About the synthesis of a high-temperature, crystalline poly[aryl ether(ketone-*co*-sulfone)]: 1. Synthetic reactions study

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The synthesis of a new poly[aryl ether(ketone-*co*-sulfone)] proceeds through a chemical mechanism similar to that in the poly(ether ether ketone) and poly(ether sulfone) polymerizations. It is basically a nucleophilic substitution of a dihalogenated species by two alkaline bisphenates. This paper considers the possibility of the occurrence of some side reactions previously observed during the synthesis of poly(ether ether ketone), poly(ether ketone) or poly(ether sulfone). Unwanted nucleophilic substitutions either by phenates (transetherifications) or by fluoride or hydroxyl anions are considered. Their effectiveness during the copolymer synthesis is demonstrated by different techniques and their influence on the final sequence distribution in the chain is discussed.

(Keywords: poly(aryl ether ketone)s; poly(aryl ether sulfone)s; synthesis)

INTRODUCTION

Semicrystalline thermoplastic matrices present numerous advantages over thermosets in the field of high-temperature composites. Easy processing and possible recycling arise from their thermoplastic character, and the crystallinity provides chemical resistance and contributes to the good mechanical properties.

The first commercial high temperature thermoplastic matrix used with fibre reinforcement was probably the poly(ether ether ketone) (Victrex PEEK), which, in the APC-2 composite, has been of considerable interest in the aerospace field. However, APC-2 is not suitable for continuous exposure at very high temperatures. In fact, a practical temperature limitation for composite materials is usually fixed at ~30°C below the matrix glass transition temperature (T_g) which is close to 150°C for Victrex PEEK.

Therefore, considerable effort has been devoted to developing semicrystalline thermoplastic matrices exhibiting a T_g around 200–210°C[1]. However, such matrices usually melt well above 400°C and cannot be processed below 450°C, leading to unacceptable degradation[2]. The ideal semicrystalline matrix would exhibit a T_g around 200°C and a melting temperature (T_m) below 400°C. We recently demonstrated that these requirements cannot be filled by a poly(aryl ether ketone) homopolymer[2].

In a recent patent[3], the synthesis has been disclosed of a poly(ether ketone-*co*-sulfone) with a high T_g (205°C) and a moderate T_m range (~400°C). A typical d.s.c. scan of such a copolycondensate is presented in *Figure 1*. The chemistry involved in this patented synthesis[3] is reminiscent of the previously published procedures for other polyaromatics such as PEEK, poly(ether ketone) (PEK)[4,5] and poly(ether sulfone) (PES)[7,8]. It is actually a similar nucleophilic substitution of a halogenated species by a phenate that leads to an ether linkage. However, in the present synthesis, three monomers are involved (*Table 1*).

The basic reaction between monomer K and a bisphenol would be expected to be as follows:

$$n\text{MO-Ar-OM} + n\text{F-}\phi\text{-CO-}\phi\phi\text{-CO-}\phi\text{-F} \rightarrow (2n\text{-}1)\text{MF} + \sim\!(\phi\text{-CO-}\phi\phi\text{-CO-}\phi\text{-O-Ar-O})_n\!- \quad (1)$$

where M is an alkaline metal (sodium or potassium) and Ar represents either $\text{-}\phi\phi\text{-}$ (D unit) or $(\text{-}\phi\text{SO}_2\phi\text{-})$ (S unit).

An *in situ* conversion into phenate using a carbonate under an inert gas was used in order to inhibit the rapid oxidation of bisphenates.

$$\sim\!\text{ArOH} + \text{M}_2\text{CO}_3 \rightarrow \sim\!\text{ArOM} + \text{MHCO}_3 \quad (2)$$

The less nucleophilic sodium carbonate is preferred for PEK whilst potassium carbonate may be used for PEEK and poly(ether ether sulfone) (PEES)[4,5]. However, no clear explanation of that choice but only property observations can be found in the quoted patent literature[6]. In the present synthesis, two bisphenols exhibiting very different nucleophilicities are used together and the proportion of sodium/potassium was

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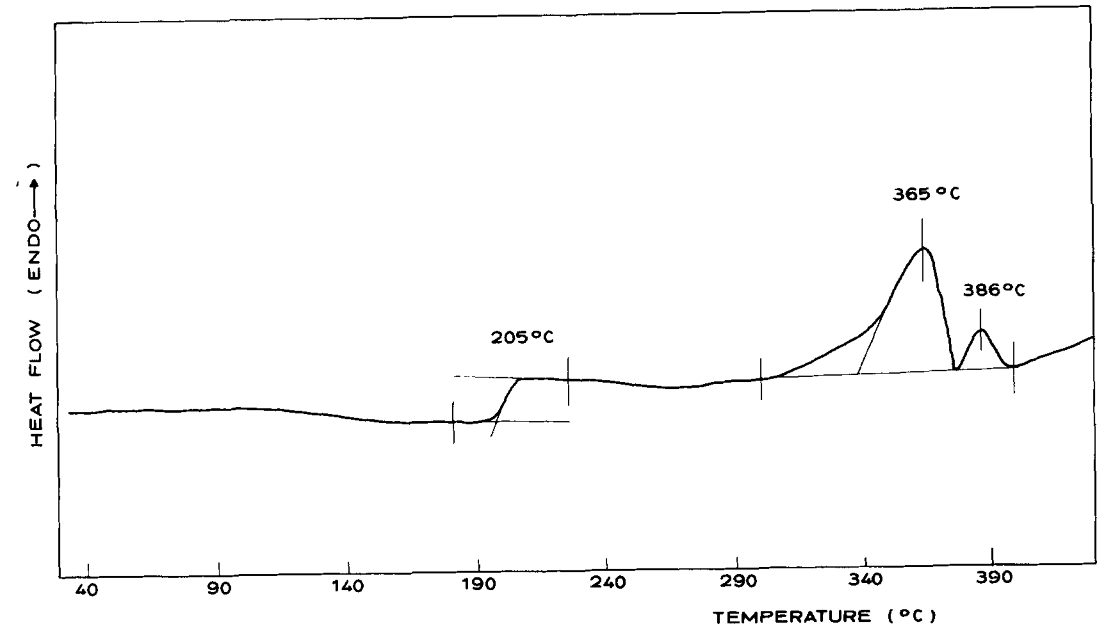

