Synthesis and characterization of segmented copolymers of aromatic polyether sulphone and a thermotropic liquid crystalline polyester

Brian C. Auman and Virgil Percec
Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106, USA
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The bulk copolycondensation of α,ω-di(acetoxy) aromatic polyether sulphone (PSU) with chlorohydroquinone diacetate and *trans*-1,4-cyclohexanedicarboxylic acid to produce segmented copolymers of amorphous PSU and thermotropic liquid crystalline poly(chloro-1,4-phenylene-*trans*-cyclohexane dicarboxylate) (PCPTCD) is described. For PSU with $\bar{M}_n = 1400$, true block copolymers were formed with PSU segments incorporated into the thermotropic liquid crystalline polyester structure. For PSU with $\bar{M}_n \geqslant 2300$, however, the products were not true block copolymers, but rather blends of PSU chain extended by short PCPTCD segments and PCPTCD homopolymer. This result can be explained by an 'apparent' molecular weight dependent reactivity of the α,ω-di(acetoxy)PSU chain ends, which is in fact the consequence of the immiscibility of the amorphous and liquid crystalline phases.

(Keywords: α,ω-di(acetoxy)PSU; thermotropic polyester; segmented copolymers; molecular composites)

INTRODUCTION

In recent years developments in ultra high strength/ultra high modulus polymer fibres have led to enlarged potential for high strength/high performance materials. Of particular interest are applications in fibre reinforced composites where the incorporation of an ultra high strength fibre in a ductile matrix has led to a new generation of advanced composites.

Although the polymeric backbone of typical semiflexible thermoplastic polymers, e.g. polyethylene (PE), poly(ethylene terephthalate) (PET) or nylon has the potential for very high strength, it is generally unrealizable because of the tendency for chain folding. Strengths near those of the theoretical limit for the polymer backbone would only be realizable by having the chains in the fully extended conformation along the direction of desired strength. It has not been until recently that special elaborate techniques, such as solid-state extrusion[1] and gel spinning[2] have been developed for PE which have allowed strengths approaching the theoretical maximum to be obtained. Further developments in these techniques may make them applicable to other semiflexible polymers as well.

Since chain folding seriously deters the formation of the extended chain conformation necessary for ultra high strength, prohibiting folding by increasing the chain rigidity would seem the most direct route to extended chain morphology. Unfortunately, increasing chain rigidity also increases the melting point and decreases the solubility so, to a great extent, rigid rod polymers which would tend readily to an extended chain conformation are insoluble and do not melt below their decomposition temperatures. Since infusible, insoluble polymers cannot be readily processed, their utility is seriously limited.

A major breakthrough in rigid rod polymers came with the development of poly(p-phenylene terephthalamide) (PPTA)[3]. This very rigid polymer, although it cannot be melt processed before decomposition, was found to be soluble in concentrated sulphuric acid and could be solution spun into high strength fibres from an anisotropic (lyotropic) solution without appreciable degradation. This solution was found to be the result of the presence of highly ordered nematic liquid crystalline (LC) domains which oriented readily under shear to give a highly ordered extended chain structure in the flow direction and therefore high strength/stiffness fibres.

Although PPTA and closely related poly(p-benzamide) (PBA), as well as other lyotropic rigid rod systems, e.g. poly(p-phenylenebenzobisthiazole) (PBT) can be solution processed and have shown widespread applicability, the fact that they must be processed from such strong acids may limit the scope of products that can be prepared from them.

A melt processable rigid rod polymer (thermotropic) would be desirable because of flexibility in fabrication. Indeed, thermotropic aromatic polyesters show great potential as high strength, melt processable materials. The polyester analogue of PPTA, namely poly(p-phenylene terephthalate), has theoretical strength that could exceed that of PPTA; however, its melting point is still too high compared to its decomposition temperature. In addition, it cannot be solution processed because it degrades rapidly in the strong acids needed for dissolution. Much work has therefore been dedicated to developing other rigid rod polyesters which could be processed below their decomposition temperatures into high strength materials[4-10].

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In order to lower the melting point of totally rigid rod aromatic polyesters like poly(*p*-phenylene terephthalate), methods for incorporating flexible spacers[5,6] rigid kinks[4-6] and bulky side-groups[6,7] or combinations thereof[8-10] have been developed. These function by disrupting to some extent the packing ability and/or cohesion of the rigid rod chains and thereby cause a decrease in melting point. These various methods have successfully reduced the melting points of rigid aromatic polyesters so that they can be processed from thermotropic melts into high strength materials.

In this paper the use of the thermotropic liquid crystalline polyester, poly(chloro-1,4-phenylene-*trans*-1,4-cyclohexane dicarboxylate) (PCPTCD)[11,12], which forms a nematic phase above its melting temperature (~320°C)[12,13], for the synthesis of block copolymers containing rod-like and flexible segments will be discussed. Rather than applying this polyester as a macroscopic reinforcement in a fibre reinforced composite, it will be sought to use this thermotropic polyester to reinforce a thermoplastic material on a much finer scale, i.e. on a molecular or supramolecular level. Such a composite material has been termed a 'molecular composite' or a 'self-reinforcing thermoplastic'. This concept has been recently reviewed[14], and developments in this area, especially as related to block copolymers of rigid rod and flexible polymers, will be briefly summarized here.

The strength of a composite material is intimately related to the ability of an applied load to be transferred from the matrix to the fibre reinforcement. This depends on several factors, most important of which is the strength of the interfacial bond between fibre and matrix. When the interfacial bond is strong, the load can be completely transferred to the fibre and failure occurs by fibre breakage at a very high load. Macroscopic (1–10 μm) fibre reinforced composites have yielded very high strengths when a good interfacial bond is present; however, the fibre strengths are still less than those predicted for the individual rigid rod chains due to fibre imperfections, the tendency towards fibrillation, and stress concentrations at the fibre ends or induced by differences in thermal expansion. It has been postulated that reinforcement on a much finer scale (i.e. 10–30 nm diam. or less) could yield more efficient reinforcement and therefore stronger materials[14,15], this being due to minimization of the aforementioned weaknesses of macroscopic reinforcement. In addition, it has been further postulated[15] that reinforcement on a much finer scale would lead to much lower reinforcement loading for equivalent strength. This would mean that molecularly reinforced materials could be processed in much the same manner as the unreinforced matrix material[15]. Hence, the current surge of interest in producing these types of materials with 'microfibrillar' (supramolecular) or even molecular scale reinforcement.

Methods aimed at achieving reinforcement on a molecular or supramolecular level can be divided into three categories: The first method entails the dissolution of the rigid rod polymer with the 'flexible' matrix polymer in a common solvent, followed by coagulation in a non-solvent. Several examples of this method include: blends of PPTA with Nylon 6, Nylon 66 or NBR rubber described by Takayanagi *et al.*[15,16]; blends of rod-like heterocyclic polymers (e.g. PBT) with coil-like heterocyclic polymers of similar structure (e.g. poly[2-5(6)-benzimidazole], PBI) described by Helminiak *et al.*[17-19] Mechanical property results from these blends show large increases in strength and stiffness over the non-reinforced material at very low reinforcement loading[15,19]. For example, Takayanagi[15,16] showed at 5% reinforcement, moduli and yield stresses for PPTA–Nylon blends which were comparable to 30% macrofibre reinforced materials. Although these results are very encouraging, the fabrication techniques are very limiting because of the dilute solutions that must be employed to obtain good dispersion. Indeed, consistent with the theoretical predictions of Flory[20], the rod-like molecules tend to aggregate and shun the coil molecules even in a common solvent, except at very low concentrations[19]. Thus, dilute concentrations were found necessary to obtain the described molecular dispersion in the coagulated films and fibres[18,19].

The second method is represented by solution block copolymerization of a rigid rod polymer with a flexible coil molecule. This is accomplished by formation of one block in the presence of the other with eventual block coupling via appropriate antagonist functions, or by direct coupling of two preformed blocks. Although this technique is severely limited because of the insolubility of rigid rod polymers, success, at least to a limited degree, has been obtained for the aromatic polyamides (PPTA, PBA) because of their solubility in salt solutions of polar aprotic solvents. Examples of these blocks are as follows: PPTA-b–Nylon 6 or 6,6 and PBA-b–Nylon 6 prepared by Takayanagi *et al.*[15,16]; PBA-b–PABH-T (PABH-T = the polyterephthalamide of *p*-aminobenzhydrazide), PPTA– or PBA-b–poly(*m*-phenylene isophthalamide) by Krigbaum *et al.*[21] The synthesis of an ABA block copolymer containing PBI and PBT segments has been also reported[18a]. The advantage of block copolymers of rigid and flexible polymers over blends is that the chemical bond between the incompatible segments provides the driving force for intermixing of the components. Thus better dispersion of rod-like polymer in the flexible matrix should be obtainable. Also, one could imagine if the coupled segments were of sufficient length, the rod-like component could be 'anchored' in the matrix by intertwining of the flexible component with the bulk matrix. Both these could be expected to give much improved properties over blends alone. Direct evidence in support of this has been given by Takayanagi *et al.*[15,16] for PPTA/nylon and PBA/nylon block copolymers blended into a nylon matrix. These block/matrix blends showed superior properties over the normal blends at equivalent rod-like loading. While the yield stress and modulus were maintained, elongation (and thereby toughness) was markedly improved in the block system[15,16]. Thus, block copolymers of rigid and flexible macromolecules appear to have great potential for use in molecular composites. Related to these are graft copolymers of which an example prepared by somewhat similar methods can be found in the literature[22,23]. Other methods for solution prepared block copolymers of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and thermotropic LC polymers have been recently revealed by Heitz *et al.*[24,25] Solution prepared polysulphone–poly(arylene terephthalate) copolymers have been described by Lambert *et al.*[26,27]

The third method also deals with block copolymers.

