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Synthesis of a poly(aryl ether sulfone)–poly(aryl ether ketone) triblock copolymer

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The synthesis of a block copolymer containing poly(aryl ether sulfone) (PAES) and poly(aryl ether ketone) (PEAK) is an interesting route combining in a single material thermal resistance (glass transition temperature, $T_g > 200°C$) and high environmental resistance. The synthesis involves the functionalization of the PAES polymer with anhydride chain ends and its further reaction with a PAEK polymer having one amine chain end. A true triblock copolymer is obtained. The block copolymer as well as all intermediates of the synthesis have been fully characterized, for example by nuclear magnetic resonance, gel permeation chromatography and viscometry. Preliminary properties of the copolymer are increased compared with the PAES polymers. Moreover, the copolymer exhibits a T_g above 200°C together with a melting temperature lower than 400°C. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(aryl ether sulfone); poly(aryl ether ketone); block copolymers)

INTRODUCTION

During the last decade, great interest has focused upon poly(aryl ether)s as matrix materials for high performance composites[1]. However, for engineering applications in the aeronautical and microelectronics fields, the polymer has to fulfil several requirements. First, it has to display a glass transition temperature (T_g) above 200°C, allowing continuous use at temperatures around 170–180°C. Moreover, the material has to be solvent-resistant and very stable against hydrolysis. The polymer must also exhibit a melting temperature (T_m) lower than 400°C in order to be processed by classical routes.

It was previously[2] demonstrated by means of a theoretical development that no polyarylether ketone or sulfone homopolymer can fulfil these requirements of a T_g higher than 200°C and T_m lower than 400°C.

For instance, commercial poly(aryl ether ketone)s (PAEKs) are high performance polymers with excellent environmental resistance[3] and good mechanical properties. These semicrystalline polymers exhibit T_m around 340–360°C but T_g around 140–160°C[4]. Owing to the decrease of elastic modulus close to T_g, PAEKs cannot be used continuously above 140°C.

Poly(aryl ether sulfone)s (PAESs) are known as thermally resistant materials exhibiting T_g above 200°C[5], but as a result of their amorphous character, they show a poorer chemical resistance than PAEKs. However, compared to PAEKs, they are considerably more fluid at high temperatures and thus more easily moulded and processed[6].

The synthesis of a block copolymer containing PAEK and PAES sequences thus seems to be an interesting route combining in a single material thermal resistance, high environmental resistance and high fluidity at elevated temperatures.

Some authors have already described the synthesis of PAES–PAEK type block copolymers. Kricheldorf and Bier[7] synthesized a block copolymer via the reaction between trimethylsilylated diphenols and activated difluoroaromatic compounds using CsF as a catalyst. Wu *et al.*[8] synthesized poly(ether sulfone) (PES) with sodium phenate end groups and reacted this PES with fluorine-ended poly(ether ether ketone) (PEEK). However, PES[9,10] and poly(ether ketone) (PEK)[11,12] polymers are known to undergo transetherification rapidly at high temperature in the presence of nucleophiles like phenates. Therefore, any synthesis involving a nucleophilic substitution reaction can lead either to molecular weight decrease and/or to molecular rearrangement ('scrambling') of structural units.

A particularly interesting route to block copolymer synthesis would be end-functionalization of PAES with anhydrides, leading, in a second step, to easy and strong linkage with amine-ended PAEK. The purpose of this article is to describe this functionalization of the PAES chain ends into anhydride and the subsequent synthesis of a true block copolymer.

The synthesis of an amine-ended PAEK has already been described in detail in a previous article[13].

Two different PAES were used throughout this work. The first one was a PAES of high thermal stability, named HTPES, containing biphenyl units leading to a high T_g. Typically, HTPES polymers of high molecular weight ($\bar{M}_n > 20\,000$) display a T_g around 260°C[14] (*Figure 1*). This polymer was originally commercially available under the tradename Victrex HTA (ICI's nomenclature)[15].

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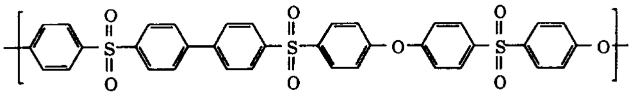


Figure 1 Repeat units of the HTPES polymer

The second PAES is a more classical random copolymer containing aryl ether and aryl sulfone linkages in the ratio 100:70. This polymer is referred to hereafter as PESC. Typically, PESC polymers of high molecular weight ($\bar{M}_n > 20\,000$) display a T_g around 210°C[16].

EXPERIMENTAL

Reagents

4,4′-bis(4-Chlorobenzenesulfonyl)biphenyl (LCDC), 4,4′-dihydroxydiphenylsulfone (Bis S), 4,4′-dichlorodiphenylsulfone, hydroquinone and diphenylsulfone (DPS) were kindly supplied by ICI and used as received. *m*-Aminophenol (Aldrich) was recrystallized twice from water. Potassium carbonate (Merck) was finely sieved and dried at 120°C under vacuum for 2 h before use. Benzene-1,2,4,5-tetracarboxylic dianhydride (or pyromellitic anhydride) (Merck) was dried at 150°C under vacuum for 12 h before use. Benzene-1,2,4,5-tetracarboxylic dianhydride (or pyromellitic anhydride) (Merck) was dried at 150°C under vacuum for 12 h before use. Acetic anhydride (Merck) and cyclopentanone (Janssen) were used as received.

