About the synthesis of a high-temperature, crystalline poly[aryl ether(ketone-*co*-sulfone)]: 2. Model compounds study

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From a detailed study of the syntheses and physical properties of semicrystalline poly[aryl ether(ketone-*co*-sulfone)] model compounds, this paper leads to a better understanding of the chemistry of the polymer synthesis and of its thermal behaviour. Long, crystallizable sequences are shown to arise from the heterogeneous nature of the synthesis. These sequences are responsible for the high melting points observed. Conclusions are drawn on the necessity for a revision of the synthesis procedure in order to avoid the appearance of such sequences.

(Keywords: poly(aryl ether ketone)s; poly(aryl ether sulfone)s; model compounds)

INTRODUCTION

Aryl ether(ketone-*co*-sulfone) polymers, patented in 1986 by ICI plc[1], are sophisticated semicrystalline thermoplastics suitable as matrices for composites. They are synthesized from the co-condensation of a long, dihalogenated ketone with two different diphenols (*Table 1*). They combine, therefore, some properties of poly(aryl ether ketone)s and poly(aryl ether sulfone)s. These polymers provide similar composite matrix mechanical performance to the poly(ether ether ketone) Victrex PEEK (APC-2) but have a higher continuous use temperature. Most mechanical properties of the preferred polymer are indeed similar to those of PEEK but its glass transition temperature (T_g), higher by ~60°C, allows it to withstand a continuous use temperature close to 180°C[2]. Some erratic high melting temperatures ($T_m > 400°C$) often appear in these high T_g polymers after synthesis and have not so far been fully explained.

The crystallinity of copolymers of this type must find its origin in homopolymer sequences which are long enough to crystallize. However, the high crystallinity levels which are often observed[1] with these polymers lead to the fully statistical character of the distribution of the moieties in their chains being questioned.

The purpose of this paper is to report on the study, by the way of model compounds, of the crystallizable entities which can be formed during synthesis of the copolymer, from either direct or secondary reactions[3], and to determine which are responsible for the observed high T_ms. From that knowledge, new strategies are suggested in order to avoid any unwanted thermal behaviour observed with these aryl ether(ketone-*co*-sulfone) copolymers.

EXPERIMENTAL

Materials

K, D, S monomers and diphenylsulfone (DPS) were provided by ICI plc (Wilton, UK) in pure form and used without further purification. 4,4'-Dihydroxy(bisbenzoyl)biphenyl, or fully hydrolysed monomer K (LKOH), was synthesized from monomer K as described elsewhere[3]. 4-Hydroxy-4'-fluoro(bisbenzoyl)biphenyl, or monohydrolysed monomer K (FLKOH), was supplied by ICI plc[4]. After recrystallization from dimethylsulfoxide (DMSO), this compound still contained some solvent molecules (0.5 mol DMSO) but its purity was >95%. Na_2CO_3, K_2CO_3, KOH and NaOH were pure compounds obtained from UCB (Brussels, Belgium). Tetrachlorethane (TCE) and toluene were distilled before use. *N*-methylpyrrolidone (NMP) and DMSO were refluxed over CaH_2 for 8 h and then vacuum distilled before use.

Phenates: separate synthesis

Bisphenols were stoichiometrically neutralized in distilled methanol solution using potassium hydroxide

Table 1 Monomers

Monomer	Abbreviation
4,4'-Bis(4-fluorobenzoyl)biphenyl	K
4,4'-Dihydroxydiphenyl	D
4,4'-Dihydroxydiphenylsulfone	S

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Table 2 Model compounds

Model compound	Structure	Abbreviation
1	F-ϕCOϕϕCOϕ-OϕϕO-ϕCOϕϕCOϕ-F	KDK
2	HOϕϕO-ϕCOϕϕCOϕ-OϕϕOH	DKD
3	F-ϕCOϕϕCOϕ-OϕSO_2ϕO-ϕCOϕϕCOϕ-F	KSK
4	HOϕSO_2ϕO-ϕCOϕϕCOϕ-OϕSO_2ϕOH	SKS
5	F-ϕCOϕϕCOϕ-O-ϕCOϕϕCOϕ-F	KK
6	F-ϕCOϕϕCOϕ-O-ϕCOϕϕCOϕ-O-ϕCOϕϕCOϕ-F	KKK

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 used immediately.

