

New polymer syntheses: II. Preparation of aromatic poly(ether ketone)s from silylated bisphenols

In honour of the 60th birthday of Dir. Dr L. Bottenbruch

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Bulk condensations of 4,4'-difluorobenzophenone and various silylated bisphenols were carried out at 220°–320°C, with caesium fluoride as catalyst. Silylated bisphenol-A, tetramethylbisphenol-A, 1,1-bis(4-hydroxyphenyl)cyclohexane or 4,4'-dihydroxydiphenylsulphone as monomers and glassy polymers were soluble in several organic solvents. Their glass transitions were determined by differential scanning calorimetry (d.s.c.) and their number molecular weights (\bar{M}_n) determined by means of vapour pressure osmometry. \bar{M}_n 's up to 10 000 were obtained. When silylated hydroquinone, 4,4'-dihydroxydiphenyl, 2,7-dihydroxynaphthalene or 4,4'-dihydroxydiphenylsulphide undergo polycondensation the resulting poly(ether ketone)s form crystals. It is demonstrated that transesterification does not take place and that block copoly(ether ketone-ether sulphone)s are synthesized. Furthermore, the thermostability of the poly(ether ketone)s in air was investigated.

(Keywords: poly(ether ketone)s; poly(ester ether ketone)s; *o,o'*-bistrimethylsilyl-bis-phenols; bulk condensation; glass transition; thermostability)

INTRODUCTION

The first synthesis of a fully aromatic poly(ether ketone) was described by Bonner¹, who obtained a low molecular weight material by the Friedel-Crafts condensation of diphenyl ether and isophthaloylchloride. The Friedel-Crafts reaction was used, with more success by Goodmain *et al.*², who condensed 4-phenoxybenzoylchloride. Iwakura *et al.*³ worked with polyphosphoric acid keeping the poly(ether ketone)s in solution. Although molecular weights were never determined, the relative viscosities reported in these three papers¹⁻³ indicate that the molecular weights were too low for technical applications. Satisfactory molecular weights for the preparation of tough films (i.e. $\eta_{inh} > 0.8$ in conc. sulphuric acid) were obtained by Marks⁴ and later by Dahl⁵ (using BF₃ as catalyst in liquid H₂F₂). The synthesis of crosslinked poly(ether ketone)s via the Friedel-Crafts method was recently reported by Marvel and coworkers^{6,7}.

A quite different approach, namely the formation of ether bonds by nucleophilic substitution of halogeno benzophenones was first investigated by a Glendinning *et al.*⁸. However, high molecular weights were not obtained when dimethylsulphoxide and sulpholane were used as reaction media with the temperature restricted to 150°–180°C. Better results, i.e. $\eta_{inh} \geq 1.0$ ($c = 1.0$ in H₂SO₄), in diphenylsulphone at reaction temperature of 300°C were obtained by Attwood *et al.*⁹. Whereas Attwood reports that fluorobenzophenones are required (because of their higher electrophilicity), Blinne and Cordes in a BASF patent claim that the condensation of sodium bis-

phenolates with chlorobenzophenones occurs in the absence of solvents¹⁰. However, the procedure has not been described in detail and the high molecular weights postulated in this patent are speculative interpretations of viscosity data. In a recent paper we have demonstrated¹¹, that polycondensations of silylated bisphenols with 4,4'-difluorodiphenyl sulphone may yield high molecular weight poly(ether sulphone)s. This procedure has the advantage that the molten polymer does not need purification from solvents or metal salts prior to processing. The purpose of the work presented here was to investigate the synthesis of poly(ether ketone)s from silylated bisphenols.

EXPERIMENTAL

Monomers

Pure 4,4'-difluorobenzophenone (m.p. 104°–106°C) was kindly donated by ICI. It was used without further purification. All bisphenols were donated by Bayer AG. The latter samples had been silylated using chromotrimethylsilane and triethylamine in boiling toluene. The precipitated triethylaminehydrochloride was removed by filtration, and the residual traces removed by refluxing the concentrated solutions of the silylated bisphenols in toluene until all the triethylamine hydrochloride had sublimed in the condenser. The silylated bisphenols were later isolated by distillation *in vacuo*. The absence of chloride ions was checked by means of AgNO₃.

Polycondensations

A silylated bisphenol (0.1 mol), 4,4'-difluorobenzophenone (0.1 mol) and caesium fluoride (~100 mg) were heated in a 250 ml three necked flask with stirring under a slow stream of nitrogen. The temperature at which a moderate and steady evolution of fluorotrimethylsilane occurred (230°–270°C) was maintained for ~30 min. When the reaction temperature was raised to 320° or 350°C a viscous foam was formed (see Table 1). After cooling the polymer was dissolved in ~600 ml methylene chloride depending on solubility. The solution was filtered, and the filtrate precipitated into 4.0l of ethanol. The polymers were dried at 80°C/12 mm. For elemental analyses small samples were dried at 185°C/12 mm.