Synthesis of amine-ended PAES

Synthesis of amine-ended HTPES. In a three-necked round-bottomed flask fitted with a mechanical stirrer, a thermoregulated electrical mantle and a nitrogen purge, LCDC (316.4 g, 0.629 mol) and DPS (420 g) were first heated up to 180°C. Potassium carbonate (108.9 g, 0.788 mol) and Bis S (123.9 g, 0.495 mol) were then slowly and successively added to the solution. The system was held for a further 30 min at 180°C. Thereafter, the temperature was steeply raised (30 min at 225°C, 90 min at 265°C and 105 min at 280°C). Then , *m*-aminophenol (30.26 g, 0.277 mol) was added and the solution was stirred for a further 45 min at 280°C. The hot solution was finally poured in an aluminium pan and allowed to cool. The crude solid product was milled and leached three times in refluxing methanol, twice in refluxing water and once again in refluxing methanol. The above procedure, aimed at producing a HTPES exhibiting $\bar{M}_n \approx 30\,000$, was later adjusted to produce other $\bar{M}_n$ values. Each polymer was characterized by ^{13}C and nuclear magnetic resonance (n.m.r.) and the molecular weight determined by gel permeation chromatography (g.p.c.).

Synthesis of the amine-ended PESC. PESC polymer was synthesized following a procedure very similar to that reported above for HTPES. 4,4′-Dichlorodiphenylsulfone was added as halogenated reagent while hydroquinone (60%) and Bis S (40%) were simultaneously used as hydroxylated co-reagents. A PESC polymer of high molecular weight was obtained.

After synthesis, the PESC–NH_2 was fractionated in order to narrow its molecular weight distribution. The batch fractionation[17] was performed at room temperature using methylene chloride and methanol as solvent and non-solvent respectively.

Synthesis of anhydride-ended PAES ($M_n \approx 30\,000$)

In a three-necked round-bottomed flask fitted with a pressure-equalized funnel, a magnetic stirrer, a thermometer and a nitrogen purge, pyromellitic anhydride (14.53 g, 0.06667 mol) was first dissolved in cyclopentanone (140 ml) at room temperature. The solution was cooled to 10°C. A solution of PAES–NH_2 (20 g) in cyclopentanone was charged to the pressure-equalized funnel and added dropwise to the anhydride solution. After complete addition, the solution was stirred for a further 2 h at 10°C. The temperature of the solution was then raised to 70°C, using a thermoregulated electrical heating mantle, and acetic anhydride (68 g, 0.6667 mol) was added. The solution was again stirred for a further 2 h. The product was then precipitated in petroleum ether and leached several times in refluxing acetone. The final powder was dried at 150°C under vacuum overnight. Characterization of the polymer was performed by ^{13}C n.m.r.

Example of a block copolymer synthesis

An anhydride-ended PAES (PESC 1, $\bar{M}_n = 10\,600$) and an amine-ended PAEK (PEK, $\bar{M}_n = 5500$) were dried at 120°C under vacuum before reaction. In a three-necked round-bottomed flask fitted with a magnetic stirrer, a condenser, a thermoregulated heating mantle and a nitrogen purge, DPS (180 g) was first heated up to 300°C. Then, the PAES (10.6 g) and PAEK (11.04 g) were added and the solution stirred for 20 min (2 h for the kinetic study). Thereafter, the solution was poured into an aluminium pan and allowed to cool. The product was then milled and leached several times in refluxing methanol. The resulting block copolymer was characterized by i.r. and ^{13}C n.mr.

Infra-red characterization

Infra-red spectra were obtained on a Perkin-Elmer FT-IR 1760X spectrometer coupled with an IBM PS2 data station provided with the IR Data Manager Program from Perkin-Elmer.

Gel permeation chromatography

PAES samples were analysed by g.p.c. using *N*-methyl pyrrolidinone (NMP) + LiBr (0.1 M) as solvent. The method is described in detail elsewhere[18,19]. The molecular weights given for the HTPES polymer are absolute molecular weights[19]. The PAES polymers were analysed using a PES calibration[18].

The PEK and HTPES used for synthesis of the block copolymer and one copolymer sample were analysed by g.p.c. at 115°C using phenol/1,2,4-trichlorobenzene (TCB) (50/50 by weight) as solvent. The method is described in detail elsewhere[20]. The molecular weights of all samples are given in polystyrene (PS) equivalent values.

Viscometry

Intrinsic viscosities of PAES were obtained using an Ubbelohde viscometer at 25°C and an NMP + LiBR solvent similar to the g.p.c. one. Intrinsic viscosity is