Figure 1 D.s.c. heating thermogram (20°C min^{-1}) of the poly(ether ketone-*co*-sulfone) with two melting endotherms below 400°C

Table 1 Monomeric reactants

Abbreviation	Chemical name	Formula
K	4,4'-Bis(4-fluorobenzoyl)biphenyl[23]	$^{F}\phi$-CO-$\phi\phi$-CO-ϕF
D	4,4'-Dihydroxydiphenyl	HO-$\phi\phi$-OH
S	4,4'-Dihydroxydiphenylsulfone	HO-ϕ-SO_2-ϕ-OH

experimentally optimized on the basis of the crystallizability of the final copolymer[3].

The high temperature solvent diphenylsulfone (DPS) is selected due to its aprotic dipolar character[7]. Increasing temperature steps during the reaction are necessary to maintain the polymer solubility and to reduce thermal degradation. A temperature scale from 200 to 330°C through 250, 265 and 300°C was retained.

It can be concluded from the above remarks that the syntheses described in this paper are very similar to the previously published ones for PEEK, PEK and PEES. Consequently, the following side reactions previously cited for PEEK and PEES polymers may be expected:

1. ether interchange or transetherification[8,9];
2. chain cleavage by the fluoride anion[8];
3. nucleophilic reactions involving the hydroxyl anion[10,11].

It is the objective of this paper to examine whether these side reactions also occur during polymerizations using the three monomers K, D and S described in this paper. Simultaneously, techniques will be discussed illustrating a semiquantitative determination of the influence of such side reactions on the polymer synthesis.

EXPERIMENTAL

Materials

K, D, S and DPS were used as received from ICI plc (Wilton, UK). Na_2CO_3, K_2CO_3, KOH and NaOH were products obtained from UCB (Brussels, Belgium). 4,4'-Dihydroxy(bisbenzoyl)biphenyl (LKOH) was prepared by the reaction of monomer K with KOH in moist dimethylsulfoxide (DMSO); the diacetate was formed by refluxing in acetic anhydride and recrystallizing from *o*-dichlorobenzene. The diacetate was finally hydrolysed using 5 M NaOH and LKOH precipitated by refluxing with HCl. After filtration the precipitate was washed with water (yield 78%; m.p. 290–292°C).

4-Hydroxy-4'-fluoro(bisbenzoyl)biphenyl (FLKOH) was supplied by ICI plc[12]. The tendency of this compound to trap the solvent of crystallization provided a sample which contained some DMSO (0.5 mol, purity > 95%). FLKOH was assigned by ^{1}H n.m.r., ^{13}C n.m.r. and mass spectrometry.

K/D/S 50/20/30 copolymer synthesis

The reaction mixture contained K monomer (11.5095 g), S monomer (4.3547 g), D monomer (2.16 g), sodium carbonate (3.075 g), potassium carbonate (0.08 g) (stoichiometric sodium/potassium carbonate ratio 100/2) and DPS (60 g). The DPS, K and D monomers were placed in the reaction flask which was purged with nitrogen. The flask was heated to 200°C and stirring was begun when the mixture became molten. Sodium carbonate was then added in a molar quantity equivalent to the phenolic groups of the D monomer present in the mixture and stirring under nitrogen was continued for 1 h. The S monomer, the rest of the sodium carbonate and all the potassium carbonate were then added. The temperature was raised to 250°C, and maintained at 250°C for 0.5 h; the temperature was then raised to 265°C for 1.5 h and then to 300°C, and maintained at 300°C for 0.5 h. Finally, the temperature was raised to 330°C and maintained at 330°C for 1.5 h. The polymer was then cooled by casting into a mortar. The solidified product was then crushed. The product was then washed with acetone, water and methanol and dried.

^{13}C nuclear magnetic resonance

^{13}C n.m.r. spectra were run on a Jeol FX270 at Wilton Materials Research Centre operating at 67.8 MHz for ^{13}C. The polymers were dissolved in 98% concentrated sulfuric acid (~10 w/w%) and the spectra were run with the polymer/solvent mix at ~30°C. Proton decoupling was achieved with the broad-band mode of decoupling and the irradiating frequency was selected to be at the centre of the proton magnetic resonances. A 5 mm capillary of d_6-DMSO, concentrically placed in the 10 mm n.m.r. tube containing the polymer solution provided a field/frequency lock signal as well as a deuterium n.m.r. signal for magnetic field homogeneity shimming.