*Model compounds **1** to **4*** (Table 2)*: DMSO procedure*

In a two-necked round-bottomed 500 ml flask, fitted with a water-cooled condenser and an argon inlet, DMSO (150 ml) was introduced, followed by, respectively:

1a 0.032 mol K monomer and 0.004 mol KOϕϕOK (potassium biphenate)
2a 0.003 mol K monomer and 0.024 mol KOϕϕOK (potassium biphenate)
3a 0.040 mol K monomer and 0.005 mol NaOϕSO_2ϕONa (sodium bisphenate)
4a 0.002 mol K monomer and 0.016 mol NaOϕSO_2ϕONa (sodium bisphenate)

The mixture was heated to reflux with magnetic stirring and the reaction continued for 5 h. The reaction mixture was then poured into deionized water, the precipitate filtered off on a number 4 sintered glass filter, and successively washed with water, acetone and methanol. In this way, the salts from the reaction and the phenates were easily eliminated. The elimination of unreacted K monomer was achieved by the procedure described below.

*Model compounds **1** to **4** and **6*** (Table 2)*: DPS procedure*

A four-necked round-bottomed 500 ml flask was fitted with a mechanical stirrer, an argon inlet, a temperature probe and, as appropriate, an air-cooled condenser, a water-cooled condenser or a Dean–Stark apparatus. As a first step, DPS (200 g) and the appropriate amounts of bisphenol and Na_2CO_3 were introduced into the reaction vessel and heated to 200°C. The mechanical stirrer was started when the mixture became molten and the temperature was then maintained at 200°C for 1 h. As a second step, the mixture was cooled and toluene was introduced in order to distil a water–toluene azeotropic mixture following a procedure described by Wu *et al.*[5]. Then the temperature was raised to 250°C and the appropriate amount of monomer K was introduced. The reaction was continued for a further 4 h. Finally the reaction mixture was cooled until it solidified, ground to a fine powder and washed successively with acetone, methanol and deionized water on a number 4 sintered glass filter. The elimination of unreacted K monomer is described below. The compounds below were obtained when the following were introduced:

1b 80 mmol K monomer, 10 mmol D monomer and 10 mmol Na_2CO_3
2b 10 mmol K monomer, 80 mmol D monomer and 80 mmol Na_2CO_3
3b 80 mmol K monomer, 10 mmol S monomer and 10 mmol Na_2CO_3
4b 10 mmol K monomer, 80 mmol S monomer and 80 mmol Na_2CO_3
6 80 mmol K monomer, 10 mmol LKOH and 10 mmol Na_2CO_3

*Model compound **5*** (Table 2)

*From presynthesized FLKOH (**5a**).* Into a two-necked round-bottomed 500 ml flask, fitted with a water-cooled condenser and an argon inlet, were introduced DMSO (400 ml), K monomer (0.02 mol), FLKOH.0.5 DMSO (0.005 mol) and K_2CO_3 (0.005 mol). The mixture was refluxed under magnetic stirring for 36 h. Upon cooling, the solution was poured into deionized water then filtered on a number 4 sintered glass filter. The precipitate was washed successively with deionized water and acetone. Unreacted K monomer was eliminated as described below.

From in situ *synthesized FLKOH (**5b**).* Into a two-necked round-bottomed 2 l flask, fitted with a water-cooled condenser and an argon inlet, were introduced: DMSO (1000 ml), K monomer (0.005 mol), K_2CO_3 (0.005 mol) and water (20 ml). The solution was refluxed for 36 h under magnetic stirring. After cooling, the precipitate was filtered off and then washed successively with NMP, deionized water and acetone.