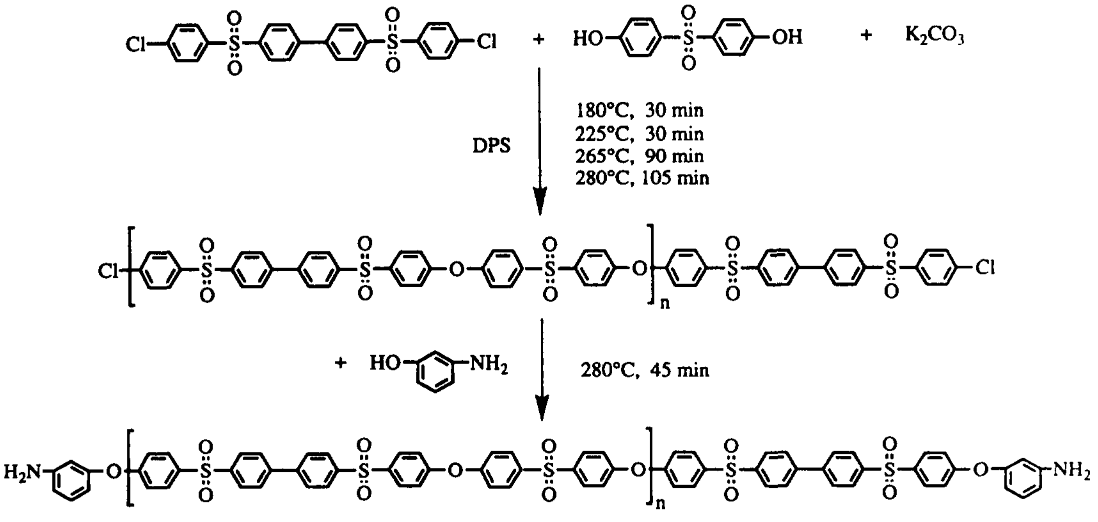


Figure 2 Synthesis of amine-ended HTPES

taken as the mean value of the reduced and inherent viscosities extrapolated to zero concentration.

The value of the molecular weight of the HTPES sample was determined using the following Mark–Houwink relationship[19]:

$$[\eta] = 33.8 \times 10^{-5} \bar{M}_{\mathrm{v}}^{0.70} \tag{1}$$

while the molecular weights of the PESC samples were obtained in PES equivalents using the following Mark–Houwink relationship[18]:

$$[\eta] = 1.33 \times 10^{-4} \bar{M}_{\mathrm{v}}^{0.77} \tag{2}$$

Both PEK and PESC samples used for the synthesis of the copolymers, and also block copolymer samples, were analysed by viscometry in sulfuric acid (99%).

Nuclear magnetic resonance

The n.m.r. spectra were taken on a Brüker AM 500 spectrometer. PAES samples were dissolved in dimethylsulfoxide (DMSO-d_6). The copolymer samples were dissolved in $D_2SO_4 + CH_3SO_3H$ (50:50).

Functional end-group titration

Titration measurements were performed using a Radiometer Standard pH meter, an ABU 80 autoburette and a Schott Gerat H61 combined electrode. The titration of the amine chain ends were performed using a solution of phenol (88%) and acetic acid (12%) as solvent and a solution of $HClO_4$ 0.1 N in acetic acid as titrating agent. For the hydroxyl end-group titration, distilled NMP was used as solvent and tetramethyl ammonium hydroxide in methanol as titrating agent.

Differential scanning calorimetry (d.s.c.)

The d.s.c. analysis was carried out on a Perkin–Elmer differential scanning calorimeter (DSC 7).

RESULTS AND DISCUSSION

Synthesis and characterization of the amine-ended PAES

Synthesis. The synthesis of the HTPES polymer proceeds by a classical nucleophilic substitution route (*Figure 2*).

Table 1 Number and weight average molecular weights and polydispersity (H) of HTPES and PESC samples

	$\bar{M}_n$	$\bar{M}_w$	H
HTPES-NH_2	2550	4700	1.82
PESC–NH_2 (before fractionation)	8800	17 200	1.95
Fraction I	23 700	34 500	1.45
Fraction II	17 200	26 100	1.52
Fraction III	14 500	20 500	1.42
Fraction IV	10 600	14 400	1.36
Fraction V	4600	7400	1.6

Concentrations of amine chain ends in synthesized PAES samples were checked carefully by titration and ^{1}H n.m.r. before anhydride end functionalization. The molecular weight of the polymer was also determined in order to ensure that the reaction of the amine-ended polymer with dianhydride led only to anhydride end functionalization and not to molecular weight increase.

G.p.c. measurements. Gel permeation chromatography was performed on the amine-ended HTPES and PESC as well as on all PESC fractions. The values of the number and weight average molecular weights are listed in *Table 1*.

For the following part of this work, fractions exhibiting molecular weights ($\bar{M}_n$) of 10 600 and 23 700 were selected and are hereafter termed PESC 1 and PESC 2.

^{1}H n.m.r. characterization. In order to determine the nature of the chain ends, ^{1}H n.m.r. characterization was performed on HTPES-NH_2 and PESC–NH_2. The chemical shifts of the protons characteristic of the HTPES and PESC backbones, the peaks corresponding to the desired amine chain ends and the peaks attributed to hydroxyl and remaining chlorine chain ends are listed in *Table 2*[21].

From the integration of all peaks, one can determine the amount of amine chain ends in the polymer and also the number average molecular weight (*Table 3*). These results confirm the $\bar{M}_n$ values previously obtained from g.p.c. analysis (*Table 1*).