However, in this case melt polymerization techniques are used. This necessitates, of course, a melt processable rigid-rod thermotropic polymer, as with the aromatic polyesters mentioned above. The advantages of these types of block copolymers in molecular composites would be expected to be the same as discussed in the preceding paragraph but would have the advantages of the flexibility of melt processing and the increased molecular weights of melt versus solution reaction[12,28]. Of course, the choice of materials is limited to those which can be coupled with the polyester either by transesterification[29] or through functional chain-ends. A further consideration is the thermal stability of the flexible polymer at the high temperatures of the melt reaction.

The procedure employed in the present study is the melt acidolysis reaction between a diacid and a diacetate. Typically, the LC segment is built up from the component monomers in the presence of the flexible segment fitted with antagonist acid or acetate functions at the chain ends. Examples of this procedure would include a copolymer of PHB [poly(hydroxybenzoate)] and PET by Jackson *et al.*[29], and copolymers of poly(arylene ether sulphones) with poly(arylene terephthalates) or poly(oxybenzoates) by Lambert *et al.*[28,30] A very recent patent[31] also cites various aromatic polyether–LC polyester block copolymers prepared by the melt acidolysis method. Unfortunately, none of these short communications or patents provides enough characterization evidence to confirm that real block copolymers containing thermotropic LC polyesters and flexible segments were obtained.

In this paper, our results concerning the synthesis of block copolymers of aromatic polyether sulphone (PSU) fitted with end-standing acetate functions and PCPTCD by a simple melt acidolysis procedure are described. Although this thermotropic polyester is not a true rigid rod polymer, owing to the semiflexible cyclohexane unit due to the chain conformation of the *trans* isomer, it readily assumes an extended chain structure and forms nematic mesophases and consequently high strength fibres[11,12]. These materials in which ideally the high strength chain extended polyester segment would be very finely dispersed in the glassy, tough, thermally stable PSU matrix have potential as high performance advanced composite materials.

EXPERIMENTAL

Materials

Bisphenol A (BPA) and 4,4′-dichlorodiphenylsulphone (DCDPS) (Aldrich) were purified by successive recrystallizations from toluene. Chlorohydroquinone diacetate (CHQDA, 99%, Rhône Poulenc) was recrystallized three times from ethanol. *trans*-1,4-Cyclohexane dicarboxylic acid (*trans*-CDA, 95%, Aldrich) (also known as hexahydroterephthalic acid) was purified as prescribed by Kwolek and Luise[12], i.e. Soxhlet extraction of any *cis* isomer with chloroform and subsequent recrystallization three times from ethanol. Anhydrous sodium acetate (Merck), *p*-chlorophenol (*p*-ClPh, Lancaster Synthesis), *N,N*-dimethylaminopyridine (DMAP, Reilly), triethylamine (TEA, Aldrich), trifluoroacetic acid (TFA), acetyl chloride, acetic anhydride (all from Fisher), and all other reagents were used as received. α,ω-Di(hydroxyphenyl) PSUs (PSU–OH) were prepared in the conventional manner[32,33] by condensation of excess disodium salt of BPA with DCDPS in anhydrous DMSO (samples 1 and 3, acetoxy derivative, *Table 1*, below) or by the DMAC/K_2CO_3 method described by Viswanathan *et al.*[34] (samples 6–8, *Table 1*). Other functional derivatives of the same PSU–OHs (vinyl benzyl and allyl ether chain ends) have been described and characterized in previous work[35,36].

Techniques

Number-average molecular weights were determined by vapour pressure osmometry (v.p.o.), ^{1}H n.m.r. and gel permeation chromatography (g.p.c.). V.p.o. measurements were performed on chloroform solutions at 35°C using a Wescan 233 instrument. N.m.r. spectra were obtained from a Varian XL-200 spectrometer using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. G.p.c. was accomplished with a Perkin–Elmer system consisting of a Series 10 pump, an LC-100 column oven set at 40°C, a PL gel column set of 10^5, 10^4, 10^3, 5×10^2, 10^2 Å, an LC-15B u.v. detector and Sigma 15 data station. Tetrahydrofuran (THF) was used as eluent at $1.0\,\text{ml}\,\text{min}^{-1}$, and the columns were calibrated with polystyrene standards. D.s.c. measurements were performed on a Perkin–Elmer DSC-4 at a heating/cooling rate of $20°\text{C}\,\text{min}^{-1}$. Indium, tin and lead were used as calibration standards. Enthalpy changes were calculated with the TADS DSC-4 standard program. I.r. analyses were performed on either a Perkin–Elmer 1330 dispersive instrument or a Digilab FTS-14 *FT*i.r. spectrophotometer. Samples were analysed as thin films on KBr discs or as powders ground with KBr powder and pressed into pellets. Inherent viscosities (η_{inh}) were obtained from solutions of the polymers in a 3:1 (v/v) mixture of *p*-chlorophenol/trifluoroacetic acid at 30°C at a concentration of 0.1 g polymer in 100 ml solvent. A Cannon–Ubbelohde viscometer was used and the flow time of pure solvent was 100 s. Hot stage optical microscopy was accomplished with a Mettler FP-52 hot stage and an Olympus BH-2 transmission microscope. Samples were viewed between cross-polarizers at a magnification of 80 ×.

Synthesis of α,ω-di(acetoxy)PSU (PSU-AC)

These bifunctional acetate terminated PSUs were prepared by two methods. The first method was similar to a previously published method for the quantitative esterification of ω-(hydroxyphenyl)PSU with methacryloyl chloride[37]. In this work, acetyl chloride was substituted for methacryloyl chloride. Samples 1, 3 and 6 were prepared in this way. A typical procedure is as follows: 10 g of α,ω-di(hydroxyphenyl)PSU-6 (PSU-6-OH) ($\bar{M}_n = 6800$ by v.p.o., 1.47×10^{-3} mol, 2.94×10^{-3} mol –OH groups) were dissolved in 50 ml

Table 1 Characterization of α,ω-di(acetoxy)PSU

	$\bar{M}_n$		G.p.c.			T_g (d.s.c.[a]) (°C)
	v.p.o.	n.m.r.	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	
PSU-1	1400	1250	1400	1800	1.3	100
PSU-7	2300	2500	2400	3900	1.6	133
PSU-8	3100	3300	3300	6000	1.8	145
PSU-3	3700	3900	4500	7600	1.7	153
PSU-6	7000	9400	9300	20000	2.1	175

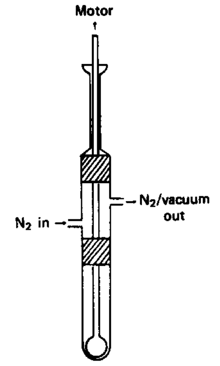
[a] $20°\text{C}\,\text{min}^{-1}$; values at $10°\text{C}\,\text{min}^{-1}$ were 1 or 2°C lower

CH_2Cl_2 along with 0.359 g DMAP (2.94×10^{-3} mol) and 0.892 g TEA (8.82×10^{-3} mol). The solution was cooled in an ice bath and 0.84 ml acetyl chloride (1.18×10^{-2} mol) was added dropwise. The reaction mixture was stirred at ice water temperature for 1 h, then allowed to warm to room temperature and stirred for an additional 5 h. The polymer was isolated by precipitation with methanol. Two additional purifications were performed by dissolution of the polymer in chloroform, filtration of the solution if necessary, and precipitation into slightly acidified (HCl) methanol. The product was dried *in vacuo* at 60°C.

The second method employed acetic anhydride as the esterifying agent. The PSU–OH was esterified using a 10-fold excess (vs. –OH groups, based on theoretical $\bar{M}_n$) of acetic anhydride prior to isolation, i.e. the acetic anhydride was added directly to the DMAC/K_2CO_3 reaction mixture used to produce the PSU–OH. Addition of the acetic anhydride was performed at room temperature and the reaction mixture was allowed to stir for 4 h. The reaction mixture was then filtered to remove the precipitated salts and the polymer was subsequently coagulated by pouring into a 50:50 (v/v) water/methanol solution. Two additional purifications were performed by dissolution in chloroform and precipitation with slightly acidified (HCl) methanol. The polymer was dried *in vacuo* at 60°C.

*Synthesis of poly(chloro-1,4-phenylene-*trans*-1,4-dicarboxylate) (PCPTCD)*

This thermotropic polyester was prepared by a melt acidolysis reaction in a similar manner to that described by Schaefgen[11] and Kwolek and Luise[12]. In a thick-walled test tube equipped with a 19/38 ground glass joint were placed 1.250 g (7.26×10^{-3} mol) of pulverized *trans*-CDA and 1.6598 g (7.26×10^{-3} mol) CHQDA along with 0.0006 g (7.26×10^{-6} mol) anhydrous sodium acetate. The reaction tube was then fitted with a 19/38 ground adapter with ports for N_2/vacuum and a high torque overhead mechanical stirrer. The glass stir-rod was designed with a paddle blade so as to just fit inside the tube in order to provide good stirring throughout the melt. The stir rod was fitted through a ground glass sleeve which could be sealed to allow vacuum be applied to the system. A sketch of the reaction vessel is given in *Scheme 1*.