Monomer K elimination

As K monomer is only sparingly soluble in common solvents, model compounds synthesized with an excess of monomer K were recrystallized from a TCE solution (6–7 g dissolved in 300 ml TCE). An alternative way to eliminate K monomer was by careful washing of the model compounds with NMP at room temperature, followed by filtration on a number 5 sintered glass filter. However, purification of **3** was unsuccessful by any procedure due to it having a solubility very close to that of K monomer.

Differential scanning calorimetry

T_g (onset), T_m (peak) and the recrystallization temperature on cooling (T_{cc}) were recorded on a Perkin–Elmer DSC-7 using a heating rate and cooling rate of 20°C min^{-1}. Data handling was performed on a 7500 Professional Computer from Perkin–Elmer with TAS-7 software.

Liquid chromatography

A special liquid chromatography procedure was used throughout this work. Size-exclusion columns were used but retention was predominantly observed. By this technique monomer K, monohydrolysed monomer K and fully hydrolysed monomer K were well separated even with very low mass difference (2 g mol^{-1}). Therefore no calibration was used.

Model compounds (soluble in NMP) were dissolved (1 mg in 50 ml) in the elution solution (NMP containing 0.1 M LiCl).

The g.p.c. device included a Waters 6000 A pump, two Waters columns (Shodex type) filled with 500 Å and 100 Å Ultrastyragel stationary phase, and a Perkin–Elmer LC 55 u.v. detector. The flow rate was 0.8 ml min^{-1} and the injected volume was 50 μl. The u.v. wavelength of the detector was set at 308 nm. Data handling was performed on a Trivector Scientific Ltd computer (from Trilab 2000).

^{19}F nuclear magnetic resonance

^{19}F n.m.r. spectra were recorded on a Bruker WM 250 spectrometer operating at 235.24 MHz for ^{19}F (spectral width 200 Hz; pulse width 13 μs (90°)). Samples were dissolved in $>99\%$ concentrated sulfuric acid (0.2 w/w%). CF_3COONa (0.01%) was added as internal standard. The method has been described previously in more detail elsewhere[6].

RESULTS

Model compound syntheses

The synthesis of the more representative model compounds is now discussed. In a previous paper[3], we showed how the copolymer synthesis gave rise to K-D, K-S, S-S, S-D and K-K sequences. However, since the corresponding polymers of -S-S- and -S-D- (*Table 3*) are known to be non-crystallizable, these sequences are not studied. Therefore, only ketone-containing -K-D-, -K-S- and -K-K- sequences will be studied. Consequently, six oligomers of different lengths (*Table 2*) based on monomer K were chosen to model the three sequences -K-D-, -K-S- and -K-K-.

The synthesis of compounds **1**–**4** in *Table 2* generally followed reactions 1 and 2, using the appropriate reactant in large excess.

$$K + {}^{-}O\phi\phi O^{-} \rightarrow K\text{-}O\phi\phi O\text{-} \quad (K\text{-}D\text{-}) \qquad (1)$$

$$K + {}^{-}O\phi SO_2\phi O^{-} \rightarrow K\text{-}O\phi SO_2\phi O\text{-} \quad (K\text{-}S\text{-}) \qquad (2)$$

For the first two compounds, KDK and DKD, the phenate is very reactive but the ether link quite inactive towards transetherification; for the third and fourth compounds, KSK and SKS, the reverse situation is true. Therefore, in order to limit such transetherification, sodium phenates were always used.

The nucleophilic substitution by the fluoride anion was also minimized by means of sodium cations. Moreover, a reaction temperature below 280°C was chosen as it has previously[9] been demonstrated that the reaction is inhibited under these conditions. In order to avoid any hydrolysis of the fluorine end groups every trace of water had to be eliminated from the reaction medium. As the transformation of phenol into phenate produces a water molecule this neutralization was achieved either in a separate vessel or in a previous reaction step followed by azeotropic distillation.

