found | 67.40 | 4.32 |
| **A** | 3 | 4 | 0.65[f] | 280 | > 340 | 400 | | Found | 67.82 | 4.52 |
| | | | | | | | | Calculated | 68.84 | 4.95 |
| **B** | 2 | 6 | 0.54 | 238 | > 340 | 330 | $C_{28}H_{24}O_8$ | Found | 68.71 | 4.79 |
| **B** | 3 | 6 | 0.76[f] | 230 | 332 | 390 | | Found | 68.91 | 4.89 |
| | | | | | | | | Calculated | 68.35 | 4.67 |
| **C** | 2 | 4 and 6[g] | 0.42 | 204 | 345 | 308 | $C_{54}H_{44}O_{16}$ | Found | 68.10 | 4.67 |
| **C** | 3 | 4 and 6[g] | 0.56 | 204 | 352 | 390 | | Found | 68.23 | 4.67 |

[a] Number of methylene units present in the polymer
[b] Inherent viscosity measured in *p*-chlorophenol at 45°C unless otherwise specified
[c] Maximum of the endothermic peak associated with the crystal to nematic transition in the d.s.c. thermogram
[d] Nematic to isotropic transition temperature as determined by POM
[e] Decomposition temperatures corresponding to 5% weight loss, as determined by thermogravimetric analysis under an $N_2$ atmosphere
[f] Measured in *p*-chlorophenol/tetrachloroethane (50/50) solution at 30°C
[g] Random copolymer containing four and six methylene units in a 1/1 ratio

was prepared by reacting methyl 4-hydroxybenzoate with terephthaloyl chloride



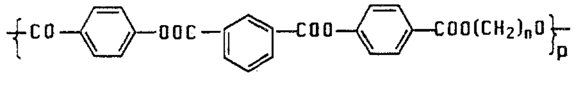
This compound was reacted with a slight molar excess of hexanediol and a catalytic amount of $Ti(OBu)_4$ under the conditions used for a different system reported earlier[7]. It was expected that the methyl ester would undergo transesterification with butanediol to form **B**. Unfortunately, all attempts to form a liquid crystalline polymer by this route failed. Preferential attack of the diol on the internal phenolic ester may have occurred, but the product was not fully characterized since only low molecular weight oligomers were obtained.

While the melt polycondensation route offers many technological advantages, there are some serious drawbacks. Because the reaction is carried out at a high temperature in the presence of a catalyst, structural modifications can occur within the polymer owing to transesterification reactions. Since complete removal of the catalyst is very difficult, thermal degradation and structural reorganization can occur during subsequent thermal treatments. As a result of this problem, the majority of the polyesters prepared for characterization in this study were obtained by solution polymerization.

### *Non-linear Triad polymers*

Non-linear Triad polymers were synthesized by reacting monomers **I-2**, **I-4** and **I-6** with isophthaloyl chloride. It has been shown previously that the polymer geometry can strongly influence the formation of a liquid crystalline morphology[8], and deviations from molecular linearity can either decrease the mesophase stability or prevent completely the formation of the mesophase. The isophthalate unit has a core angle of 120°, and this unit has been introduced to lower the transition temperatures and improve the processability of blends of such TLCPs containing these units.

Polymers **D**, **E** and **F** containing the central isophthalate unit with either two, four or six methylene spacers were prepared and characterized



Polymers **D** ($n = 2$), **E** ($n = 4$) and **F** ($n = 6$)

All the non-linear polymers synthesized by us are listed in *Table 2*. They had high inherent viscosities except for polymer **D**. The elemental analyses of the polymers were in agreement with the calculated values. The $^{1}$H n.m.r. and $^{13}$C n.m.r. data for the polymers were also in agreement with the structures and are consistent with peak assignments previously reported[9]. Polymers **D**, **E**, **F** and **G**, containing an isophthalate unit instead of a terephthalate group in some cases in the Triad moiety, showed some differences. In the linear Triad system, the four terephthalate ring protons are equivalent and appear at 8.4 ppm. The isophthalate protons in polymer **E** are non-equivalent and appear as a singlet at 9.1 ppm, a doublet at 8.6 ppm and a triplet at 7.8 ppm. The non-equivalent nature of the central isophthalate carbons may also be seen in the $^{13}$C n.m.r. spectrum where the peaks appear at 139.02 ppm, 135.05 ppm, 132.48 ppm and 131.97 ppm, compared to the terephthalate carbon chemical shifts for the linear Triad-containing polymers at 136.2 ppm and 133.42 ppm.