Scheme 1 Melt acidolysis reaction vessel

The contents of the reaction tube were purged well with N_2 for at least several hours, then the tube was placed in a Wood's metal bath at 100°C. After the CHQDA had completely melted (av. m.p. = 71°C) stirring was begun and the bath temperature was quickly raised to 250°C and allowed to remain there for 1 h. The byproduct acetic acid which distilled from the molten mass was removed under a steady N_2 flow via the N_2 exit port. Stirring was kept rather brisk during this cycle to aid in byproduct removal and to allow for good mixing of the components. After 1 h at 250°C, the flux of acetic acid had substantially subsided and the bath temperature was raised to 280°C to facilitate further acetic acid removal. After 1 h at 280°C stirring was halted and vacuum was applied to the system over a 10–15 min period. The pressure was reduced to 0.2 mm Hg, and at this point the temperature was raised to 305°C and held there either for 1 h (sample H1, *Table 2*, below) or 0.5 h (sample H2, *Table 2*). Afterwards, the reaction vessel was brought to atmospheric pressure by bleeding in N_2, the stir rod was lifted out of the melt, and the tube was removed from the metal bath and allowed to cool under N_2. The solidified polymer was removed by cutting the tube and slicing the polymer away from the glass with a sharp knife followed by crushing. In the case of sample H1, the polymer was subsequently heat treated at 170°C for 48 h and then extracted with hot acetone for several hours. In the case of sample H2, the polymer was not heat treated, only extracted with acetone. Both samples were dried at 60°C *in vacuo* for several days prior to analysis.

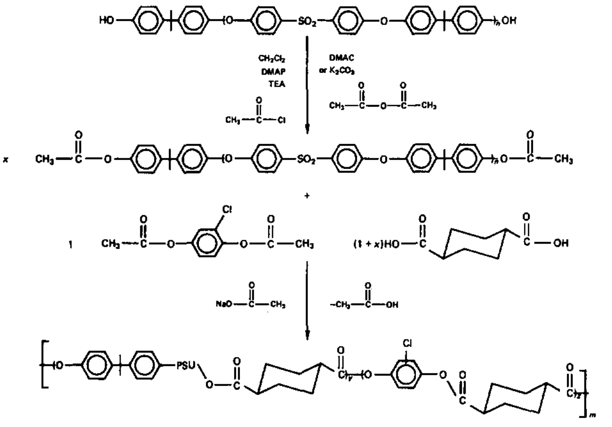
Table 2 Synthesis and characterization of PCPTCD and PSU–PCPTCD segmented copolymers

Sample	Wt% PSU[a]	PSU No. ($\bar{M}_n$)	η_{inh} (dl g^{-1})	T_{kk} (°C)	T_{kn} (°C)	ΔH_{kn} (cal g^{-1})[d]	Wt% soluble[c]
H1	0	–	3.0	188	306	1.04	–
H2	0	–	2.6	203	310	1.6	–
C1	25	6 (7000)	–	193	309	0.48 (0.64)	31.3
C2	50	6 (7000)	2.4	197	324	0.12 (0.24)	51.6
C3	75	6 (7000)	1.1	(189)[b]	–	–	87.3
C4	25	3 (3700)	–	197	318	0.62 (0.83)	24.5
C5	50	3 (3700)	2.5	191	301	0.15 (0.30)	48.4
C6	25	1 (1400)	–	187	306	0.58 (0.77)	0.9
C7	50	1 (1400)	–	(175)[b]	–	–	4.4
C8	25	8 (3100)	2.9	203	326	0.73 (0.97)	28.5
C9	50	8 (3100)	1.4	197	323	0.30 (0.60)	64.7
C10	25	7 (2300)	2.5	199	321	0.66 (0.88)	31.5
C11	50	7 (2300)	2.6	198	322	0.18 (0.36)	63.5

[a] Based on feed ratio
[b] T_g
[c] In chloroform
[d] Values in parentheses are corrected for the wt% of crystallizable material (polyester) in the copolymer

Synthesis of segmented copolymers of PSU and PCPTCD

The procedure was essentially the same as for the homopolymers described in the previous section. In these cases, the CHQDA was partially replaced by an appropriate molar amount of PSU–AC. The stoichiometry of acid to acetate groups was kept at 1:1. The v.p.o. $\bar{M}_n$ of the PSU–AC was used to determine molar quantity and the PSU–AC was introduced as a fine powder. Samples C1–C7 (*Table 2*) were produced and purified in the same manner as the homopolyester H1, (except C5, C6 not heat treated); while samples C7–C11 were synthesized and treated similarly to H2. The use of acetone to swell the copolymers facilitated their removal from the reaction vessel. Purification by extraction with hot acetone was performed in the same manner as for the homopolymers. Yield of recovered polymer was >90%. The overall weight per cent of PSU in the copolymers was varied between 25 and 75% as noted in *Table 2*.



Scheme 2 Synthesis of PSU–PCPTCD segmented copolymers

RESULTS AND DISCUSSION

The reaction pathway employed for the synthesis of PSU–PCPTCD segmented copolymers is outlined in *Scheme 2*. The PSU–OH prepared by the conventional techniques[32–34] was quantitatively esterified after isolation with acetyl chloride in the presence of catalyst/acid acceptors[37], or prior to isolation by acetic anhydride addition to the DMAc/K_2CO_3 reaction mixture used to produce the PSU–OH. Although this esterification reaction could also be performed *in situ* prior to the melt acidolysis reaction[28], prior acetate formation was chosen. As with PTC etherification of PSU–OH discussed in previous papers[35,36], the quantitative nature of the esterification reaction can be shown by both n.m.r. and i.r. spectroscopies. *Figures 1* and *2* show 200 MHz ^{1}H n.m.r. spectra of PSU–OH and PSU–AC, respectively. As before, quantitative reaction of the –OH chain ends results in downfield shifts of signals 1, 2 and 3. In this case, signal 3 moves from 1.64 to 1.68 ppm, while signals 1 and 2 essentially disappear from the spectrum of PSU–AC by moving under the other aromatic signals. In the i.r. spectra the rather large, broad –OH stretch (3448 cm^{-1}, *Figure 3a*) completely disappears after esterification (*Figure 3b*). The strong signal of the carbonyl group ($\nu_{C=O}$, 1760 cm^{-1}) now appears in this latter spectrum. The remainder of the i.r. spectrum of PSU–AC is given in *Figure 4b*. The results were the same by either esterification method.

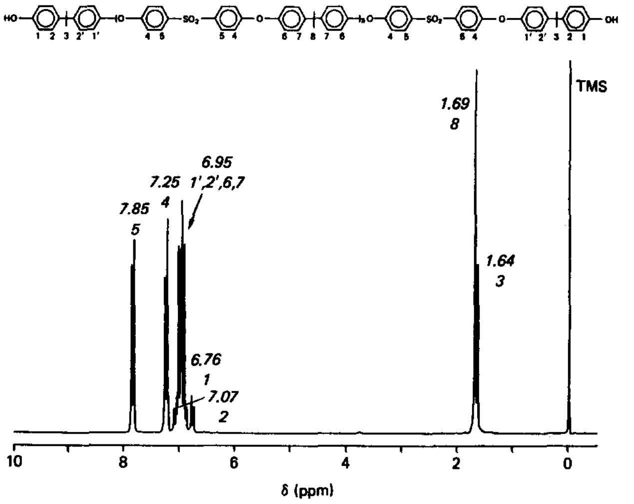


Figure 1 200 MHz ^{1}H n.m.r. spectrum of PSU-3-OH

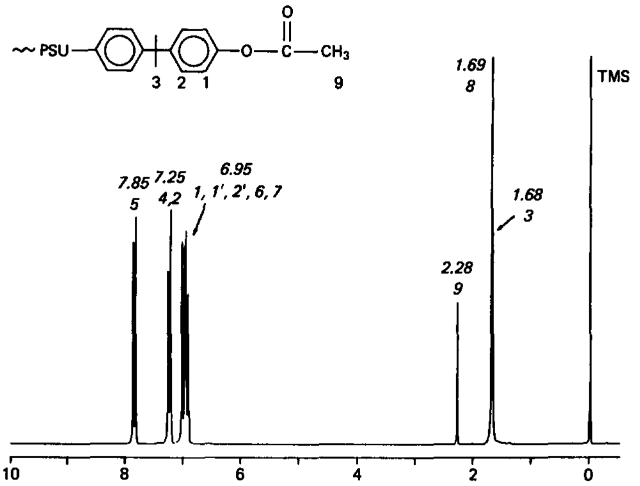


Figure 2 200 MHz ^{1}H n.m.r. spectrum of PSU-3-AC

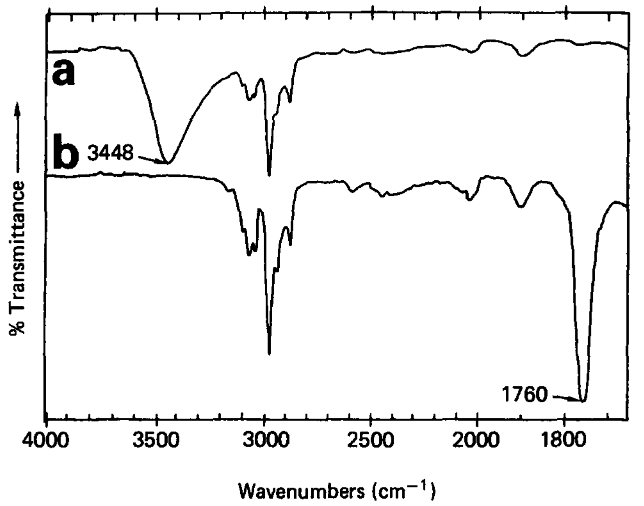


Figure 3 I.r. spectra of: (a) PSU-1-OH; (b) PSU-1-AC

Table 1 presents the characterization data for the various molecular weight PSU–AC materials produced. Samples 1, 3 and 6 have been utilized in previous work[35,36] (although with different chain ends) and the data are in good general agreement with previous results. Samples 7 and 8 were synthesized as necessitated by the work described in this paper and again show the consistency between v.p.o. and n.m.r. $\bar{M}_n$ results attributable to their good functionality. The v.p.o. and n.m.r. $\bar{M}_n$ results show quite good agreement up to 4000