Table 2 Chemical shift assignments (ppm) of the backbone and chain ends of PAES samples

	HTPES	PESC
Backbone	7.27	7.2
	7.98	7.95
-NH_2	6.18	6.15
	6.25	6.25
	6.44	6.45
-Cl	7.61	7.6
-OH	6.68	6.7

Table 3 Number average molecular weights of the PAES samples and percentage of amine chain ends calculated from ^{1}H n.m.r. analysis

	$\bar{M}_n$	% NH_2 Chain Ends
HTPES-NH_2	2500	47
PESC 1-NH_2	9900	>90
PESC 2-NH_2	25 000	>90

Table 4 Chemical shift assignments (ppm) of the carbon atoms close to the amine chain ends

Atom No.	HTPES	PESC
13	134.0	134.3
14	129.9	ND[a]
15	117.7	ND[a]
16	161.9	161.8
17	155.3	155.3
18	104.3	105.0
19	150.8	150.8
20	110.8	110.8
21	130.3	130.4
22	106.8	106.8

[a] ND, not detected

^{13}C n.m.r. characterization of amine-ended PAES. The PAES polymers were also characterized by ^{13}C n.m.r. The assignment of the carbon atoms of the main chain are given in the literature for the HTPES polymer[22] as well as for the PESC polymer[23]. The assignment of the carbon atoms close to the amine chain ends was performed by Maes *et al.*[24]. Molecular structure and ^{13}C n.m.r. spectra of both polymers together with peak assignments are presented in *Figures 3* and *4* and in *Table 4.*

Titration of amine and hydroxyl chain ends. In order to further confirm the results obtained by ^{1}H n.m.r. titration of amine and hydroxyl end groups was also performed. $\bar{M}_n$ was also calculated in this way, assuming there were no other end groups (*Table 5*).

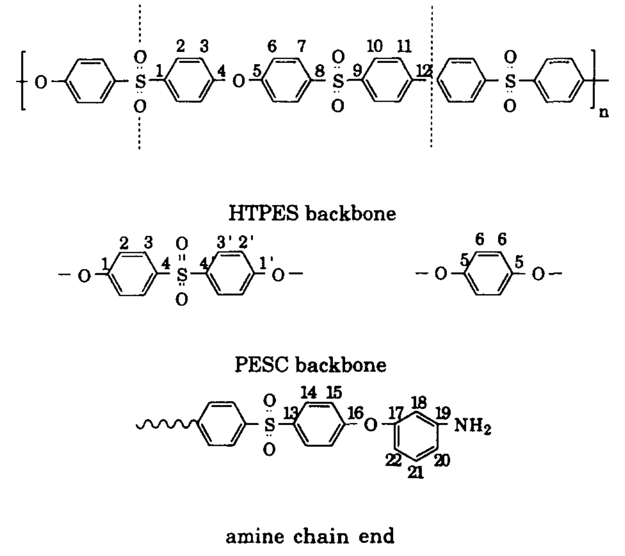


Figure 3 Molecular structure of the HTPES and PESC backbone and of the amine chain end

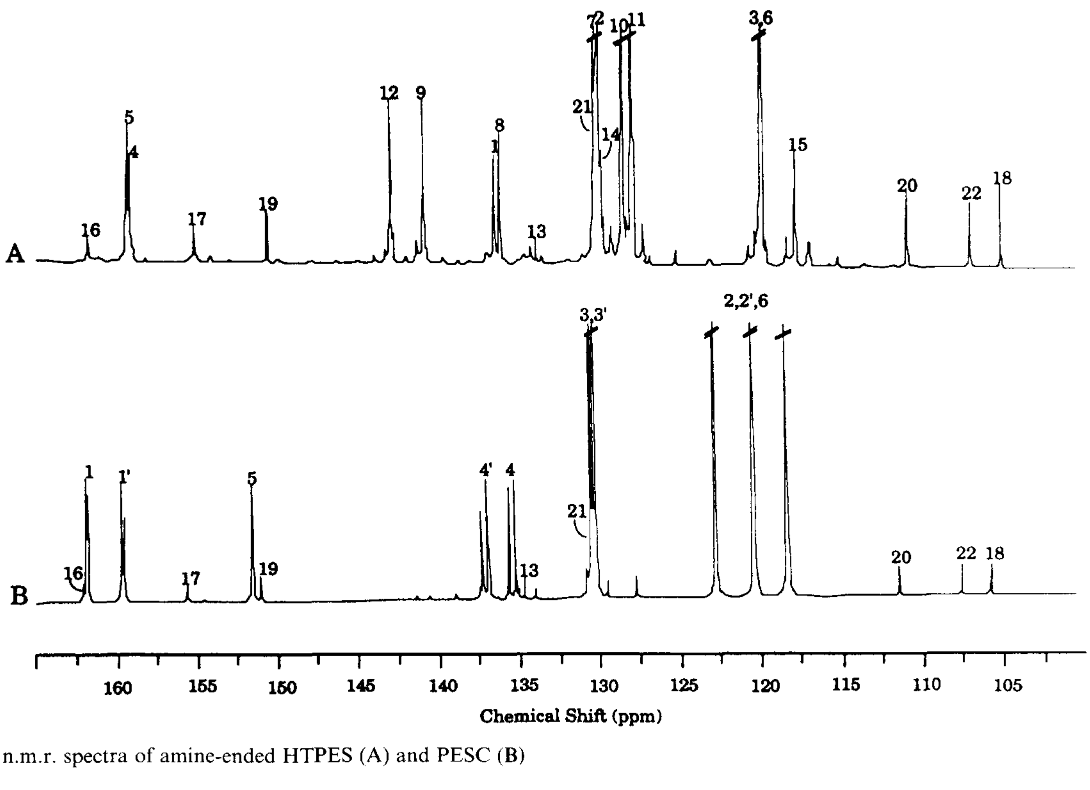


Figure 4 ^{13}C n.m.r. spectra of amine-ended HTPES (A) and PESC (B)

Table 5 Concentration of amine and hydroxyl chain ends and number average molecular weight calculated from titration