Polymers **D**, **E** and **F** were examined by POM and all were found to be non-liquid crystalline. All three polymers melted directly to form dark isotropic phases. These observations were confirmed by differential scanning calorimetry (d.s.c.). These polymers showed a single melting peak during the first heating scan (see *Table 2* for the respective peak temperatures), and on cooling they did not show a crystallization exotherm but they exhibited a shift in the baseline associated with the glass transition. During the second heating scan, unlike polymers **D** and **F**, polymer **E** had two cold crystallization exotherms followed by a melting peak at the same temperature as in the first scan. Polymers **D**, **E** and **F** had glass transition temperatures at 100°C, 91°C and

**Table 2** Properties of non-linear Triad polymers prepared from solution

| Polymer | $n^a$ | $\eta_{inh}$ (dl g$^{-1}$) | $T_g{}^b$ (°C) | $T_{k-i}{}^c$ (°C) | $T_{n-i}{}^d$ (°C) | Liquid crystalline behaviour | Empirical formula | Elemental analyses | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | C (%) | H (%) |
| **D** | 2 | 0.22 | 100 | 207 | | None | | | | |
| **E** | 4 | 0.59 | 91 | 222 | | None | $C_{26}H_{20}O_8$ | Calculated | 67.82 | 4.38 |
| | | | | | | | | Found | 67.83 | 4.37 |
| **F** | 6 | 0.74 | 64 | 158 | | None | $C_{28}H_{24}O_8$ | Calculated | 68.84 | 4.95 |
| | | | | | | | | Found | 68.66 | 4.72 |
| **G**$^e$ | 6 | 0.72 | | 205$^f$ | 340 | Nematic | $C_{28}H_{24}O_8$ | Calculated | 68.84 | 4.95 |
| | | | | | | | | Found | 68.68 | 5.09 |

[a] Number of methylene units present per repeating unit of the polymer
[b] Measured during the second d.s.c. heating cycle
[c] Maximum of the melting endotherm obtained during the first d.s.c. heating cycle
[d] Nematic to isotropic transition temperature as determined by POM
[e] Random copolymer prepared from a 75/25 mixture of terephthaloyl and isophthaloyl chlorides
[f] Crystal to nematic transition temperature observed during the first d.s.c. heating cycle

**Table 3** Properties of random copolymers

| Polymer | $n^a$ | Monomer feed ratio I-4/BHBT/TCl$^b$ | $\eta_{inh}{}^c$ (dl g$^{-1}$) | Content of moieties determined by $^1$H n.m.r. (mol%) | | | $T_m{}^d$ (°C) | $T_{n-i}{}^e$ (°C) | Liquid crystalline behaviour |
|---|---|---|---|---|---|---|---|---|---|
| | | | | BT | Diad-4 | Triad-4 | | | |
| **H** | 4 | 3/1/4 | 0.60 | 27 | 33 | 40 | 276 (14) | > 340 | Nematic |
| **J** | 4 | 1/1/2 | 0.84 | 50 | 32 | 18 | 211 (8)<br>249 (6) | 290 | Nematic |
| **K** | 4 | 1/3/4 | 0.60 | 77 | 20 | 3 | 209 (49) | | None |

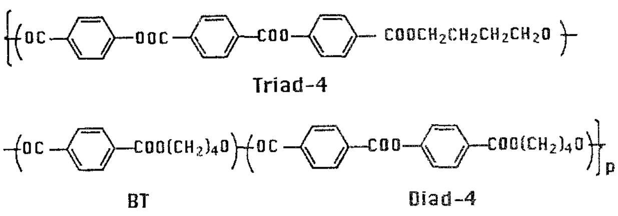
[a] Number of methylene units attached to the Triad moiety
[b] TCl = terephthaloyl chloride
[c] Inherent viscosity measured in 60/40 *p*-chlorophenol/tetrachloroethane solution
[d] Maximum of the endotherm observed in the first d.s.c. heating cycle; the heat of fusion (in J g$^{-1}$) of each transition is given in parentheses
[e] Isotropization temperature as observed by POM

64°C, respectively, during the second heating cycle. This decrease in the $T_g$ may be attributed to the increase in chain flexibility which develops as the number of methylene spacers is increased.