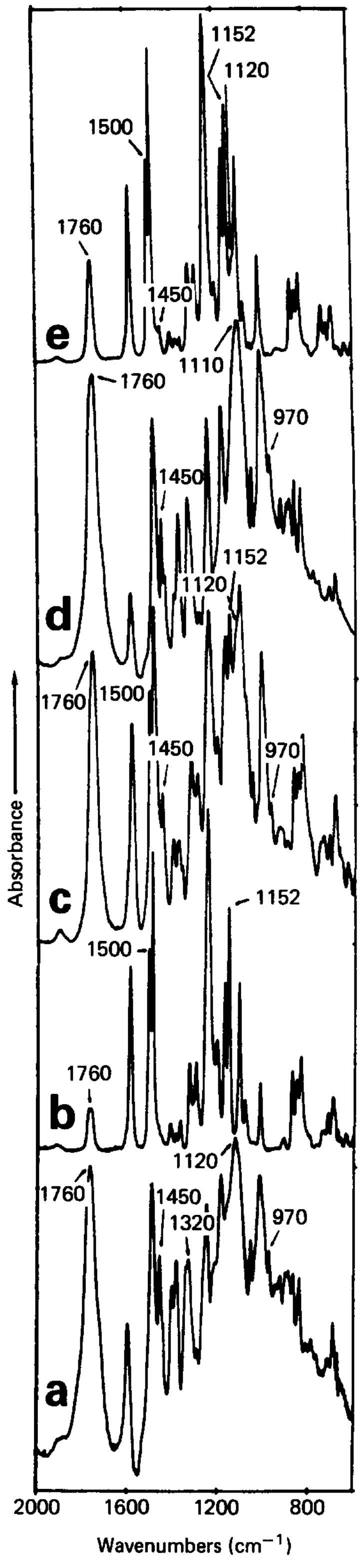


Figure 4 *FT*-i.r. spectra of: (a) PCPTCD; (b) PSU-7-AC; (c) copolymer of PSU-1-AC and PCPTCD (C7, *Table 2*); (d) chloroform-insoluble fraction of the copolymer of PSU-7-AC and PCPTCD (C11, *Table 2*); (e) chloroform-soluble fraction of copolymer in (d)

daltons, which is better than that previously obtained[35,36]. This is probably due to the more intense signal of the acetate protons (signal 9, *Figure 2*), and to the fact that the *FT*-n.m.r. integrals were obtained from only one scan as against the 16 to 64 used previously. This avoids relaxation time differences between signals, which can distort the integrals used for $\bar{M}_n$ calculations. The n.m.r. $\bar{M}_n$ was calculated via the equations:

$$DP = \frac{A(9)}{A(8+3)} - 1 \quad \text{and}$$

$$\bar{M}_n = DP\,[MW(\text{repeat unit})] + MW(\text{BPA} - 2\text{H}) + MW(\text{acetate end-groups})$$

The homopolyester, PCPTCD, and the PSU–PCPTCD segmented copolymers were synthesized via a melt acidolysis reaction[38–40] of *trans*-CDA with CHQDA[11,12] or *trans*-CDA with CHQDA and PSU–AC, respectively, as illustrated in *Scheme 2*. Although there are several other methods for polyester synthesis, e.g. a solution reaction of a diacid chloride with a diol in the presence of an acid acceptor[41], an interfacial or phase-transfer catalysed reaction of a diacid chloride[26,27,42] in an organic solvent with aqueous phenolates or alcoholates, the melt acidolysis procedure has been noted by several authors[28,31] as being the most versatile method for the production of thermotropic block copolyesters. Polymers prepared by solution or even interfacial methods usually exhibit low inherent viscosities due to their very low solubility in the solvents employed. The melt acidolysis route, which involves reaction of a diacid with a diacetate in the melt at high temperature (250 to 300 + °C) with loss of acetic acid, has been shown[12] to give much higher molecular weights versus low temperature solution methods. The melt acidolysis method was thus employed in the work described here.

The characterization of the homopolyesters H1 and H2 is presented in *Table 2*. The inherent viscosities of both are consistent with literature data[12,13]. The difference between these two samples lies in the fact that sample H1 was held for 1 h during the vacuum cycle at 305°C (only 0.5 h for H2) and that it was subsequently heat treated (post-polymerized)[40] at 170°C for 48 h. As would be expected from this treatment, the inherent viscosity of H1 is higher than that of H2, indicating a higher molecular weight; however, the degree of crystallinity as indicated by the d.s.c. transition temperatures (T_{kk} = crystal→crystal, T_{kn} = crystal→nematic)[12,13] and ΔH_{kn} is surprisingly lower. This may be due to some difference in their thermal histories, the effect of polymorphism[12], or possibly due to some small amount of crosslinking or branching at elevated temperatures, noted by Jackson for chlorohydroquinone containing copolyesters[7]. This crosslinking reaction involving the chlorine groups is facilitated by the presence of oxygen but, according to Jackson[7], can even occur in an inert atmosphere in relatively short times at ca. 300°C. Although Schaefgen[11] has reported chlorohydroquinone containing copolyesters synthesized in excess of 300°C for several hours, reaction times above 300°C are typically kept short ($\sim$0.5 h). For this reason, in later experiments (H2, C8–C11) reaction times at 305°C were reduced to 0.5 h. Whether any crosslinking or branching has taken place in any of the samples is not known, but if it has, its extent is small as evidenced by the solubility of the homo- and copolymers.

The thermal characterization of the homopolymers is also presented in *Table 2*. Consistent with the data presented by other authors[12,13] this thermotropic polyester exhibits a crystal–crystal transition (T_{kk}) in the

200°C range and a crystal–nematic endotherm (T_{kn}) above 300°C. The nematic mesophase at $T > 300$°C was verified by optical microscopy, which will be discussed later. The nematic state exists up until the decomposition temperature of this polymer (ca. 400°C)[12,13]. The d.s.c. transitions are highly dependent on the thermal history of the sample[12,13] and therefore for comparison purposes both homo- and copolymers were analysed in the same manner by d.s.c. All the thermal data listed in *Table 2* were recorded during the second heating scan at 20°C min^{-1}. The second heated scan followed: (1) a 20°C min^{-1} heating scan from 30 to 370°C (first heating scan) which was immediately followed by (2) a slow cool from 370 to 30°C at 20°C min^{-1}. Examples of the various d.s.c. scans for a homopolyester are given in *Figures 5a–5c*. The cooling curve (*Figure 5b*) of the PCPTCD shows the reversibility of the two transitions at lower temperatures than on heating. It is noted from the given example, and data from the copolymers as well, that the transitions during the first heating scan were always accompanied by a larger enthalpy change and occurred at higher temperatures than those of subsequent scans.