Table 3 Thermal transitions for $(\text{-S-S-})_n$ and $(\text{-S-D-})_n$ homopolymers

Homopolymer	T_g (°C)	T_m (°C)	Ref.
$(\text{-}\phi SO_2\phi O\text{-})_n$	223–230	–	7
$(\text{-}\phi SO_2\phi\text{-}O\phi\phi O\text{-})_n$	232	–	8

The synthesis of the fifth model compound (KK) needed the use of monohydrolysed K monomer (FLKOH). The latter was generated either *in situ* by control of reaction 3, or by separate synthesis.

$$\underset{\text{K monomer}}{F\text{-}\phi\text{-}CO\text{-}\phi\phi\text{-}CO\text{-}\phi\text{-}F} + OH^{-} \rightarrow \underset{\text{FLKOH}}{HO\text{-}\phi\text{-}CO\text{-}\phi\phi\text{-}CO\text{-}\phi\text{-}F} + F^{-} \qquad (3)$$

In both cases, the final step was an etherification:

$$\underset{\text{FLKOH}}{HO\text{-}\phi\text{-}CO\text{-}\phi\phi\text{-}CO\text{-}\phi\text{-}F} + \underset{\text{K monomer}}{F\text{-}\phi\text{-}CO\text{-}\phi\phi\text{-}CO\text{-}\phi\text{-}F} \xrightarrow{Na_2CO_3} \underset{\text{KK}}{F\text{-}\phi\text{-}CO\text{-}\phi\phi\text{-}CO\text{-}\phi\text{-}O\text{-}\phi\text{-}CO\text{-}\phi\phi\text{-}CO\text{-}\phi\text{-}F} + NaF \qquad (4)$$

The sixth model compound was synthesized using reaction 4 but with fully hydrolysed K monomer (LKOH) instead of FLKOH.

Model compound analyses

Different techniques were used to characterize the synthesized products.

D.s.c. and solubility. The results of the d.s.c. analysis of all the starting and synthesized compounds are reported in *Table 4* together with their solubility in NMP. The latter technique sometimes allows two fractions to be distinguished from a single reaction product. Several values are reported for compounds exhibiting multiple melting behaviour. Recrystallization temperatures on cooling are also reported.

Liquid chromatography. Using a g.p.c. technique, the compounds are not only separated by size exclusion but more predominantly by their affinity for the mobile or stationary phase[3]. The results are presented in *Table 5* (for NMP-soluble compounds only).

^{19}F nuclear magnetic resonance. The fluorine concentration level of each compound was determined from the ratio between the area of its ^{19}F n.m.r. spectrum and that of the internal standard peak. The results are reported in *Table 6* together with a theoretical value calculated from the expected structure.

DISCUSSION

Before discussing the melting points of the model compounds and attempting to learn from them about the thermal behaviour of the preferred K/D/S copolymer, the first part of this section will be devoted to discussing the correlation between actual and expected model compound structures. Discrepancies are observed (*Tables 4–6*) not only with regard to that criterion but

Table 4 Thermal transitions and solubility of model compounds

Model compounds	Expected structure	Solubility in NMP	T_m (°C)	T_{cc} (°C)
K monomer		sol.	268	248
FLKOH.0.5 DMSO		sol.	213, 247	184
LKOH		sol.	296	–[a]
1a	KDK	insol.	404	366
2a	DKD	insol.	401	347
3a	KSK	sol.	287	247
1b	KDK	insol.	404	390
2b	DKD	sol.	393	351
		insol.	436	414
3b	KSK	sol.	290	267
4b	SKS	sol.	256	–[b]
6	KKK	insol.	366, 414, 433	391, 400
5a	KK	insol.	387	357, 366
5b	KK	insol.	391	368, 377

[a] Not recorded
[b] Amorphous

Table 5 Retention times for NMP-soluble compounds

Model compound	Expected structure	Retention time (s)
K monomer		1252
FLKOH.0.5 DMSO		1096
LKOH		1060
2b (sol. in NMP)	DKD	1012
3a and **3b**	KSK	1052 and 1270
4b	SKS	934