The following spectrometer parameters were used: pulse width 15 μs (90° 25 μs); acquisition time 0.5 s; spectral width 16 000 Hz; pulse delay 0.1 s; line broadening normally zero; number of accumulated scans, typically 50 000–100 000 requiring overnight collection; accumulation 16 K points Fourier transformed.

^{19}F nuclear magnetic resonance

^{19}F n.m.r. spectra were run on a Bruker WM 250 spectrometer at Louvain-la-Neuve operating at 235.24 MHz for ^{19}F. The polymers were dissolved in 99% concentrated sulfuric acid (~4 w/w%). Sodium trifluoroacetate was dissolved in sulfuric acid (~0.01 w/w%) as internal standard. The following spectrometer parameters were used: spectral width 2000 Hz; pulse width 13 μs (90°). The procedure was similar to the one previously published for PEEK[13].

Gel permeation chromatography of low molecular weight compounds

After dissolution of the sample in the eluent [*N*-methylpyrrolidone (NMP) with 0.1M LiCl, ~1 mg per 50 ml], 50 μl were injected and circulated on two columns (Waters Ultrastyragel 500 Å and 100 Å) by a pump (Waters 6000A solvent delivery system). The signal was detected by a Perkin–Elmer (LC-55) u.v. detector and analysed by a Trivector Scientific Ltd computer (from Trilab 2000). The following conditions were applied: pressure < 6.9 MPa; flow 0.8 ml min^{-1}; quantitative results were obtained by means of a benzoylacetone reference (0.1 g l^{-1} in sample solvent); u.v. wavelength 308 nm; columns at room temperature.

G.p.c. of the high molecular weight copolymer followed the technique proposed for PEEK[14].

High temperature g.p.c. A high temperature Waters 150 C chromatographic apparatus equipped with two Shodex columns (styrene–divinylbenzene) from Showa Denko was used at 115°C. A phenol-1,2,4-trichlorobenzene mobile phase was circulated at a flow rate of 1 ml min^{-1}. The refractive index (r.i.) signals were recorded and analysed by a Trivector Scientific Ltd computer. The sample concentration was 0.2% and the injected volume was 80 μl.

Room temperature g.p.c. The same chromatographic system was used at room temperature but the eluent (NMP with 0.1 M LiCl) was circulated at a flow rate of 0.8 ml min^{-1}. R.i. and u.v. (270 nm) signals were recorded. The sample concentrations were, respectively, for u.v. and r.i. 0.05% and 0.2%. The injected sample volume was 50 μl. The dissolution was performed for 30 min at 120°C on sulfonated samples.

Phenates solubility study

Bisphenols were stoichiometrically neutralized in distilled methanol using potassium hydroxide or sodium hydroxide. After stirring for 2 h, the phenates were recovered by evaporation of the solvent under vacuum followed by drying for 3 h in a vacuum oven at 90°C. They were immediately introduced into DPS solvent in a three-necked round bottom flask fitted with an argon inlet, a temperature probe and a vigorous mechanical stirrer. After stirring for 2 h at the selected temperature, the stirring was stopped to allow the insoluble fraction to be decanted. After a few minutes, sampling was carried out with Teflon tubing fitted with a number 3 glass sintered filter (porosity 16–40 μm). The samplings were carefully performed on the surface and solubilized at a concentration of 6 mg per 50 ml in a water–acetonitrile solution (50/50 v/v) including benzoylacetone as reference (25 mg l^{-1}).

H.p.l.c. analyses were then performed: water–acetonitrile (50/50 v/v) was circulated at a flow rate of 1 ml min^{-1} on a column (Merck Lichrocart RP18) by a Waters pump. The signal was detected by a Perkin–Elmer LC-55 u.v. detector (fixed at 270 nm) and analysed by a Trivector Scientific Ltd computer. The solution sampling was filtered off and 50 μl was injected.

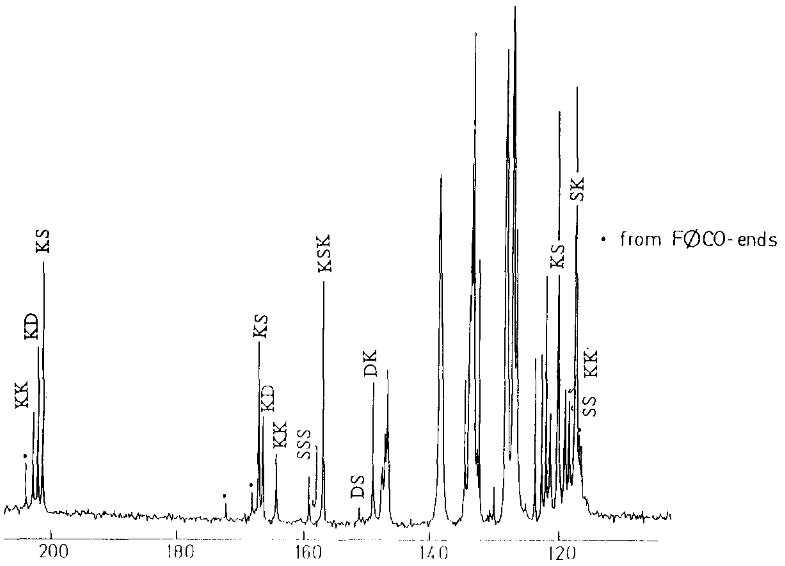

Figure 2 ^{13}C n.m.r. spectrum of a K/D/S 50/20/30 copolymer, following the method of Bunn *et al.*[15–19]

RESULTS AND DISCUSSION

The formation of a polymer from the K, D, S monomers with PEK or PES side reactions involves additional reactions to reaction 1. New sequences must arise. Effectively, they can be identified and quantified by ^{13}C n.m.r. analyses as described in previous papers[15–19].