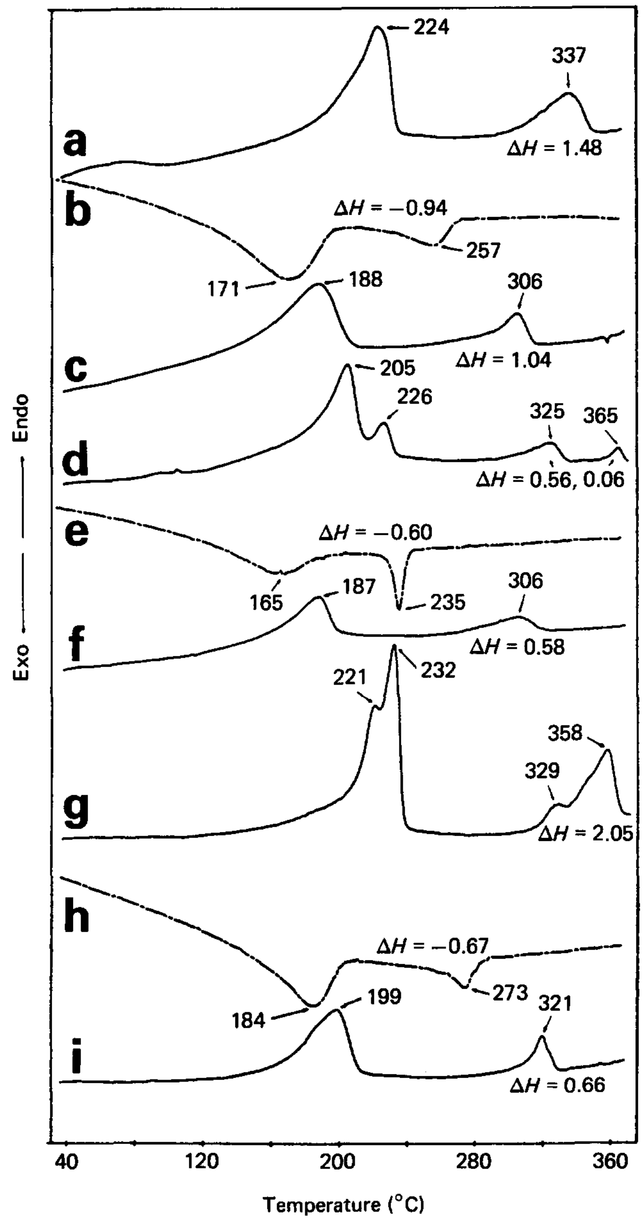
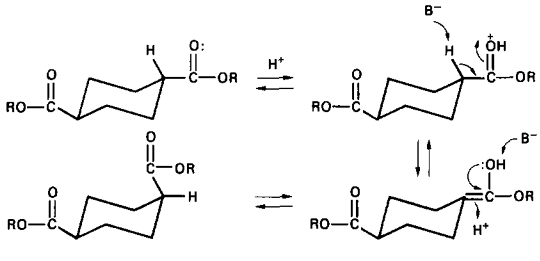


Figure 5 D.s.c. curves of: (a), (b), (c) PCPTCD (Sample H1, *Table 2*), first heating, first cooling and second heating scan, respectively; (d), (e), (f) the copolymer of PSU-1-AC and PCPTCD (C6, *Table 2*), first heating, first cooling and second heating scans, respectively; (g), (h), (i) the copolymer of PSU-7-AC and PCPTCD (C10, *Table 2*), first heating, first cooling and second heating scans, respectively

The PCPTCD was insoluble in typical organic solvents, making characterization somewhat difficult. The polymer was, however, analysed by *FT*-i.r. and a spectrum is given in *Figure 4a*. In addition to the very strong band due to the carbonyl group of the ester linkages present (1760 cm^{-1}, $\nu_{C=O}$), bands at 1320 cm^{-1} and 970 cm^{-1}, typical of the *trans* cyclohexane units, are readily observed. The *cis* version of this polyester does not show these bands[12]. Additionally, strong absorptions at 1450 cm^{-1} and 1120 cm^{-1} are present which do not appear in the spectrum of PSU–AC. These bands will later be used for copolymer analysis.

The PCPTCD homopolymer is somewhat of a complex material. In addition to being thermotropic and displaying a crystal–crystal transition, it is also known to be polymorphic and subject to *cis–trans* isomerization at elevated temperatures[12]. It has been shown that the crystal structure in polymer can be in a triclinic, as well as a hexagonal form[12], depending on the thermal history of the polymer. The triclinic structure has been shown to yield better mechanical properties[12]. Likewise, *cis–trans* isomerization (via enol/enolate intermediate) of the cyclohexane dicarboxylate units is possible at the high melt temperatures employed in the reaction (as with the acid monomers). This isomerization is acid/base catalysed and is outlined as follows:



The *trans* isomer is highly favoured in this system and it was noted that the solution-prepared *cis* polymer converts to the *trans* form rather quickly in the melt at $T \geqslant 280$°C[12]. This fact allows thermotropic polyesters to be prepared from either *cis*- or *trans*-CDA because the non-thermotropic *cis* form converts readily to *trans* in the melt, giving an essentially pure *trans* polymer[12]. Very recent data in this regard from Schwarz *et al.*[43] have shown that independent of the *cis–trans* monomer ratio, at temperatures of 290–320°C, $98 \pm 2\%$ of the *trans* structure is evident in crystalline and liquid crystalline phases of the formed polyester. In isotropic phases this preference is reduced to $66 \pm 2\%$. Obviously, crystallinity or liquid crystallinity provides a thermodynamic driving force for the *trans* isomer. In the homopolymer used here, this preference is very high; however, copolymers may, perhaps, exhibit somewhat different behaviour. The polymorphism and isomerization potential for this homopolymer make its thermal characterization complex, especially for copolymers and this will be discussed further below.

Segmented copolymers of PSU and PCPTCD were prepared from *trans*-CDA and CHQDA by replacement of some of the CHQDA by a polymeric diacetate, namely PSU–AC as defined in *Scheme 2*. Depending on the molecular weight of the PSU–AC, different copolymer morphologies could be envisioned. A low molecular weight PSU–AC could be viewed as a non-mesogenic bisphenol modifier in much the same way as various non-mesogenic bisphenol monomers have been used to modify thermotropic polyesters[5,44]. The short block length of the 'bisphenol' becomes essentially incorporated into the polyester structure and thereby modifies its thermal transitions and mechanical properties. At the opposite end, the use of a high molecular weight PSU telechelic could be ideally viewed as giving rise to a true block copolymer with long PSU segments chemically bound to, but physically distinct from, the thermotropic polyester segments. This physical segregation would be due to microphase separation owing to the incompatibility of the two polymers. Ideally, the extended chain, highly oriented polyester segments would be embedded and chemically bound to a PSU amorphous matrix. Whether this situation can be realized under the conditions described will be discussed further below.

The weight per cent of PSU in the copolymers was varied between 25 and 75% and the $\bar{M}_n$ between 1400 and 7000, as noted in *Table 2*. Inherent viscosities of most of the copolymers were obtained and show that reasonably high molecular weight copolymers were produced. Typical methods of molecular weight determination are difficult for the aromatic polyesters due to their insolubility in most solvents other than strong acids. For reference purposes, however, the inherent viscosities of PSU-6-AC (v.p.o. $\bar{M}_n = 7000$, g.p.c. $\bar{M}_w = 20\,000$) and commercial PSU (from Aldrich, g.p.c. $\bar{M}_w = 54\,000$) were measured in the same solvent as for the homo- and copolymers (ClPh/TFA, 3:1 v/v). PSU-6-AC had an inherent viscosity of 0.25 dl g^{-1}, while the commercial sample gave 0.64 dl g^{-1}. The copolymers all show values quite a bit higher than this, indicating a high degree of polymerization.

The *FT*-i.r. spectrum of a typical copolymer is given in *Figure 4c*. This spectrum shows the bands characteristic of the homopolyester (970, 1120, 1450 cm^{-1}) mentioned before (*Figure 4a*), as well as bands exclusive to PSU (1152 cm^{-1}, ν_{SO_2} sym, 1500 cm^{-1} aromatic C–C vibration). Additionally, the intense carbonyl band of the ester linkages is noted at 1760 cm^{-1}. This spectrum is typical of all the copolymers obtained, with variation via intensities due to the different weight ratios of PSU/PCPTCD.

The thermal characterization of the copolymers by d.s.c. is also included in *Table 2*. It is seen that in most cases, thermal transitions very similar to those of the homopolyester were observed. The nature of the transitions at least for T_{kn} was verified by optical microscopy, which is discussed in the next paragraph. Only in two cases was the absence of transitions due to crystalline or liquid crystalline components noted in the second heating scan. These are C3 (75% PSU-6-AC, $\bar{M}_n = 7000$) and C7 (50% PSU-1-AC, $\bar{M}_n = 1400$). For these cases, only a single T_g was evidenced during the second heating scan. A small d.s.c. endotherm (~329°C) was noted, however, on the first heating scan for sample C7, ($\Delta H = 0.13$ cal g^{-1}) but this was not found on subsequent runs. Apparently, the high weight per cent of PSU coupled in the latter case with the low PSU molecular weight (functions as a bisphenol modifier) gave systems with low degrees of crystallinity or liquid crystallinity. The appearance of only one T_g in sample C7 suggests a single-phase material for this low molecular weight PSU. At lower weight per cent of PSU-1, however, (C6, 25 wt% PSU-1-AC) crystallinity was readily observed (see *Figures 5d–5f*). It was generally noted as well that with 50 wt% PSU, for the whole range of molecular weights, ΔH_{kn} was significantly lower than at 25 wt%, even when the values were corrected for the amount of crystallizable component (*Table 2*, values in parentheses). It seemed obvious that the higher the weight per cent of PSU in the copolymer the less of the component polyester was crystallizable.