	Number of NH_2 chain ends (mol g^{-1})	Number of OH chain ends (mol g^{-1})	Calculated $\bar{M}_n$
HTPES	4.761×10^{-4}	1.6715×10^{-4}	3100
PESC 1	2.096×10^{-4}	ND^a	9500
PESC 2	1.033×10^{-4}	ND6*a*	19400

^{a} ND, not detected

Table 6 Assignment of the i.r. peaks characteristic of the amine chain ends

Wavenumber (cm^{-1})	Assignment
3472	asymmetric N–H stretching
3381	symmetric N–H stretching
1627	N–H deformation

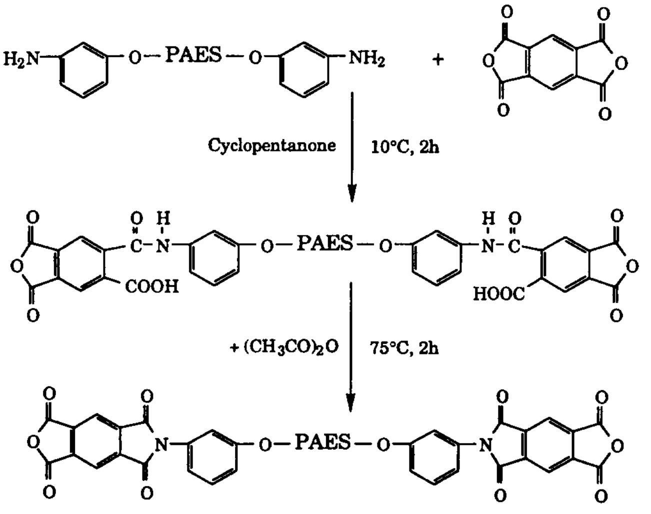


Figure 5 Synthesis of anhydride-ended PAES

Table 7 Assignment of the i.r. peaks characteristic of anhydride and imide linkages

Wavenumber (cm^{-1})	Assignment
1856	C=O anhydride: symmetric mode
1782	C=O anhydride: asymmetric mode
1798	C=O imide: symmetric mode
1729	C=O imide: asymmetric mode

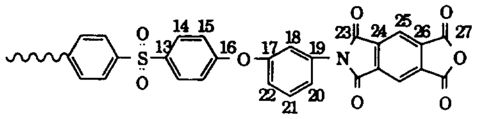


Figure 6 Molecular structure of anhydride chain end of PAES

Table 8 Chemical shift assignments (ppm) of the HTPES and PESC anhydride chain ends

Atom No.	HTPES	PESC
13	134.8	134.3
14	ND^a	ND^a
15	117.7	ND^a
16	160.9	161.8
17	154.6	154.6
18	118.3	118.3
19	160.9	160.8
20	ND^a	ND^a
21	130.5	130.5
22	123.7	123.7
23	165.5	165.4
24	133.3	133.2
25	123.3	122.8
26	135.0	135.7
27	167.1	167.2

^{a} ND, not detected.

It is noteworthy that, for the PESC polymer, the concentration of hydroxyl chain ends was too low to be detected by titration.

Infra-red characterization. The interpretation of the infra-red spectrum of the PESC backbone was reported by Ellis *et al.*[25]. The HTPES spectrum displays the peaks characteristic of sulfone, ether and *para*-disubstituted phenyl groups.

The presence of amine chain ends on the PAES polymers was further evidenced by the infra-red spectra (*Table 6*).

It is pointed out here that the peak located at 1627 cm^{-1} can only be observed for deconvolution of the spectrum.

Synthesis and characterization of anhydride-ended PAES

Synthesis. The synthesis procedure is described in *Figure 5*. Its first step involves the formation of an amic acid. This is an exothermic reaction which is thermodynamically favoured at low temperature (10°C). In the second step, the amic acid is dehydrated in the presence of acetic anhydride leading to an imide link.

Infra-red characterization. The i.r. spectra of all samples of anhydride-ended PAESs show clearly the absence of amine peaks, together with other peaks characteristic of imide and anhydride groups. The assignment of these peaks[26] is reported in *Table 7*.

Again, the peaks located at 1782 and 1798 cm^{-1} have been assessed by deconvolution of the spectrum.

^{13}C n.m.r. characterization of the anhydride-ended PAESs. The ^{13}C n.m.r. results fully confirm the i.r. observations: the peaks characteristic of the amine chain ends disappear and new anhydride and imide peaks are observed. The structure of the anhydride chain end is given in *Figure 6*. *Table 8* and *Figure 7* give the chemical shifts of the carbon atoms close to this chain end.

Viscometry. As anhydride end functionalization of PAES proceeds by reaction with a dianhydride, and it is important to verify that no chain extension has occurred. Thus, the molecular weight of the anhydride-ended polymer must be compared with the molecular weight of the starting amine polymer.

However, no g.p.c. measurement could be performed on the anhydride-ended PAES as the presence of anhydride end groups led to retention of the material on the stationary phase of the g.p.c. columns.