Table 6 Recorded and expected fluorine contents (%)

		^{19}F content	
Model compound	Expected structure	Recorded	Expected
K monomer		10.1	9.5
FLKOH.0.5DMSO		5.2	4.8
LKOH		0	0
1a	KDK	4.2	4.3
1b	KDK	2.0	4.3
2a	DKD	4.0	0
2b (sol. in NMP)	DKD	0	0
2b (insol. in NMP)	DKD	0.3	0
4b	SKS	0	0
6	KKK	3.0	3.3
5a	KK	3.3	4.9
5b	KK	4.7	4.9

also between compounds synthesized using different procedures [DMSO (**a**) or DPS (**b**)].

Chemical structures of model compounds

Model compounds 1a and 1b. The K-D-K structure would be expected from the excess K monomer introduced in both syntheses. D.s.c. results for compounds **1a** and **1b** are indeed very similar (*Table 4*). However, from ^{19}F n.m.r. analysis (*Table 6*) a loss of fluorine is observed for compound **1b**. This result probably originates in partial hydrolysis of monomer K (reaction 3). Therefore, only model compound **1a** will be considered below for the K-D-K structure.

Model compounds 2a and 2b. For both methods of synthesis, the excess D monomer would be expected to lead to the D-K-D structure. However, large discrepancies are observed from solubility, d.s.c. (*Table 4*) and ^{19}F n.m.r. (*Table 6*) results. Since there is no fluorine in the structure, only the NMP-soluble fraction of **2b** appears to fit the D-K-D formula. Moreover, the liquid chromatography results (*Table 5*) reveal only one peak, suggesting fairly good purity for this compound. Consequently, the soluble part of the **2b** compound only will be considered to represent the D-K-D structure. Problems encountered during the synthesis will be detailed below and will give some explanation for the production of the **2a** and **2b** (insoluble fraction) compounds.

Model compounds 3a and 3b. Model compound **3**, having the expected formula K-S-K, was never obtained in a sufficiently pure form. The explanation lies in its solubility which is so close to that of K monomer that neither TCE nor NMP methods could be used to purify the reaction product. This is confirmed by liquid chromatography (*Table 5*) which reveals the presence of residual K monomer in both **3a** and **3b** products (retention time 1270 s).

Model compounds 4a and 4b. Model compound **4**, with the expected structure S-K-S, was only successfully synthesized through the **4b** procedure. Indeed, no fluorine is observed in the ^{19}F n.m.r. spectrum (*Table 6*). Also, liquid chromatography reveals only one peak (*Table 5*). No recrystallization peak was observed during the d.s.c. cooling step (*Table 4*).

Model compounds 5a and 5b. The synthesis of model compound **5**, with the expected structure K-K, was attempted by the two ways described above. Both products **5a** and **5b** exhibit similar d.s.c. results. However, here again, compound **5a** had to be discarded for its low fluorine content (*Table 6*). A loss of fluorine during the **5a** synthesis may be due to a hydrolysis reaction (reaction 3) but another explanation may be found in the self-condensation of FLKOH:

$$2\text{HO-}\phi\text{-CO-}\phi\phi\text{-CO-}\phi\text{-F} \xrightarrow{\text{Na}_2\text{CO}_3} \text{F-}\phi\text{-CO-}\phi\phi\text{-CO-}\phi\text{-O-}\phi\text{-CO-}\phi\phi\text{-CO-}\phi\text{-OH} \quad (5)$$

Therefore, only the model compound **5b** is considered to fit the K-K structure.

Model compound 6. From the ^{19}F n.m.r. results (*Table 6*) the synthesis of the model compound **6** (expected structure K-K-K) seems to have been successful. However, since multiple melting and recrystallization peaks are observed by d.s.c. (*Table 4*) its actual structure remains doubtful. It could indeed be a mixture of K-K, K-K-K and K-K-K-K oligomers in such a ratio as to fit the correct fluorine content. Model compound **6** will, therefore, be discussed later.