Optical micrographs taken at 330°C of PCPTCD homopolymer, H1 and a representative segmented copolymer (C10, *Table 2*) are given in *Figures 6* and *7*, respectively. As expected, the schlieren nematic textures observed in the molten state were very similar to the nematic textures found by other authors[13] for the PCPTCD homopolymer. In all cases in which crystalline/liquid crystalline transitions were noted by d.s.c., birefringence was apparent in the melt (between cross polarizers), and the melt could be readily sheared and aligned by movement of the cover glass. Qualitatively, birefringence was observed to decrease with an increase in PSU content, as expected. For samples C3 and C7 in which crystalline transitions were

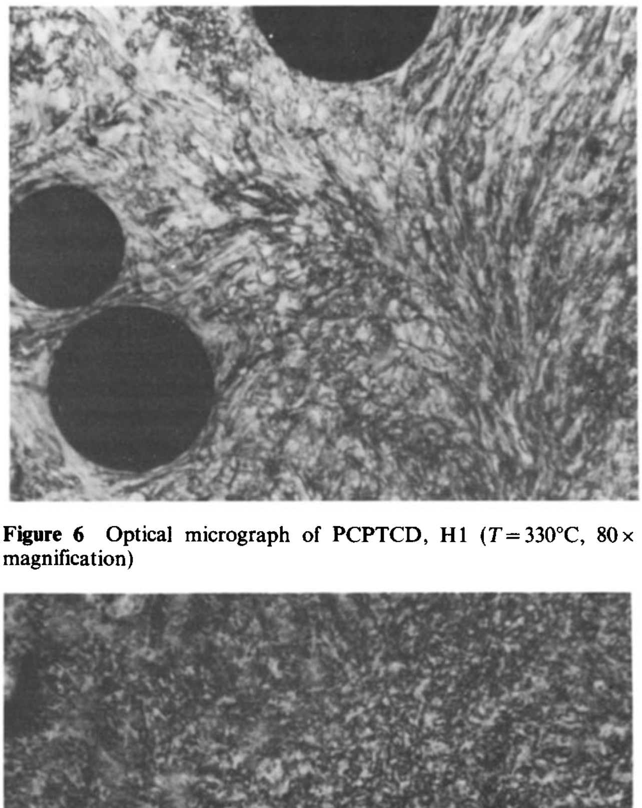


Figure 6 Optical micrograph of PCPTCD, H1 ($T = 330$°C, 80× magnification)

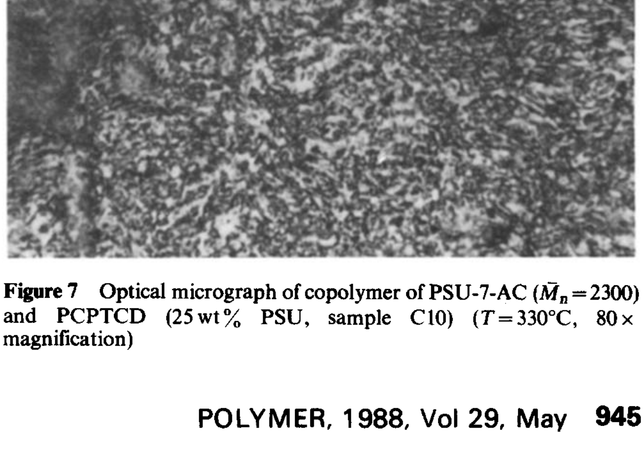


Figure 7 Optical micrograph of copolymer of PSU-7-AC ($\bar{M}_n = 2300$) and PCPTCD (25 wt% PSU, sample C10) ($T = 330$°C, 80× magnification)

absent in the d.s.c., the melts were essentially nonbirefringent and were not readily sheared, indicating the general lack of liquid crystallinity in these samples. These optical microscopy observations confirm the existence of the liquid crystalline state above 300°C for most copolymers, as has been suggested by d.s.c. and the findings of other authors[12,13] for the PCPTCD homopolymer.

Another interesting feature of the thermal data in *Table 2* is that, despite lower ΔH_{kn} for the co- versus homopolymers, often T_{kn} transitions occurred at somewhat higher temperatures. The reason for this, however, is not clear at this point. It should be mentioned as well that although values for T_{kk} have been recorded for the copolymers in *Table 2*, overlapping with the polysulphone T_g occurred (as discussed later) making these values approximate. This fact also makes assessment of phase separation difficult because the PSU T_g cannot be clearly discerned from the T_{kk} of PCPTCD when both are present in the copolymer.

Typical d.s.c. traces for the copolymers are given in *Figures 5d–5i*. As with all the copolymers both T_{kk} and T_{kn} showed a 'bimodal' nature on the first heating scan and, in some cases, to some extent on the subsequent cooling scan. The reason for this is not quite known; however, it can be speculated that it is the result of the polymorphism discussed above, or due possibly to some *cis–trans* isomerization, or even some influence of incorporated PSU segments. In any case, this bimodal nature was essentially absent in the second heating scan of all the copolymers. The reversibility of the transitions on cooling and subsequent heating was also evident for the copolymers as for the homopolymer. The transitions on cooling always occurred at lower temperature than on the subsequent heating scan. The exact temperature and magnitude of the transition varied from copolymer to copolymer.

Interestingly, two copolymers (C1, C4) were noted to be inhomogeneous on a macroscopic scale. Regions of tan coloured polymer were intermixed with white regions. At first it was thought that the tan regions were composed of PSU that had phase separated from the highly ordered, crystalline PCPTCD. A whitening effect in anisotropic polymer melts is often seen upon shearing[4], however, and in the copolymers this may have resulted from stirring of the melt after the anisotropic phase had formed, and this whitening of some anisotropic domains remained in the polymer. To check this, it was possible to mechanically separate the two forms of polymer in C4. The tan regions were swollen by acetone, but the white areas were not. D.s.c. analyses were performed for both forms and compared to the bulk sample. While the bulk sample exhibited the typical bimodal nature of T_{kk} and T_{kn} present in all copolymers during the first heating scan, the separated forms showed a high preference for only one mode. The white polymer showed almost exclusively T_{kk} and T_{kn} corresponding to the higher temperature peaks and the tan region due to the lower temperature peaks. Since both phases show crystalline transitions, the tan portion is not just PSU, but it is PSU-rich, as evidenced by the swelling in acetone. The inhomogeneity noted on a macroscopic scale for these two copolymers (C1, C4) is probably present in the other copolymers as well, but on a much smaller scale. This could explain the bimodal nature exhibited by all copolymers in d.s.c.

Although the inherent viscosities measured and recorded in *Table 2* indicate that reasonably high molecular weight copolymers are formed, the question remains whether these materials are true block copolymers. This was the desired goal because, as mentioned in the introduction, this should lead to the best dispersion of rod-like polymer in flexible matrix and thereby probably the best properties. In order to assess this, it was realized that unreacted PSU–AC, as well as PSU-rich copolymer could be extracted from the highly insoluble PCPTCD-containing chains with chloroform (a good solvent for PSU). Essentially, if all block copolymer is present, and the PCPTCD segments are of sufficient length, very little material should be extractable because the insoluble PCPTCD blocks chemically attached to the PSU would prevent dissolution. The block copolymer should swell but not dissolve. On the other hand, if substantial unreacted PSU–AC or PSU-rich copolymer is present it should be readily solubilized by chloroform. A 0.5 g sample of all copolymers was vigorously stirred in $CHCl_3$ overnight at room temperature and then carefully filtered. The $CHCl_3$ was removed from the filtrant using a rotary evaporator and the resultant films were dried at 60°C *in vacuo*. As can be seen in *Table 2*, except for the cases of copolymers from the lowest $\bar{M}_n$ PSU-1-AC, where only small amounts of material were extracted, the chloroform-soluble fraction of the copolymers equals or exceeds the wt % PSU in the feed. Characterization of this soluble fraction will be described in the next paragraphs. This result indicates that for PSU $\bar{M}_n \geqslant 2300$ true block copolymers were not formed under the simple melt acidolysis conditions described. The same phenomenon has been observed by Krigbaum *et al.*[21] in the synthesis of rigid rod/flexible coil aromatic block copolyamides by solution techniques. It was noted that substantial fractions of soluble material could be extracted from the copolymers, in many cases depending on the reaction method, and that this fraction has essentially flexible homopolymer which was not coupled with the rigid rod block[21]. This situation may be present in other melt acidolysis prepared blocks as well[28,30,31], but insufficient data were presented to ascertain this.

In order to understand the nature of the copolymers produced, the chloroform-soluble fraction was characterized by g.p.c., n.m.r., i.r. and d.s.c., and the insoluble fraction by i.r. and d.s.c. *Table 3* summarizes the g.p.c. and d.s.c. results for the soluble fraction. As seen from

Table 3 Characterization of the chloroform-soluble fraction of PSU–PCPTCD segmented copolymers

Sample	PSU No. ($\bar{M}_w$[g.p.c.])/wt %[a]	Wt % soluble	$\bar{M}_w$ (g.p.c.)	T_g (°C)
C1	6(20000)/25	31.3	78 000	183
C2	6(20000)/50	51.6	103 000	182
C3	6(20000)/75	87.3	111 000	183
C4	3(7600)/25	24.5	125 000	179
C5	3(7600)/50	48.4	155 000	175
C6	1(1800)/25	0.9	10 500	–
C7	1(1800)/50	4.4	16 000	155
C8	7(6000)/25	28.5	59 000	169
C9	7(6000)/50	64.7	182 000	176
C10	8(3900)/25	32.0	56 000	167
C11	8(3900)/50	63.5	107 000	177

[a] Based on feed ratio

g.p.c. $\bar{M}_w$ values reported here as compared to *Table 1*, a fair amount of chain extension of the PSU has taken place during the melt acidolysis reaction, and this increases for a given PSU with an increase in PSU weight fraction in the feed. Graphically, this chain extension is illustrated by the g.p.c. traces in *Figures 8a* and *8b*. *Figure 8c* shows the fraction extracted from the copolymer by acetone purification. This extracted amount was always small ($\leqslant$2.5 wt%) and was composed of cyclic PSU[32] and low molecular weight linear copolymer.