Therefore, the weight average molecular weight of the anhydride-ended PAESs as well as the amine-ended PAESs were compared via their intrinsic viscosities. *Table 9* gives the intrinsic viscosities and viscometric molecular weights ($\bar{M}_v$) of the PAES samples. The

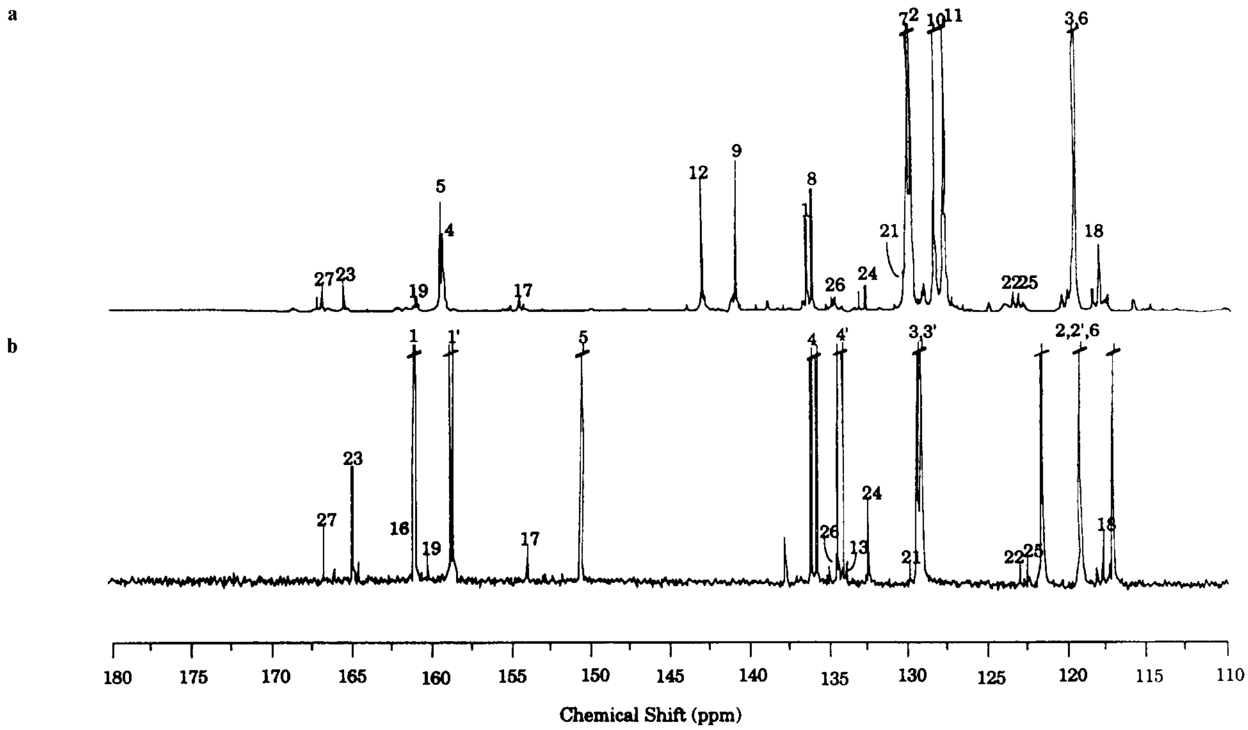


Figure 7 ^{13}C n.m.r. spectra of anhydride-ended HTPES (A) and PESC (B)

Table 9 Intrinsic viscosities and viscometric molecular weights of the amine and anhydride ended PAES samples

Polymer	Intrinsic viscosity [η] (g dl^{-1})	$\bar{M}_v$
HTPES-NH$_2$	0.12	4400
HTPES-anh	0.125	4700
PESC 1-NH$_2$	0.25	17 900
PESC 1-anh	0.28	20 400
PESC 2-NH$_2$	0.47	40 700
PESC 2-anh	0.54	48 600

Table 10 Sequence length of the different block copolymers synthesized

	PEK sequence length ($\bar{M}_n$)	PAES sequence length ($\bar{M}_n$)
PEK–PESC–PEK		
Copo 1	5500	10 600
Copo 2	5500	23 700
Copo 3	2600	10 600
PEK–HTPES–PEK		
Copo 4	1500	2550

molecular weight of the HTPES could be obtained from a Mark–Houwink relationship established for HTPES while the molecular weights of the PESC samples could be calculated from a Mark–Houwink relationship established for PES (see Experimental section).

The results obtained by viscometry confirm that the reaction between amine-ended PAES and pyromellitic dianhydride leads mostly to anhydride end functionalization and that chain extension remains very limited. As the value of $\bar{M}_v$ is more sensitive to chain extension than the value of the $\bar{M}_n$, the increase of $\bar{M}_n$ will thus be neglected hereafter.

Synthesis and characterization of the PEK–PAES–PEK block copolymer

Synthesis. Amine-ended PEK polymers of molecular weights 1500, 2600 and 5500 were synthesized, following the procedure described in a previous paper[13]; they will be referred to as PEK 1, 2 and 3, respectively. The purpose of this study was to react these amine-ended PEKs with the anhydride-ended PAES samples in order to obtain triblock copolymers.

When the amine-ended PEK and the anhydride-ended PAES are blended together in DPS at high temperature (300°C), two different reactions may occur. Firstly, the amine groups can react with the anhydride end groups of the PAES polymer. Secondly, however, as an unwanted reaction, amine functions can also react with ketone links of the PEK chain[27]. Nevertheless, the synthesis of the PEK–PAES–PEK block copolymer can be achieved as the reaction between amine and anhydride proceeds much more rapidly than the reaction between the amine and the ketone groups along the chain.

In this work, four block copolymers with different sequence lengths were synthesized (*Table 10*).