An example of a ^{13}C n.m.r. spectrum of a K/D/S 50/20/30 copolymer is shown in *Figure 2*. The -K-D-, -K-S-, -K-K-, -S-S- and -S-D- sequences are assigned. Each type of side reaction can explain the appearance of the new sequences. The actual impact of each one during the copolymer synthesis is now discussed separately.

Ether interchange

The most powerful nucleophile present in the DPS solution is the phenate $\text{-O}\phi\phi\text{O}^-$ (-D^-) but the bisphenate $\text{-O}\phi\text{SO}_2\phi\text{O}^-$ (-S^-) can also play a role. Therefore, six possible nucleophilic substitutions can be written:

$$\begin{aligned}&\text{-K-S-} + \text{-D}^- \rightarrow \text{-D-S-} + \text{-K}^- &&\text{(i)}\\ &\text{-K-S-} + \text{-D}^- \rightarrow \text{-K-D-} + \text{-S}^- &&\text{(ii)}\\ &\text{-K-D-} + \text{-D}^- \rightarrow \text{-K-D-} + \text{-D}^- &&\text{(iii)}\end{aligned}$$

and

$$\begin{aligned}&\text{-K-S-} + \text{-S}^- \rightarrow \text{-S-S-} + \text{-K}^- &&\text{(iv)}\\ &\text{-K-S-} + \text{-S}^- \rightarrow \text{-K-S-} + \text{-S}^- &&\text{(v)}\\ &\text{-K-D-} + \text{-S}^- \rightarrow \text{-K-S-} + \text{-D}^- &&\text{(vi)}\end{aligned} \qquad (3)$$

From the six possible ether interchanges listed above, (i) and (iv) lead to new chain sequences D-S and S-S together with a new phenate -K^-. The latter can also be involved in secondary transetherifications leading, for instance, to -K-K- sequences. Following that transetherification mechanism, the occurrence of -S-D- sequences should be higher than that of -S-S- sequences and the -K-K- concentration at its maximum should reach the sum of the S-D and S-S concentrations.

Figure 2 shows S-S and K-K sequences whilst there is no evidence for S-D sequences. This observation is a contradiction to the above deductions. As a consequence, the transetherification mechanism does not appear to be predominant.

Chain cleavage by the fluoride ion

Transposition of this cleavage described for PES to the polymers studied in this paper can be directly derived only for the -S-S- linkages which are themselves by-products of the main reactions. Therefore, that nucleophilic substitution should be of little importance. However, its occurrence on K-S or even on -K-K- links cannot be excluded. Very recent work in our laboratory[20] has been devoted to identifying the temperatures at which the nucleophilic attack of -S-S-, -K-S- and -K-K- links by the fluoride ion take place at a significant rate. Appropriate model compounds and polymers were reacted with potassium fluoride in DPS at different temperatures. Significant chain cleavage was found to occur from 280°C upwards for -S-S-, 300°C for -K-S- and above 300°C for -K-K-.

In the K/D/S copolymers synthesis, temperature steps up to 330°C are involved, therefore, at least -S-S- and -K-S- attacks by the fluoride ion should be observed. Three reactions can be written involving the three activated phenyl carbons mentioned above:

$$\begin{aligned}&\text{-S-S-} + \text{F}^- \rightarrow \text{-S-F} + \text{-S}^- &&\text{(i)}\\ &\text{-K-S-} + \text{F}^- \rightarrow \text{-K}^- + \text{F-S-} &&\text{(ii)}\\ &\text{-K-S-} + \text{F}^- \rightarrow \text{-K-F} + \text{S}^- &&\text{(iii)}\end{aligned} \qquad (4)$$

From these reactions, the new -S-F end group and the K^- phenate can be involved in subsequent reactions leading to -S-S-, -S-D- or -K-K- or back to -K-S- sequences.

In order to verify the effectiveness of chain cleavage in the above K/S/D copolymers studied, ^{19}F n.m.r. spectra were recorded. *Figures 3* and *4* report the ^{19}F n.m.r. spectra of a K/D/S copolymer sampled during the synthesis before the 300°C step and after the 330°C step, respectively. These spectra reveal unambiguously that $\text{F-}\phi\text{SO}_2\phi\text{-}$ end groups only appear after the highest temperature steps. They arise, therefore, most probably from the nucleophilic cleavage of the -K-S- link, which is far more abundant than the -S-S- link. Indeed, the latter should already be cleaved at 300°C but, as no peak is observable in *Figure 3*, the resulting $\text{F-}\phi\text{SO}_2\phi\text{-}$ concentration is very low, either as a result of the very low amount of -S-S- involved or because the consumption of the $\text{F-}\phi\text{SO}_2\phi\text{-}$ group is too fast.