A typical n.m.r. spectrum of the chloroform-soluble fraction is presented in *Figure 9* with an expansion of the aromatic region given in *Figure 10*. The spectrum in *Figure 9* is similar to that of PSU–AC in *Figure 2*. The differences lie in the appearance of small signals due to *trans* cyclohexane units of the polyester (signals A), those due to chlorophenylene units (signals B, see also *Figure 10*), and in the large decrease in the signal 9 (PSU acetate end-groups) at least to the point where it can no longer be distinguished from the resonances of the cyclohexane units. These data demonstrate the incorporation of some PCPTCD segments into the PSU, forming a segmented copolymer. Quantification of the amount incorporated was difficult due to overlapping of the resonance but it was obviously small and decreased with increasing molecular weight of the PSU segment. D.s.c. measurements of the soluble fraction revealed only a T_g that indicated a completely amorphous polymer. These T_g values are listed in *Table 3*. Interesting to note is that although the T_g values showed significant increases over the starting PSU–ACs, they were lower than the 190°C value typical of high molecular weight PSU, even though high $\bar{M}_w$ values were given by g.p.c. This is due to the flexible but non-crystalline cyclohexane units that were incorporated in the chain.

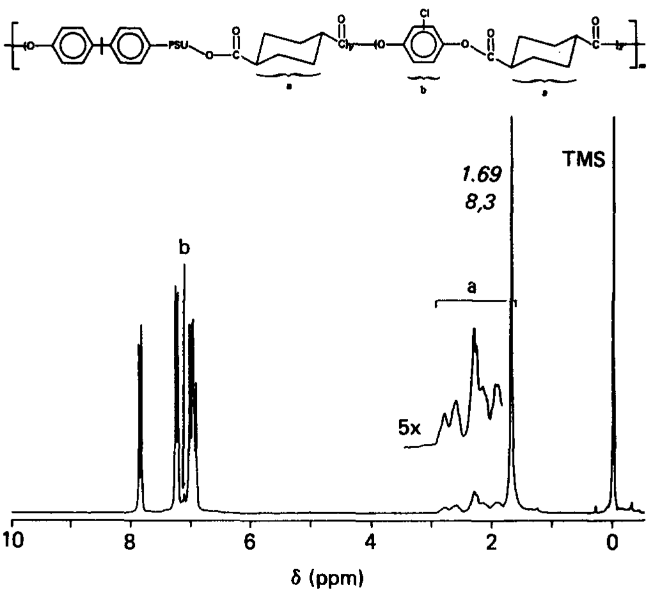


Figure 9 200 MHz ^{1}H n.m.r. spectrum of the chloroform-soluble fraction of the copolymer from PSU-7-AC and PCPTCD (C11, *Table 2*)

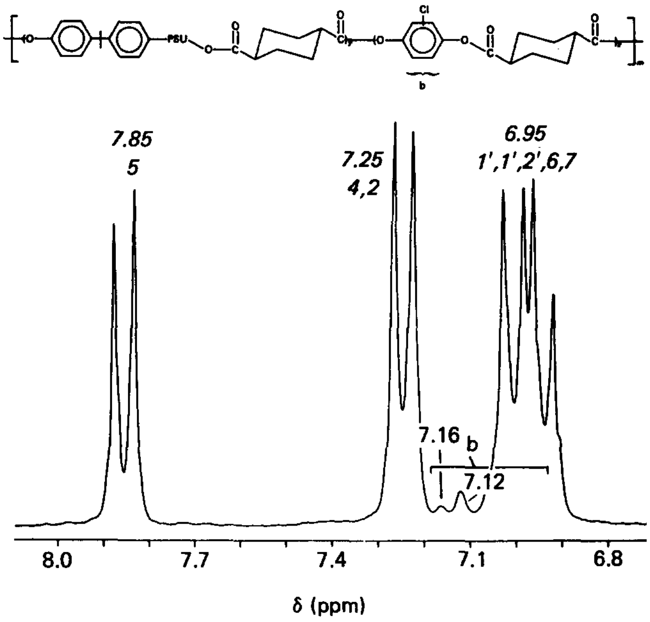


Figure 10 200 MHz ^{1}H n.m.r. expansion of the aromatic region of the copolymer in *Figure 7*

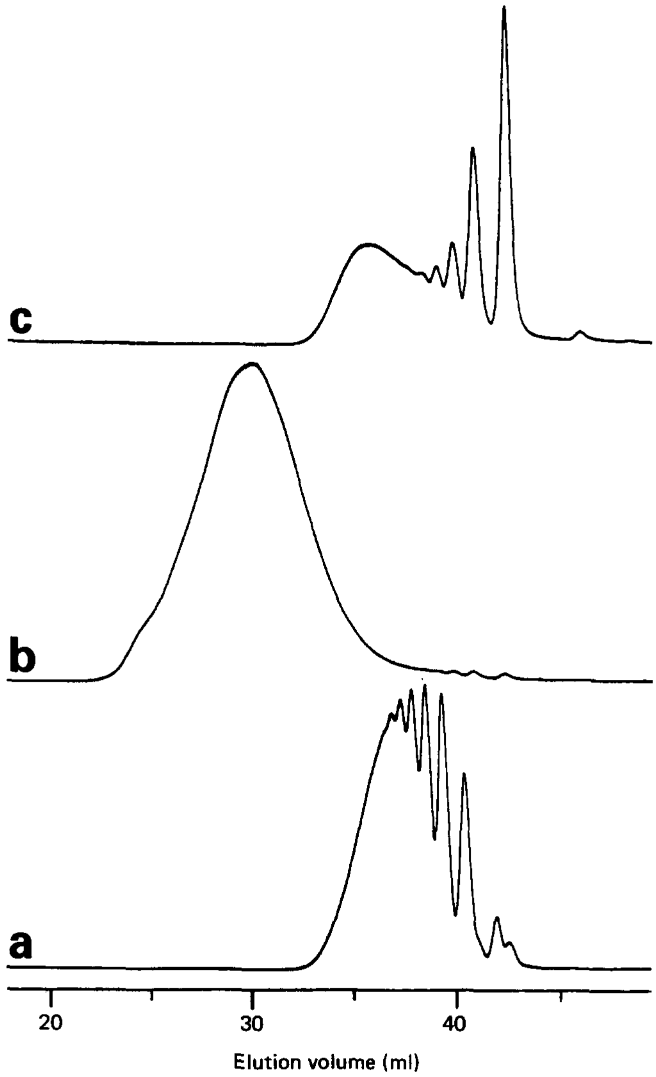


Figure 8 G.p.c. chromatograms of: (a) PSU-7-AC ($\bar{M}_w$ = 3900); (b) the chloroform-soluble fraction of the copolymer of PSU-7-AC and PCPTCD (C11, $\bar{M}_w$ = 107 000); (c) the acetone extracted fraction of the copolymer in (b) ($\bar{M}_w$ = 3000)

Typical *FT*-i.r. spectra of the chloroform-insoluble and soluble fractions of PSU–PCPTCD copolymers are shown in *Figures 4d* and *4e*, respectively. As was shown by n.m.r. in *Figure 9*, a small amount of PCPTCD segments was present in the soluble fraction, as evidenced by the small bands at 1120 and 1450 cm^{-1} (compare to *Figure 4a*), although this spectrum was otherwise largely equivalent to that of the PSU (*Figure 4b*). The insoluble fraction (*Figure 4d*), on the other hand, is largely equivalent to the homopolyester in *Figure 4a*. In most cases, no evidence of the bands at 1152 or 1500 cm^{-1} typical of the PSU was seen. This indicated that essentially the insoluble fraction was homo-PCPTCD with little or no PSU incorporated, at least that could be detected by *FT*-i.r. D.s.c. analysis of this fraction gave thermal data similar to the homopolymers. Only in the case of the lowest molecular weight PSU-1 ($\bar{M}_n = 1400$) (C6, C7) did the i.r. spectrum of the insoluble fraction show bands due to both PCPTCD and PSU. The spectrum was essentially equivalent to that of the unextracted copolymer (as in *Figure 4c*). For this low molecular weight, the PSU was almost completely incorporated into the polyester structure (as for a bisphenol), and very little material was soluble in $CHCl_3$. These data then demonstrate that, except for the lowest molecular weight PSU, the reaction produced a highly chain extended PSU coupled by short PCPTCD segments as flexible amorphous high T_g matrix, and a crystalline PCPTCD homopolyester containing little PSU as a reinforcement. Although to some extent a segmented copolymer is formed, under the chosen reaction conditions, the copolymers produced (for PSU $\bar{M}_n \geqslant 2300$) were largely 'blends' of matrix and reinforcement.