G.p.c. could not be performed for Copo 1, 2 and 3, as the PEK polymers with $\bar{M}_n$ greater than 2000 are not soluble in any suitable solvent. In order to follow the increase of molecular weight after the coupling reaction, the block copolymers as well as the starting polymers were then analysed by viscometry in H_2SO_4. No Mark–Houwink relationship has been reported yet for the PESC and PEK polymer in H_2SO_4. Therefore, the comparison of the intrinsic viscosities gives only a qualitative idea of the increase in molecular weight. *Table 11* lists the intrinsic viscosities determined for the block copolymers and for the starting polymers.

The intrinsic viscosity of Copo 1 was also compared with the viscosity of a blend of PESC 1–anhydride and PEK–NH_2 ($\bar{M}_n = 5500$) having the same composition as Copo 1. Certainly, no reaction was to be expected in H_2SO_4 solution at room temperature. The viscosity of the blend is lower than the viscosity of Copo 1. This result strongly indicates the formation of a block copolymer.

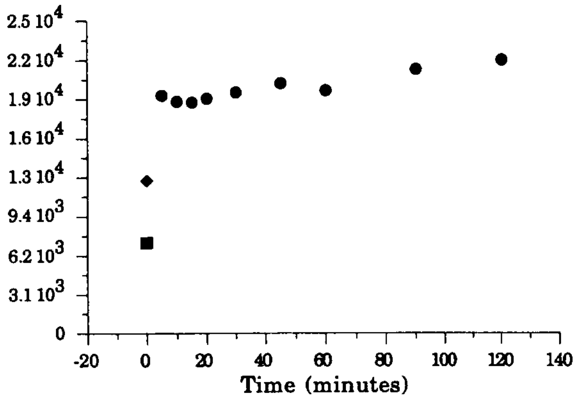


Figure 8 Changes in the molecular weight of the block copolymer during synthesis: ◆, anhydride-ended PAES; ■, amine-ended PEK; ●, block copolymer

Table 11 Intrinsic viscosities of Copos 1, 2 and 3 compared to those of the starting polymers and that of the blend

Polymer	Intrinsic viscosity [η] ($g\,dl^{-1}$)
PESC 1–anhydride	0.22
PESC 2–anhydride	0.45
PEK 2–NH_2	0.11
PEK 3–NH_2	0.26
Copo 1	0.49
Copo 2	0.50
Copo 3	0.28
Blend	0.24

Copo 4, synthesized from HTPES and PEK sequences having $\bar{M}_n$ around 1500, appeared to be soluble in phenol/TCB (50/50) g.p.c. solvent. Therefore, a kinetic study was performed during the coupling reaction. Samples of the reaction mixture were taken after different times and the changes in the molecular weight were followed by g.p.c. As no standards of HTPES and PEK polymers were available, the calibration was performed using PS standards. All the molecular weights are thus only given in PS equivalents.

The molecular weight values of the copolymers formed were compared to the molecular weights of the starting polymers (*Figure 8*). Although this comparison is only qualitative, as the interaction between polymer and solvent is different for each sequence, *Figure 8* shows clearly that the block copolymer is formed during the first 5 min of reaction. This g.p.c. measurement also confirms the stability of the copolymer in DPS at high temperature (300°C).

^{13}C n.m.r. of block copolymers. ^{13}C n.m.r. analysis was performed on the block copolymers. For instance, a spectrum of Copo 4 is presented in *Figure 9*. The molecular structure of Copo 4 is given in *Figure 10* and the chemical shift assignments are reported in *Table 12*. It can be seen from the spectrum that all amine chain ends of PEK polymer as well as all anhydride chain ends of HTPES polymer have reacted. Two imide carbon resonances can be identified, corresponding to one on the HTPES side (peak 18) and another on the PEK side (peak 22).

The spectra of the other block copolymers are comparable with that of Copo 4, despite the presence of some peaks due to sulfonation of OΦO units of the PESC polymer.