Polymer **G**, which was prepared by the polycondensation of terephthaloyl chloride and isophthaloyl chloride in the molar ratio 75/25 with monomer **I-6**, formed a liquid crystalline melt with a nematic texture. The d.s.c. thermogram of polymer **G** showed a single melting peak at 205°C, which is lower than the melting transition of the linear Triad-6 polymer **B** but higher than that of its non-linear analogue **F**. When the polymer was observed by POM, a birefringent texture was seen on melting. When the sample was heated to 280°C certain regions became dark, but the birefringent domains remained until 340°C. Therefore, incorporation of 25 mol% of isophthaloyl units does not inhibit the liquid crystalline behaviour, but in fact it helps in widening the liquid crystalline range.

### *Triad-4*-co-*BT random copolymers*

Three copolymers **H**, **J** and **K** were prepared by the polycondensation of terephthaloyl chloride with varying molar ratios of the monomers **I-4** and BHBT in order to examine the effect of varying the content of butylene terephthalate (BT) moieties on the liquid crystalline behaviour. All three polymers had relatively high inherent viscosities. These copolymers consisted of random distributions of BT, Diad-4 and Triad-4 units. Their properties are summarized in *Table 3*.



Random copolymers **H**, **J** and **K**

The n.m.r. spectra of copolymers **H**, **J** and **K** were consistent with their structures. *Figure 1* shows the $^1$H n.m.r. spectrum of polymer **J**. The aromatic region contains peaks at 8.4 ppm and 8.1 ppm, and these are associated with the terephthalate protons of Triad and BT moieties, respectively. Peaks between 8.4 ppm and 8.2 ppm correspond to the presence of tetramethylene-4-terephthaloyl-4′-oxybenzoate (Diad-4) moieties which are formed during the polycondensation[9]. The molar percentages of Triad-4, Diad-4 and BT moieties were calculated from the integral values of the peaks at 8.4 ppm, 7.3 ppm and 4.5 ppm using a calculation