Measurements

The viscosities were measured using Ostwaldt viscosimeters thermostatically controlled at 25°C. Solutions of 1% (w/v) were measured after filtration through a glass frit. The measurements were repeated with freshly prepared and filtered solutions to test the reproducibility.

The vapour pressure osmometry measurements were conducted in chloroform with a Perkin Elmer Md. 115. The individual measurements were repeated to test their reproducibility.

The differential scanning calorimetry (d.s.c.) curves were obtained on a 'Du Pont 990 Thermal Analyzer' at a heating rate of 20 K/min. In all cases the first heating was followed by rapid cooling (quenching of the sample, then by a second heating annealing above T_g (~30 min) and finally by a third heating.

The thermogravimetric analyses were measured at a heating rate of 8 K/min in air. These measurements were conducted by Bayer Werke (4150 Krefeld-Urdingen) on a Perkin Elmer TGS-2.

The gel permeation chromatography (g.p.c.) measurements were conducted with a Waters GPC-200 using Styragel columns with dry tetrahydrofuran as solvent

(and fractionated polystyrene samples (Waters Co) for calibrations).

The ^{13}C n.m.r. spectrum in Figure 1 was measured with a Bruker WP-80 FT-spectrometer at 28°C in a 10 mm (outer diameter) sample tube. The poly(ester-ether-ketone) XIV (300 mg) was dissolved in deuterated chloroform (2 ml) containing TMS for shift referencing. The following acquisition parameters were used: pulse width 5 μs (~35°); 16 K data points/5000 H spectral width; 2.4 s relaxation delay; experimental line broadening 1.0 Mz; ~12 000 transients.

RESULTS AND DISCUSSION

Synthesis

When the syntheses of poly(ether sulphone)s from silylated bisphenols were investigated, it was found that

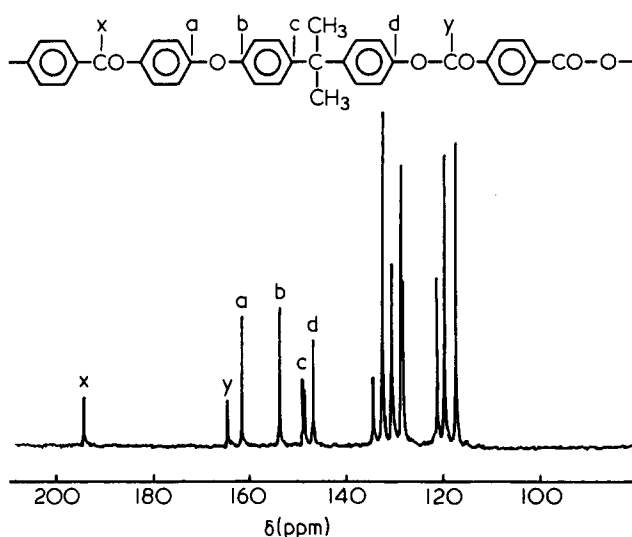


Figure 1 20, 15 MHz ^{13}C n.m.r. spectrum of poly(ester-ether-ketone) XV dissolved in CDCl_3

Table 1 Reaction conditions and results of bulk condensations 4,4'-difluorobenzophenone with various silylated diphenols