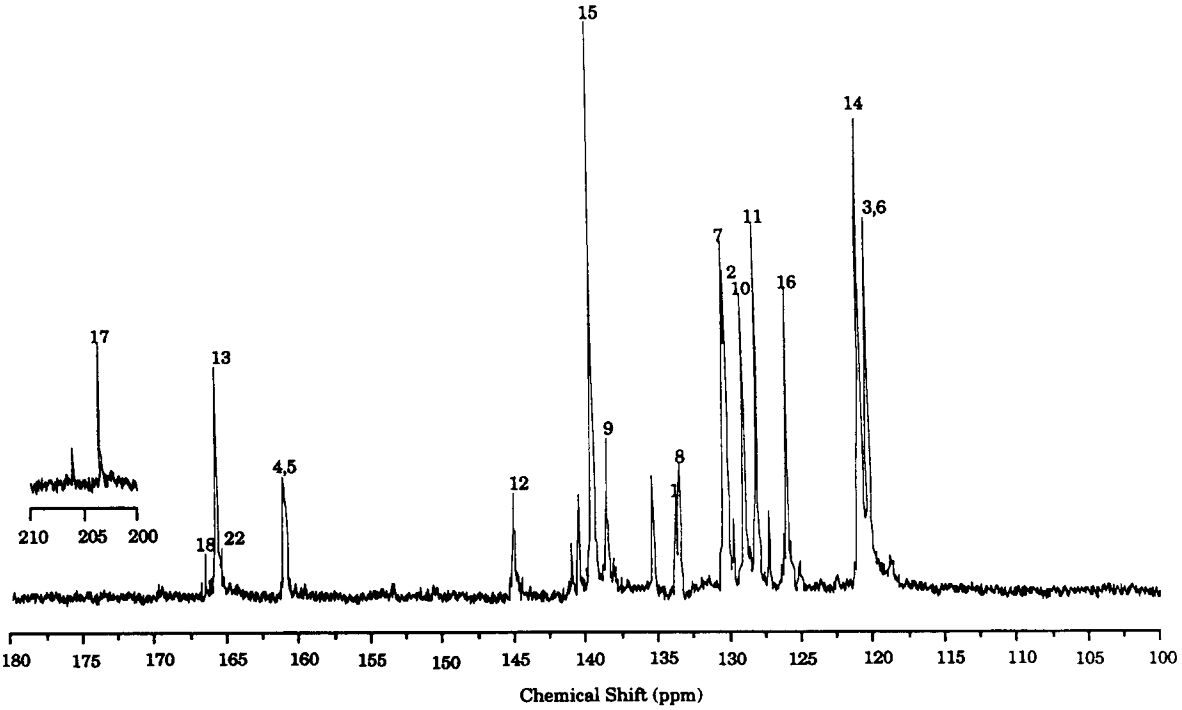
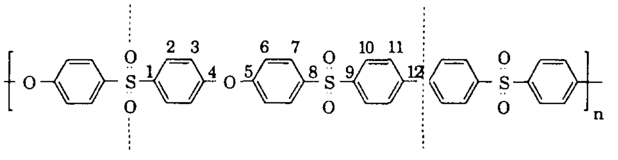
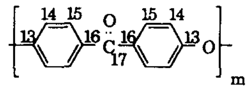


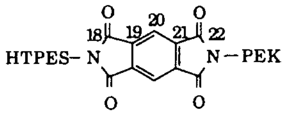
Figure 9 ^{13}C n.m.r. spectrum of the HTPES–PEK block copolymer in a solution of D_2SO_4 (50%) and CH_3SO_3H (50%)



HTPES backbone



PEK backbone



imide bond

Figure 10 Molecular structure of the HTPES–PEK block copolymer

Table 12 Chemical shift assignments of the carbon atoms of Copo 4

Atom no.	Chemical shift (ppm)
HTPES backbone	
1	134.17
2	130.66
3	120.82
4	161.27
5	161.27
6	120.82
7	130.80
8	133.93
9	138.93
10	129.47
11	128.56
12	145.38
PEK backbone	
13	165.87
14	121.40
15	139.95
16	126.49
17	202.54
Imide bond	
18	166.70
19	–
20	–
21	–
22	165.50

Copolymer solubility. As seen in the molecular characterization of the block copolymers, the copolymers are no more soluble in the PAES solvents for g.p.c. (NMP) and n.m.r. (DMSO). Indeed, the copolymers are no more soluble in common PAES solvents than the parent PEK material. The solvents of the block copolymers are typical solvents of PEK.

Thermal properties. Preliminary results from d.s.c. analyses of block copolymers as well as of the starting polymers are reported in *Table 13*.

Table 13 Thermal characteristics of the block copolymers and the starting homopolymers on heating at 10°C min^{-1}

HTPES–NH_2	224.2	
PESC 1–NH_2	203.8	–
PESC 2–NH_2	213.4	–
HTPES–anh	231.9	–
PESC 1–anh	209.8	–
PESC 2–anh	218.3	–
PEK 1–NH_2	ND[a]	348
PEK 2–NH_2	ND[a]	354.7
PEK 3–NH_2	150.2	361.8
Copo 1	203.7	356.4
Copo 2	204.2	343.5
Copo 3	198.8	326.6
Copo 4	208.9	331.9

[a] ND, not determined

The T_g difference observed between amine- and anhydride-ended PAESs of similar $\bar{M}_n$ may be attributed to a physical coupling between anhydride end groups. It is also to be noted that only one heating cycle can be performed on the amine-ended PEK due to ketimine formation at high temperature. Therefore, no T_g was observed for the PEK–NH_2 of $\bar{M}_n$ = 1500 and 2600, as the crystalline level of these polymer was very high after synthesis.

However, the d.s.c. results for the block copolymers seem to be promising as the block copolymers fulfil the requirements: a T_g above 200°C together with a T_m around 350°C. In these copolymers, the T_g of the PEK phase cannot be observed due either to miscibility of the amorphous PEK in the PESC phase or to the low signal of the amorphous PEK caused by a very high degree of crystallinity of the PEK sequence.

CONCLUSIONS

A triblock copolymer consisting of one poly(aryl ether sulfone) block linked to two poly(aryl ether ketone) blocks has been synthesized avoiding any transetherification. The synthesis involves the functionalization of the PAES polymer with anhydride chain ends and its further reaction with a PAEK polymer having one amine chain end. The block copolymer as well as all intermediates of the synthesis have been fully characterized, for example by n.m.r., g.p.c. and viscometry.

Preliminary properties of the copolymer seem very encouraging. The solvent resistance of the block copolymer is increased compared with the PAES polymers.

Moreover, the thermal properties of the block copolymer also fulfil the engineering requirements for a high performance composite matrix. The copolymer displays a T_g above 200°C together with a T_m lower than 400°C. Of course, a more extensive characterization of the block copolymer in terms of crystallization kinetics and morphology has to be performed; this will be the subject of a future paper.

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