In order to understand why this takes place the reaction must be further considered. In the melt acidolysis reaction for the production of the segmented copolymers several 'sub' reactions can be postulated. These include the chain extension of the PSU by the diacid; the build up of homopolyester, and the linking of polyester blocks with PSU. These reactions would be suspected to be highly influenced by the molecular weight of the PSU and its weight per cent in the reaction mixture, not only from the point of view of the concentration of its end-groups, but also from a PSU/PCPTCD incompatibility standpoint. The PSU and polyester segments are expected to be highly incompatible and this could have a profound effect on whether or not the respective end-groups can come together to react to form the desired block copolymer. As noted by Flory[20], the extended chain molecules would tend to reject the flexible coil molecules and form their own discreet phase free of flexible molecules. This tendency would increase with concentration. In the melt the concentration is maximum, so it would seem likely that when PCPTCD molecules of sufficient length are formed, they tend to aggregate and phase separate from the flexible PSU matrix. Of course, although the weight per cent of PSU can be high in the reaction, the end-group concentration is still usually very low; statistically therefore, it would be suspected that significant reaction between only diacid and diacetate monomers could take place before a PSU acetate end group is encountered. This could lead to a sufficient length of nematic PCPTCD which would then tend to shun the flexible matrix. If this occurs, reaction between PCPTCD and PSU molecules becomes highly improbable because they exist in different phases. As with PSU–PDMS block copolymers discussed in previous papers[35,36], reaction between molecules in different phases can be very difficult. This then is a suspected reason for the lack of formation of true block copolymer. Additionally, it is also possible that if block copolymer was initially formed, crystallization-induced re-organization reactions of liquid crystalline polyesters demonstrated by Lenz *et al.*[45] could have resulted in a restructuring of the block copolymer. These ester interchange reorganization reactions would favour a separation of the liquid crystalline PCPTCD segments from the non-crystalline PSU segments.

Although conversions of reactive groups in the simple melt acidolysis procedure is high, as noted from the degree of PSU chain extension and the inherent viscosities, the procedure used here does not seem satisfactory to produce true block copolymer for higher PSU molecular weights ($\bar{M}_n \geqslant 2300$). This may possibly be altered by changes in reaction time, temperature cycles, or the use of a processing aid as described in a very recent patent[31], but this is beyond the scope of the present investigation.

The mechanical properties of these copolymers, although they are not true blocks, may still be very interesting, considering that the copolymers may be intimate blends. As was noted previously, intimate blocks of rigid rod and flexible molecules[15,19] are molecular composites and can show marked improvements in properties over macroscopically reinforced materials. The mechanical properties as well as the morphological characterization of these copolymers is left for future work.

CONCLUSIONS

Segmented copolymers of PSU and PCPTCD were produced by a melt acidolysis procedure. Degrees of chain extension were high, and for PSU with $\bar{M}_n = 1400$ the desired block copolymers were obtained. For PSU with $\bar{M}_n \geqslant 2300$, on the other hand, true block copolymers were not achieved. The resulting copolymers were found to be largely 'blends' of amorphous PSU chain extended to a high degree by short PCPTCD segments, and PCPTCD homopolymer. Thermal characterization of copolymers by d.s.c. showed crystal–crystal and crystal–nematic transitions similar to PCPTCD homopolymer in most cases, indicating the presence of crystalline domains and liquid–crystalline mesophases. Optical microscopy verified the presence of the nematic liquid crystalline mesophase. The enthalpies of the transitions, corrected for the amount of crystallizable component, decreased with increasing weight per cent PSU.

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REFERENCES

1 Zachariades, A. E., Mead, W. T. and Porter, R. S. in 'Ultra High Modulus Polymers', (Eds. A. Ciferri and I. M. Ward), Applied Science Publishers, London, 1979, p. 77

2 Smith, P. and Lemstra, P. J. *Makromol. Chem.* 1979, **180**, 2983

3 Schaefgen, J. R., Bair, T. E., Ballou, J. W., Kwolek, S. L., Morgan, P. W., Pafar, M. and Zimmerman, J. in 'Ultra High Modulus Polymers', (Eds. A. Ciferri and I. M. Ward), Applied Science Publishers, London, 1979, p. 203

4 Griffin, B. P. and Cox, M. K. *Br. Polym. J.* 1980, **12**, 147

5 Jin, J.-I., Antoun, S., Ober, C. and Lenz, R. W. *Br. Polym. J.* 1980, **12**, 132

6 Jackson, W. J., Jr *Br. Polym. J.* 1980, **12**, 154

7 Jackson, W. J., Jr, in 'Contemporary Topics in Polymer Science', (Ed. E. J. Vandenberg), Plenum Press, New York, 1984, Vol. 5, p. 177

8 Jackson, W. J., Jr, *J. Appl. Polym. Sci., Appl. Polym. Symp.* 1985, **41**, 25
9 Jackson, W. J., Jr *Macromolecules* 1983, **16**, 1027
10 McFarlane, F. E., Nicely, V. A. and Davis, T. G. in 'Contemporary Topics in Polymer Science', (Eds. E. M. Pearce and J. R. Schaefgen), Plenum Press, New York–London, 1977, p. 109
11 Schaefgen, J. R., US Patent 4 118 372, 3 Oct. 1978
12 Kwolek, S. L. and Luise, R. R. *Macromolecules* 1986, **19**, 1789
13 Kyotani, M. and Kanetsuna, H. *J. Polym. Sci., Polym. Phys. Edn.* 1983, **21**, 379
14 Prevorsek, D. C. in 'Polymer Liquid Crystals', (Eds. A. Ciferri, W. R. Krigbaum and R. B. Meyer), Academic Press, New York, 1982, p. 329
15 Takayanagi, M. *Pure Appl. Chem.* 1983, **55**, 819
16 Takayanagi, M., Ogata, T., Morikawa, M. and Kai, T. *J. Macromol. Sci., Phys. (B)* 1980, **17**, 591
17 Helminiak, T. E., Benner, C. L., Arnold, F. E. and Husman, G. E. US Patent 4 207 407, 10 June 1980
18 Hwang, W.-F., Wiff, D. R., Helminiak, T. E. and Adams, W. W. *Prepr. Am. Chem. Soc. Div. Polym. Mat. Sci. Eng.* 1983, **48**, 929; (a) Tsai, T. T., Arnold, F. E. and Hwang, W. F. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* 1985, **26**(1), 144
19 Krause, S. J., Haddock, T., Price, G. E., Lenhert, P. G., O'Brien, J. F., Helminiak, T. E. and Adams, W. W. *J. Polym. Sci., Polym. Phys. Edn.* 1986, **24**, 1991
20 Flory, P. J. *Macromolecules* 1978, **11**, 1138
21 Krigbaum, W. R., Preston, J., Ciferri, A. and Shufan, Y. *J. Polym. Sci., Polym. Chem. Edn.* 1987, **25**, 653
22 Ogata, N., Sanui, K., Watanabe, M. and Yahagi, I. *J. Polym. Sci., Polym. Lett. Edn.* 1985, **23**, 349
23 Yahagi, I., Watanabe, M., Sanui, K. and Ogata, N. *J. Polym. Sci., Polym. Chem. Edn.* 1987, **25**, 727
24 Fradet, A., Eckel, J. and Heitz, W., Makromolekulares Kolloquium Freiburg, Freiburg, March 1987, Abstr., p. 45
25 Risse, W. and Heitz, W., German Offen. 3 505 142, 14 August 1986
26 Lambert, J. M., Webster, D. C. and McGrath, J. E. *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* 1984, **25**(2), 14
27 Lambert, J. M., Webster, D. C. and McGrath, J. E. in 'Advances in Polymer Synthesis', (Eds. B. M. Culbertson and J. E. McGrath), Plenum Press, New York, 1985, p. 93
28 Lambert, J. M., McGrath, B. E., Wilkes, G. L. and McGrath, J. E. *Prepr. Am. Chem. Soc. Div. Polym. Mat. Sci. Eng.* 1986, **54**, 1
29 Jackson, W. J., Jr and Kuhfuss, H. F. *J. Polym. Sci., Polym. Chem. Edn.* 1976, **14**, 2043
30 Lambert, J. M., Yilgor, E., Yilgor, J., Wilkes, G. L. and McGrath, J. E. *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* 1985, **26**(2), 275
31 Matzner, M. and Papuga, D. M., US Patent 4 619 975, 28 Oct. 1986
32 Johnson, R. N., Farnham, A. G., Clendinning, R. A., Hale, W. F. and Merriam, C. N. *J. Polym. Sci. (A-1)* 1967, **5**, 2375
33 Gagnebien, D., Madec, P. J. and Marechal, E. *Eur. Polym. J.* 1985, **21**, 289
34 Viswanathan, R., Johnson, B. C. and McGrath, J. E. *Polymer* 1984, **25**, 1827
35 Auman, B. C., Percec, V., Schneider, H. A., Jishan, W. and Cantow, H.-J. *Polymer* 1987, **28**, 119
36 Auman, B. C., Percec, V., Schneider, H. A. and Cantow, H.-J. *Polymer* 1987, **28**, 1407
37 Percec, V., Rinaldi, P. L. and Auman, B. C. *Polym. Bull.* 1983, **10**, 215
38 Kleinschuster, J. J., US Patent 3 991 014, 9 Nov. 1976
39 Hamb, F. L. *J. Polym. Sci. (A-1)* 1972, **10**, 3217
40 Sorenson, W. R. and Campbell, T. W., 'Preparative Methods of Polymer Chemistry', 2nd Edn., J. Wiley and Sons, New York, 1968, pp. 148–150
41 Osman, M. A. *Macromolecules* 1986, **19**, 1824
42 Eareckson, W. M., III *J. Polym. Sci.* 1959, **40**, 399
43 Schwarz, G., Koziel, H. and Kricheldorf, H. R., Makromolekulares Kolloquium Freiburg, Freiburg, March 1987, Abstr., p. 28
44 Lenz, R. W. and Jin, J.-I. *Macromolecules* 1981, **14**, 1405
45 Lenz, R. W., Jin, J.-I. and Feichtinger, K. A. *Polymer* 1983, **24**, 327