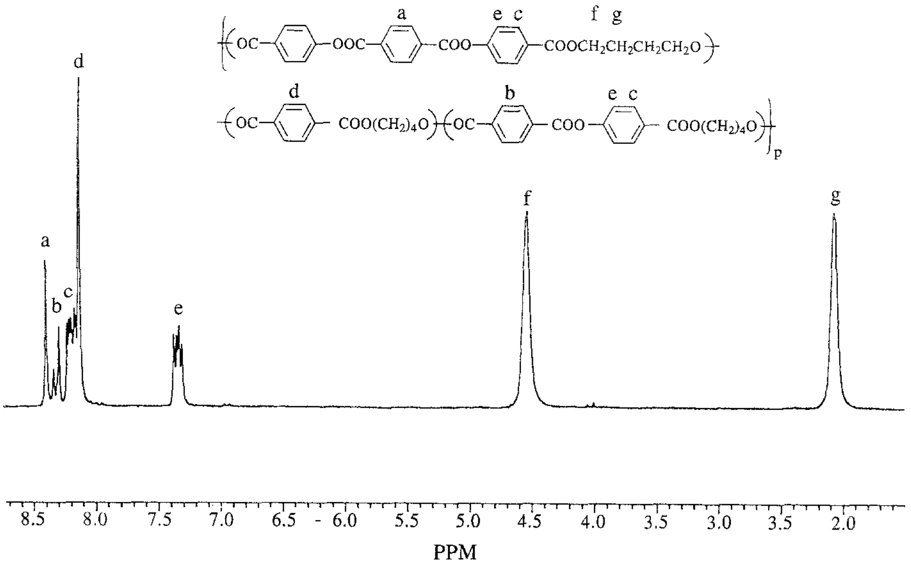


**Figure 1** $^1H$ n.m.r. spectrum (200 MHz) of polymer **J**

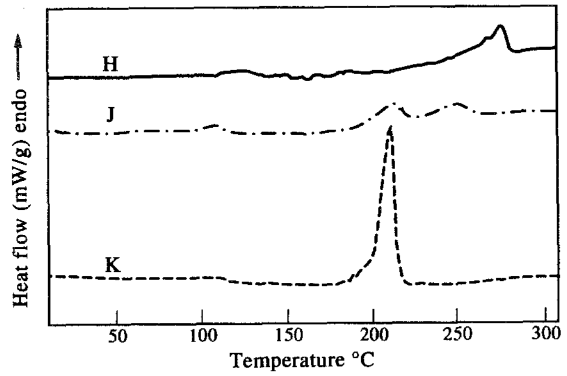


**Figure 2** Normalized d.s.c. traces obtained during the first heating scans of polymers **H**, **J** and **K**

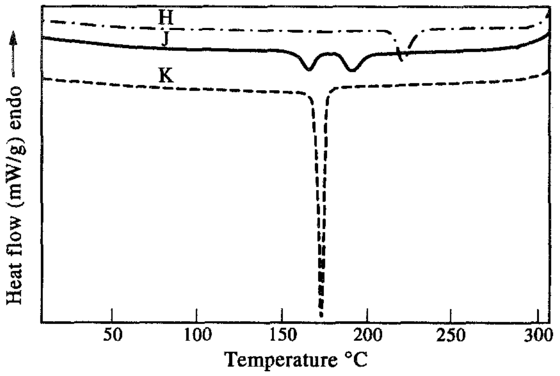


**Figure 3** Normalized d.s.c. traces obtained during the first cooling scans of polymers **H**, **J** and **K**

discussed previously[9]. The results in *Table 3* show that a significant number of Diad-4 units were formed during the polycondensation reactions. The formation of Diad-4 units was expected from the use of the premesogenic monomer **I-4**[9].

The formation and stability of the mesophase depended on the amount of BT present in the copolymer. Polymers **H** and **J**, containing respectively 27 mol% and 50 mol% of BT moieties, formed liquid crystalline phases with a nematic texture above their melting transitions, but polymer **K**, with 77 mol% of BT segments, was not liquid crystalline and melted to an isotropic state. Similarly, the isotropization temperatures also depended on the amount of BT present. Polymer **H** became isotropic well above 340°C, while polymer **J** had a nematic to isotropic transition temperature of 280°C.

*Figure 2* shows the normalized d.s.c. thermograms obtained during the first heating scans of polymers **H**, **J** and **K**. Polymer **H** showed a broad melting peak at 276°C, and polymer **J** had two melting peaks at 211°C and 249°C which are probably associated with separate melting of the BT-rich and liquid crystalline domains. The thermogram of polymer **K** had a sharp peak at 209°C, which is lower than the melting point of pure high molecular weight PBT ($T_m = 222°C$)[9]. The heat of fusion associated with this transition was the highest of the three copolymers, in agreement with the highest BT content.

Among the three random copolymers, only copolymer **J** showed a glass transition at 54°C comparable to that observed in the case of segmented block copolymers containing BT and Triad-4 segments ($T_g = 50°C$). Even for the latter block copolymer, which clearly exhibited a microphase-separated behaviour, only one $T_g$ was discernible either because the $T_g$ values of the two segments were close together or because the $T_g$ of the Triad-4 segment could not be determined by d.s.c. Melot and Macknight[10] made use of dynamic mechanical thermal analysis (d.m.t.a.) measurements since the Triad-4 homopolymer ($\eta_{inh} = 0.5\,dl\,g^{-1}$) did not exhibit a $T_g$ by d.s.c. In d.m.t.a. the Triad-4 homopolymer showed an $\alpha$ transition at 56°C at 1 Hz and at a heating rate of $4°C\,min^{-1}$.

The normalized d.s.c. thermograms which were obtained on cooling the polymers **H**, **J** and **K** from 310°C are shown in *Figure 3*. Polymer **H** exhibited one crystallization exotherm at 221°C, which was a few degrees lower than that for pure Triad-4 homopolymer[9]. The presence of 27 mol% of BT units lowered the crystallization temperature of Triad-4 domains in the copolymer. Similarly, the crystallization temperature of polymer **K** was 173°C, which was slightly higher than that for high molecular weight PBT[9]. There were two distinct crystallization exotherms at 166°C and 191°C in the thermogram of polymer **J**, which contained equal amounts of BT and rigid units. These exotherms are probably associated with the separate crystallization of the two domains. Unequivocal assignments of the thermal transitions to the various phases have not been made owing to the complex microstructures of these copolymers.

## CONCLUSIONS

Liquid crystalline polyesters containing aromatic Triad units were prepared by melt and solution polymerization. Acidolysis is the method of choice for the melt polycondensation since transesterification using the methyl ester of the Triad diacid only formed low molecular weight products. The Triad polymers made in solution from the acid chloride monomers were more thermally stable than the melt-generated samples. In addition, the solution-generated polymers have a more predictable chemical structure and are preferred for characterization of their physical properties.

Polymers with a central isophthalate unit in the Triad moiety were not liquid crystalline. Replacing some of the isophthalate units by terephthalate units restored liquid crystallinity. Other copolymers were prepared with a random distribution of Triad-4, Diad-4 and BT moieties. These were shown to be liquid crystalline with transition temperatures that were dependent on the BT content. At high BT content, liquid crystallinity was no longer evident.

## ACKNOWLEDGEMENT

Financial support from AKZO America Inc. is gratefully acknowledged.

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