In *Figure 4*, three different peaks appear in the region of 24 ppm which are attributed to the $\text{F-}\phi\text{SO}_2\phi\text{-}$ end groups. The attribution of that splitting to -K-S-F, -D-S-F and -S-S-F end sequences is logical owing to the fact that an analogous but less clear splitting can be observed for the peak attributed to -K-F ends (-S-K-F, -D-K-F, -K-K-F) around 8.5 ppm. Such a long distance shielding effect was indeed already observed on PEEK in sulfuric acid[13]. However, in the present study, the peaks lie so close to each other (0.1 ppm) that no quantitative analysis can be undertaken.

The first conclusion to be drawn from the above observation is that the nucleophilic cleavage of ether links by the fluoride anion has to be taken into account at temperatures above 300°C. In those conditions, the ether links were shown to exhibit different reactivities towards further nucleophilic substitution by the fluoride ion in the following order: -K-K- < -K-S- < -S-S-. Therefore, -S-S- sequences will more easily undergo subsequent exchange reactions whilst, conversely, -K-K- links will appear considerably more stable. As a consequence, the final result of the nucleophilic substitution of ethers for a fluoride anion will be an enrichment in -K-K- sequences within the copolymer chain.

Nucleophilic reactions involving the hydroxyl anion

Hydrolysis of the halogenated monomer and hydrolysis of the previously formed ether linkage can also explain the appearance of new sequences observed by n.m.r. Those side reactions are effective even at low temperature. Two kinds of relevant reactions should be:

$$\sim\text{K-F} + \text{OH}^- \rightarrow \sim\text{K-OH} + \text{F}^-$$

and

$$\begin{aligned}&\sim\text{K-D}\sim + \text{OH}^- \rightarrow \sim\text{K-OH} + {}^-\text{D}\sim\\ &\sim\text{K-S}\sim + \text{OH}^- \rightarrow \sim\text{K}^- + \text{HO-S}\sim\end{aligned}$$

or

$$\sim\text{K-S}\sim + \text{OH}^- \rightarrow \sim\text{K-OH} + {}^-\text{S}\sim \qquad (5)$$

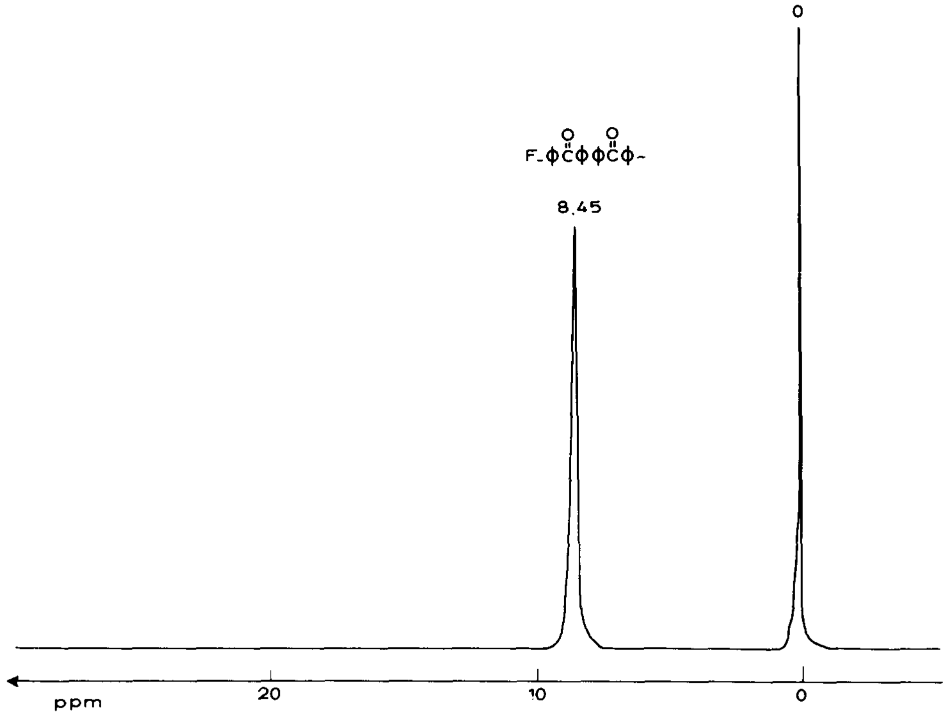

Figure 3 ^{19}F n.m.r. spectrum of a K/D/S 50/20/30 copolymer before the 300°C step, following the technique proposed by Devaux *et al.*[13]