From the above discussion, it is apparent that four model compounds from the six attempted ones (*Table 2*) were actually obtained in a reasonably pure form. These are reported in *Table 7* together with their T_m values. The results recorded in *Table 7* show directly that model compounds even as short as K-D-K, D-K-D or K-K exhibit very high T_ms, close to 400°C. It should also be noted that the T_m of the S-K-S model compound is only 12°C below that of K monomer itself ($T_m = 268$°C). Therefore, it can be assumed that the addition of two S moieties on both ends of a crystallizable long-ketone structure has only a limited effect on its melting point. However, it must be remembered that the crystallization rate is significantly decreased.

From these two observations it seems that crystallizable sequences within the preferred K/D/S copolymer chain can be considered as being responsible for the high melting peaks observed in the d.s.c. Effectively, PEEK studies[10,11] have recently shown that the thickness of the polymer crystalline core and the length of extended model compounds control in the same way the T_m (first T_m of an isothermally crystallized PEEK). A PEEK lamellar thickness of ~5 nm is related to a first T_m of ~320°C and a second T_m of 335°C while the corresponding monodisperse trimer (same extended length 5.6 nm) exhibits melting points up to 315°C.

The next part of this discussion deals with an extrapolation of the melting points of the oligomers towards longer structures in order to gain a better idea of the longest admissible sequences within the K/D/S copolymer chain.

Extrapolation of melting points

In another paper[12], a linear extrapolation technique was proposed to estimate the thermodynamic melting point (T_m°) of a polymer on the basis of the melting points and lengths of its first oligomers.

$$T_m = T_m^\circ\left(1 - R\frac{\ln l}{l}\frac{T_m^\circ}{\Delta h^\circ}\right) \qquad (6)$$

where l is the oligomer length (in Å), T_m is the oligomer melting temperature, T_m° is the thermodynamic melting temperature and Δh° is the thermodynamic melting enthalpy.

Table 7 Isolated model compounds and their melting points

Model compound	Abbreviation	Solubility in NMP	T_m (°C)
1a	K-D-K	insol.	404
2b	D-K-D	sol.	393
4b	S-K-S	sol.	256
5b	K-K	insol.	391

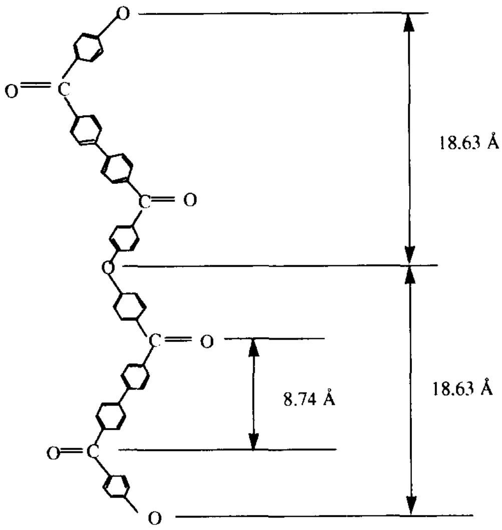

Figure 1 K-K repetitive length

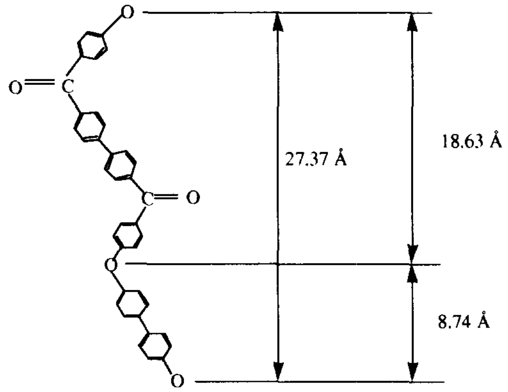

Figure 2 K-D repetitive length

Therefore, it is now possible to perform such an extrapolation on the basis of the melting points of monomer K and LKOH (*Table 4*) and of the synthesized model compounds (*Table 7*).