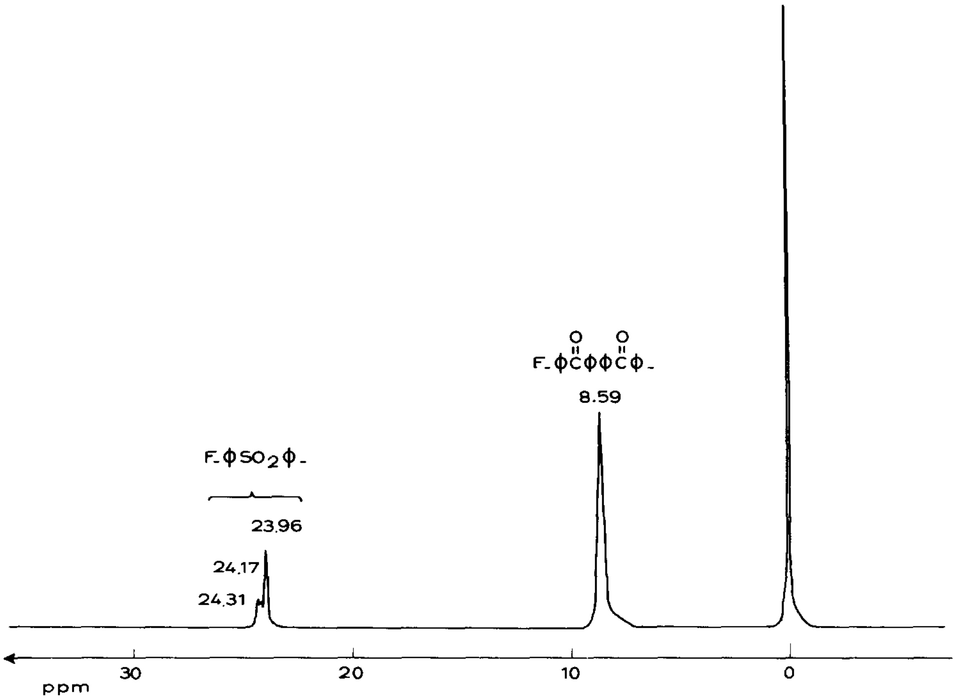

Figure 4 ^{19}F n.m.r. spectrum of a K/D/S 50/20/30 copolymer after the 330°C step, following the technique proposed by Devaux *et al.*[13]

In each case, ~K-OH or ~K$^-$ end groups would be obtained, leading via condensation with a halogenated K end to the ~K-K~ sequence.

In order to demonstrate the possibility of hydrolysis of the monomer K, two series of experiments were undertaken. First, monomer K was reacted with NaOH in NMP at the reflux temperature for different periods of time. A gel permeation chromatograph of the soluble phase from this reaction leads to chromatograms such as the one reported in *Figure 5*. Besides the reference (benzoylacetone), three peaks are observed; the first one on the right-hand side was identified as pure monomer K and was observed to decrease with time. Of the two other peaks, the last one was identified as completely hydrolysed monomer K (HO-ϕ-CO-$\phi\phi$-CO-ϕ-OH), referred to as LKOH, by comparison with a pure sample. The intermediate peak was, therefore, assumed to be the half-hydrolysed product, F-ϕ-CO-$\phi\phi$-CO-ϕ-OH, referred to as FLKOH. That identification was later confirmed after a separate synthesis of FLKOH.

The good separation observed even with mass

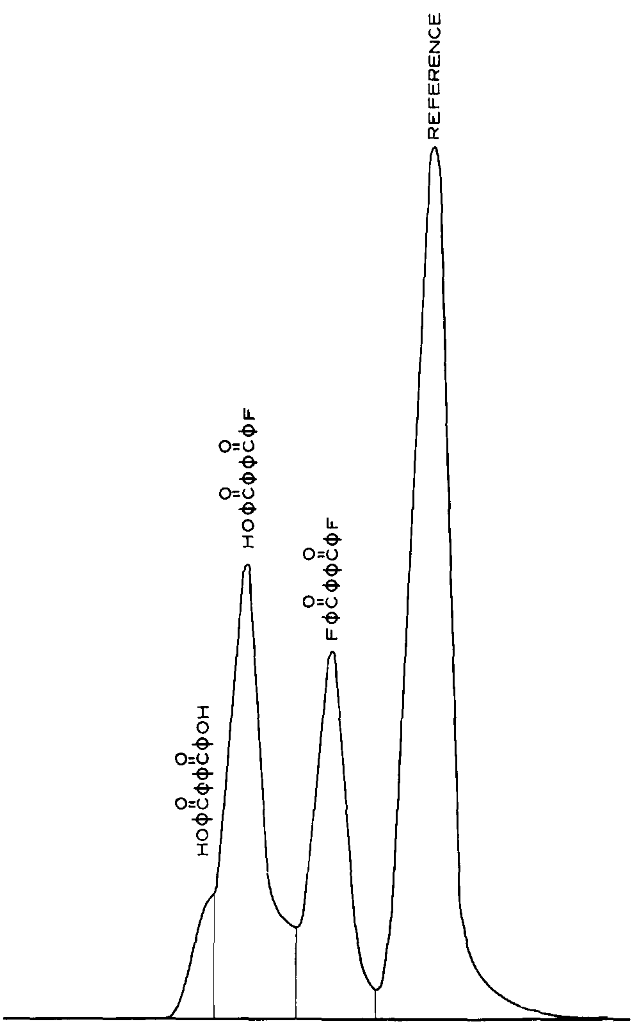

Figure 5 Gel permeation chromatograph of the soluble phase from the reaction: monomer K + NaOH in NMP

differences as low as 2 g mol^{-1} (between K monomer and FLKOH) should be noted. Only an important retention on the g.p.c. column can explain this result.