While it can be shown (*Figures 1* and *2*) that the shapes of the -K-K- and -K-D- sequences in their extended forms are not perfectly isomorphous, similar chain–chain interactions and packing can be expected to lead to similar Δh° values. On the other hand, both extrapolated T_m°s were found to be (within <1%) close to 570°C. Therefore, the superimposition of the extrapolation straight lines shown in *Figure 3* seems reasonable.

Of course, due to the very limited number of available oligomers, the value of T_m° (around 570°C) represents only an approximation, but the use of an extrapolation to estimate the melting points of oligomers just a few units longer than the synthesized model compounds should lead to fairly accurate values. Results of such estimations are reported in *Table 8*.

It can be observed in *Tables 7* and *8* that the hypothesis that the actual composition of the product **6** is a mixture of K-K, K-K-K and K-K-K-K is not far from reality since it shows melting peaks at 366, 414 and 433°C. These

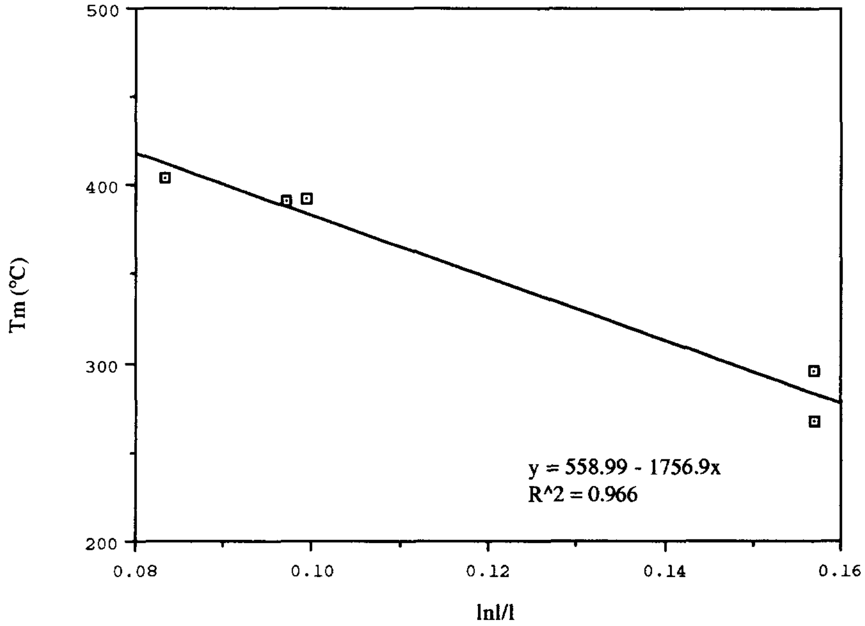

Figure 3 $(K\text{-}D)_n$ and $(K\text{-}K)_n$ coextrapolation

Table 8 Extrapolated melting points for longer compounds

Longer compound	l (Å)	Extrapolated T_m (°C)
D-K-D-K	54.7	430
D-K-D-K-D	63.5	444
K-K-D-K	64.6	445
K-D-K-D-K	73.4	456
K-K-K	55.9	432
K-K-K-K	74.5	457

are close to the expected values (*Tables 7* and *8*) taking into account a reasonable cryoscopic effect.

It is remarkable that all the calculated melting points reported in *Table 8* lie largely above 400°C. Therefore the sequences K-D-K (model compound **1**) and K-K (model compound **5**) theoretically represent the longest admissible crystallizable sequences within the K/D/S copolymer chain.

The last part of this discussion will be devoted to a reaction mechanism, so far unidentified, which may lead to the formation of these long, crystallizable sequences.