A second series of experiments was aimed at demonstrating that this hydrolysis effectively took place during the K/D/S copolymer synthesis. In order to achieve the sequence of reactions leading to the hydrolysis of monomer K, the presence of carbonates and phenols in the solvent is required. It was verified that carbonates alone appear to be unable to promote any hydrolysis of monomer K in DPS. Similarly, water alone (in NMP) will not react with monomer K. Therefore the generation of water *in situ* and its ionization by phenates seems to be the most likely route to the hydrolysis of monomer K. Two systems were, therefore, examined to confirm this view, namely:

System 1	$K + D + Na_2CO_3$ in DPS	(250°C)
System 2	$K + S + Na_2CO_3$ in DPS	(250°C)

Gel permeation chromatographic analysis of the soluble phase, sampled after increasing periods of reaction time, detected K monomer and FLKOH as shown in *Figures 6* and *7*. No evidence of LKOH formation was found using this technique.

From the hydrolysis studies of monomer K described above it can now be concluded that the mechanism proposed by Johnson and Farnham[10,11] for the role of water in the synthesis of PES is equally applicable to polymers of the K/D/S type. Despite no experimental work being done to show chain cleavage by the hydroxyl anion, the similarity of the mechanism involved in every nucleophilic substitution makes it reasonable to predict that it will occur but to a lesser extent than the hydrolysis of halogenated end groups.

This nucleophilic substitution by a hydroxyl anion was, however, previously discarded as a possible side reaction in K/D/S copolymer synthesis due to the imbalance of the reactive species which would result. Indeed, all molecular weight characterizations indicate higher molecular weight products than would be expected from the initial stoichiometry (*Table 2*).

The explanation of this apparent anomaly was found to lie in the very poor solubility of the bisphenate monomer S in the DPS solvent. This phenate mainly precipitates as a separate solid phase and, upon progressive redissolution maintains a constant but very low concentration level in solution. In this way, the balance of reactants actually in solution exhibits a permanent excess of halogenated species up to the formation of a high molecular weight polymer.

Low solubility of phenate monomers

Attwood *et al.*[21] have previously described the benzophenone phenate as insoluble in DPS, even at high

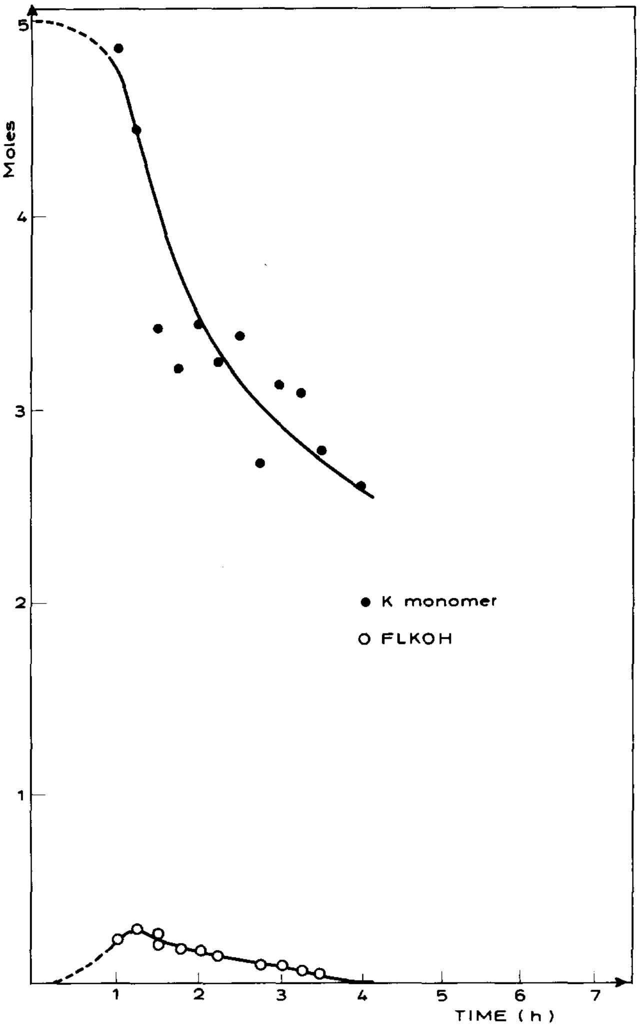

Figure 6 Plot of the appearance of FLKOH and disappearance of K monomer with increasing reaction time for the system K/D 50/20

temperature (335°C). They reported a solubility as low as 0.1%.

During K/D/S copolymer synthesis, a large insoluble phase was observed which led to a phenate solubility study. The four phenates $KO\phi\phi OK$, $KO\phi SO_2\phi OK$, $NaO\phi\phi ONa$, $NaO\phi SO_2\phi ONa$ were synthesized in methanol and isolated. Their solubility in DPS was immediately studied by sampling on the surface soluble phase, through a glass sintered filter. *Table 3* gives the soluble phenate concentrations measured by h.p.l.c. analyses. The given concentrations must be considered to be maximum values because small very fine solid particles must be suspended in solution and drawn in through the filter (porosity 16–40 μm). The accuracy of the technique is estimated to be <0.2%. S phenates show very low solubility at all temperatures, whilst D phenate solubilities vary with the cation type and the temperature. Potassium phenates are significantly soluble above 300°C, while sodium phenates show an intermediate solubility over the temperature range studied.

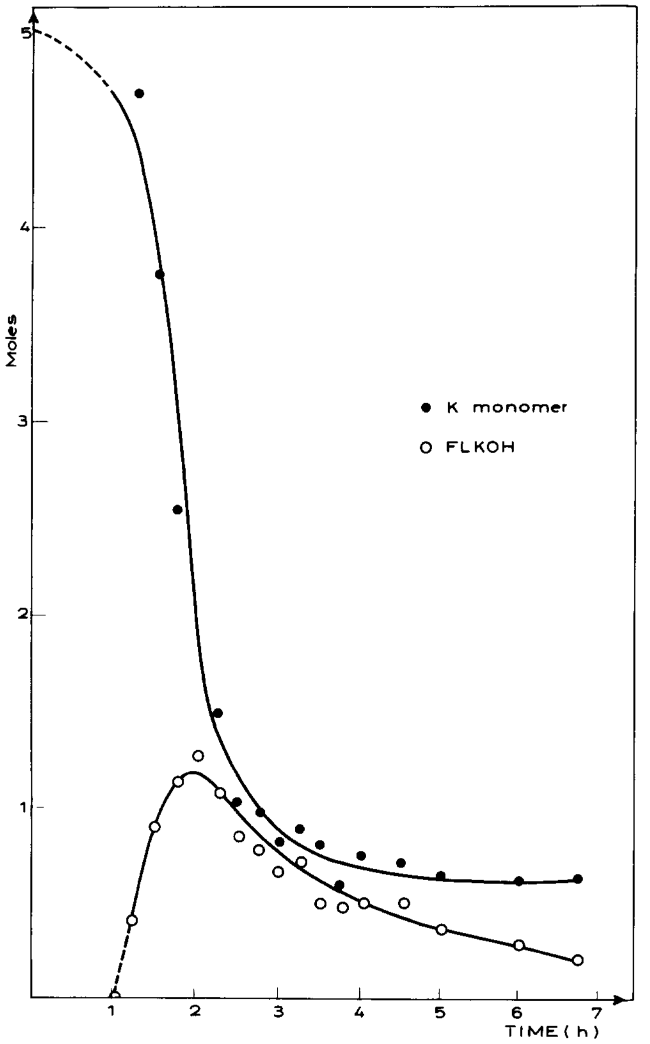

Figure 7 Plot of the appearance of FLKOH and disappearance of K monomer with increasing reaction time for the system K/S 50/30

CONCLUSIONS

The mechanism for the synthesis of copolymers from K, D and S monomers appears very similar to that for PEEK and PES, despite the competitive reaction of the halogenated monomer with two different phenates. The main reaction is the nucleophilic substitution of the halogen by the bisphenate ions leading to ether sulfone and ether ketone moieties. However, the aromatic ethers in the polymer are activated by either the sulfone or ketone linking groups, so they constitute potential sites for subsequent substitutions (side reactions). Different nucleophilic species already described in the literature for PEK and PES are present in the reaction medium and lead to chain rearrangements by side reactions.

The present study clearly demonstrated in the K/D/S polymer synthesis that:

- transetherification by the phenates is greatly reduced by the low solubility of these nucleophiles in the reaction solvent DPS.
- chain cleavage by the fluoride ion seems very effective but only above 300°C.

Table 3 Solubility of phenates with increasing temperature

Phenate	Temperature (°C)	Maximum solubility (w/w%)
Potassium S monomer	200	0.1
	250	0.3–0.5
	265	0.0–0.2
Sodium S monomer	200	0.2–0.4
	250	0.2–0.4
	265	0.2–0.9
Potassium D monomer	200	0.1–0.5
	250	0.2–0.7
	265	0.1–0.8
	300	3.0–3.6
Sodium D monomer	200	1.1–1.3
	250	1.1–1.3
	265	0.9–1.6
	300	1.3

Table 2 Comparison between molecular weights obtained by different techniques for the K/D/S copolymer

Copolymer samples	Synthesis M_n	^{19}F n.m.r. M_n	High temperature g.p.c.^{a} M_p	Room temperature g.p.c.^{b} M_w	M_n	M_p	H
A	5000	6000	11 100	16 500	7600	13 500	2.2
B	7500	8800	15 100	21 700	9700	18 400	2.2
C	10 000	12 700	20 600	26 900	11 700	26 600	2.3
D	12 000	14 200	22 200	30 700	13 200	30 800	2.3
E	15 000	16 800	28 100	34 500	14 500	35 600	2.4

^{a} PEEK calibration

^{b} K/D/S 50/20/30 copolymer calibration

M_w, weight average molecular weight; M_n, number average molecular weight; M_p, peak molecular weight; H, polydispersity

- hydrolysis of the halogenated end groups (and possibly the chain cleavage) by the hydroxyl ion plays a significant role in the copolymer synthesis from the monomers K, D and S.

It is, therefore, clearly established that this synthesis will lead to -S-S-, -S-D- and -K-K- linkages in addition to the expected -K-D- and -K-S- sequences. Since any such structural modification may lead to changes in final properties, side reactions of this type would probably result in poor reproducibility of the properties of K/D/S copolymers unless they were closely controlled. In the next paper[22], the melting behaviour of model compounds of each crystallizable sequence will be studied. The results of that study will be useful in designing an optimized microstructure for future polymer chains synthesized from K, D and S monomers.

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