Formation of high melting sequences during K/D/S copolymer synthesis

Several secondary reactions likely to produce long, crystallizable sequences during the K/D/S copolymer synthesis have been described and discussed elsewhere[3]. Methods to minimize the effects of such reactions were used throughout this work. Nevertheless, a number of syntheses appeared unsuccessful, leading to products exhibiting properties different from the one expected.

From the series of syntheses in DMSO, as recorded in *Tables 4* and *6*, products **1a** and **2a** look so similar that they must have the same K-D-K structure. If that structure was, indeed, expected for the **1a** product it seems very improbable that it would be obtained from the **2a** product, owing to the large excess of monomer D used in this synthesis. It appears, therefore, that ending an oligomer with a D unit is very difficult in DMSO.

In DPS, the D-K-D model compound was actually synthesized (i.e. the fraction of product **2b** soluble in NMP). However, it was isolated from a large amount of a product (the fraction of product **2b** insoluble in NMP) which exhibited a melting point largely above 400°C. From *Figure 3*, the latter product has, therefore, to be identified as higher $(K\text{-}D)_n$ oligomers. In the same solvent, the K-D-K model compound was also synthesized but with a loss of fluorine and in very low yield (product **1b**).

It is now proposed to explain these observations through a new mechanism, different from the secondary reactions described above and leading to unwanted long, crystallizable sequences. A tentative explanation can be based on two assumptions:

- in DMSO, the potassium phenate deriving from monomer D is poorly soluble whilst the potassium phenate from the K-D intermediate is a little more soluble.
- in DPS, the sodium phenate of monomer D is quite soluble. The sodium phenate from intermediate K-D is likely to agglomerate in the form of clusters with the organic K moiety in the external layer.

Therefore, in DMSO, whatever the amount of D monomer introduced, the concentration of the corresponding phenates in solution will remain exceedingly low. However, this is not the case for the K-D phenates which can therefore preferentially react with K monomer, resulting in the production of K-D-K. In contrast, in DPS, after formation of the sodium salt of K-D, only further reaction with D monomer can occur because of phenate-end protection by clustering, therefore D-K-D oligomers will be produced. As the only further possibility for the latter is to add one or two K units, higher oligomers will necessarily be formed (D-K-D-K, D-K-D-K-D, K-D-K-D-K,...). This proposed mechanism is likely to be of prime importance in the synthesis of K/D/S copolymers (in DPS) because it will lead, without the need for any secondary reaction, to unwanted long $(K\text{-}D)_n$ sequences, melting above 400°C, even at the expense of the copolycondensation statistics.

CONCLUSIONS

From their synthesis, as well as from their physical properties, the detailed study of K/D/S copolymer model compounds has led to some useful conclusions. From the physical point of view, the thermal analysis of model compounds representing $(\text{K-D})_n$ and $(\text{K})_n$ sequences has shown that entities even as short as K-D-K or K-K exhibit melting points close to 400°C. Moreover, an extrapolation from these T_ms has demonstrated that sequences of analogous structure, just one or two units longer, should melt at a temperature considerably higher than 400°C. Also, the measurement of the melting point of the S-K-S model compound has shown that S entities on both ends of a crystallizable model compound do not depress its melting point sufficiently to allow the incorporation of long, crystallizable sequences within the K/D/S copolymer chain while keeping its melting point below 400°C. Consequently, all $(\text{-K-D})_n\text{-K-}$ and $(\text{-K})_n\text{-K-}$ sequences where $n > 1$ would preferably be avoided.

From the chemical point of view, the synthesis of D-K-D and K-D-K model compounds has led to the observation that long, crystallizable sequences not only arise from secondary reactions but also tend to form spontaneously in DPS, the solvent used for the synthesis of K/D/S copolymers. Therefore, in order to produce K/D/S copolymers free from high-melting species it is necessary to avoid the secondary reactions which lead to them and this necessitates a profound revision of the initially used synthetic procedure in order to either suppress the sharing of reactive intermediates between the two phases or to enhance the exchange of reactive intermediates between the two phases.

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