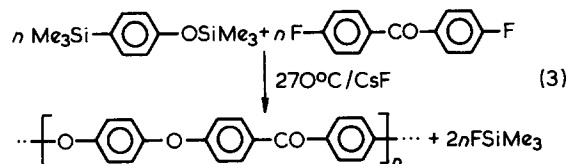
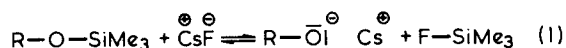
No.	Bis-trimethylsilyl derivative of	Temperature (°C)	Time (h)	Yield ^a (%)	Element. formula (mol. weight)	Elemental analysis		
						Calcd.	Found ^a	
1	Bisphenol-A	220	0.5	96.5 ^a	$\text{C}_{28}\text{H}_{22}\text{O}_3$ (406.48)	Calcd.	82.73	5.45
		270	4.0			Found ^a	82.76	5.35
2	Bisphenol-A	230	0.5	98.0 ^a	$\text{C}_{28}\text{H}_{22}\text{O}_3$ (406.48)	Calcd.	82.73	5.45
		320	1.5			Found ^a	82.41	5.48
3	3,3',5,5'-tetramethyl bisphenol-A	250	0.5	82.5 ^a	$\text{C}_{32}\text{H}_{30}\text{O}_3$ (462.59)	Calcd.	83.09	6.54
		320	1.5			Found ^a	82.33	6.42
4	1,1-Bis(4-hydroxyphenyl)cyclohexane	230	0.5	97.0 ^a	$\text{C}_{30}\text{H}_{26}\text{O}_3$ (434.54)	Calcd.	82.92	6.03
		320	1.0			Found ^a	83.05	6.08
5	4,4'-Dihydroxydiphenylsulphide	250	1.0	97.0 ^b	—	Calcd.	—	—
		320	0.5			Found.	—	—
6	4,4'-Dihydroxydiphenylsulphone	300	1.0	91.0 ^a	$\text{C}_{25}\text{H}_{16}\text{SO}_5$ (428.47)	Calcd.	70.08	3.76
		320	0.5			Found	69.60	3.50
7	4,4'-Dihydroxydiphenylsulphone	300	0.5	96.0 ^a	$\text{C}_{25}\text{H}_{16}\text{SO}_5$ (428.47)	Calcd.	70.08	3.76
		340	5.0			Found	69.28	3.55
8	2,7-Dihydroxynaphthalene	270	0.5	95.0 ^b	$\text{C}_{23}\text{H}_{14}\text{O}_3$ (338.36)	Calcd.	81.64	4.17
		350	1.0			Found ^a	80.95	4.34
9	Hydroquinone	270	0.5	95.0 ^b	$\text{C}_{19}\text{H}_{12}\text{O}_3$ (288.31)	Calcd.	79.15	4.19
		350	1.0			Found ^b	78.08	4.03
10	4,4'-Dihydroxydiphenyl	270	0.5	97.0 ^b	$\text{C}_{25}\text{H}_{16}\text{O}_3$ (364.40)	Calcd.	82.40	4.42
		350	1.0			Found ^b	81.19	4.23

^a after reprecipitation from methylenechloride/ethanol

^b after washing with hot ethanol

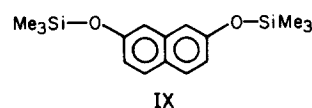
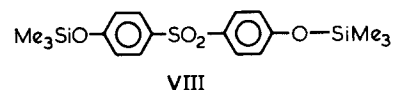
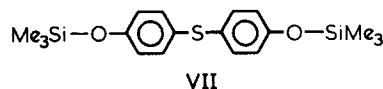
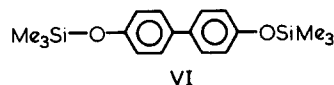
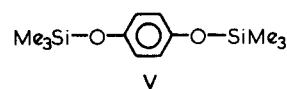
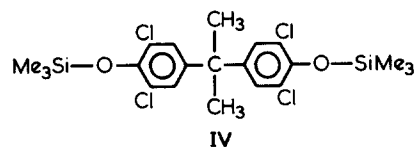
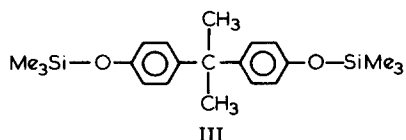
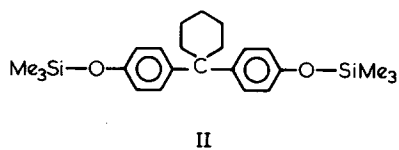
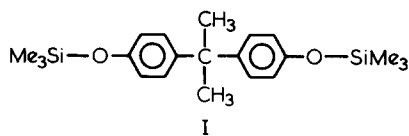
^c after recrystallization from boiling 1-chloronaphthalene

the starting materials are inert up to temperatures above 350°C unless a suitable catalyst was added. Caesium fluoride was found to be the most effective catalyst and the reaction mechanism of equation (1) and (2) was formulated:



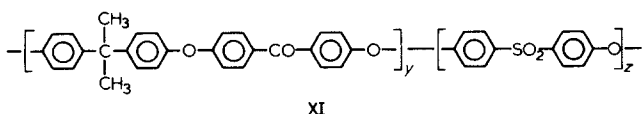
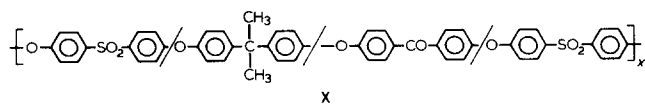
Since 4,4'-difluorobenzophenone is less reactive than 4,4'-difluorodiphenylsulphone, caesium fluoride was also required for all synthesis of poly(ether ketone)s. Its quantity must be of the order of 0.1 wt% relative to the sum of both monomers. The effectiveness of the catalyst depends on the formation of dissolved fluoride ions, which according to equation (1) cleave the Si-O bond of the silylated bisphenols. Fluoride ions are the most effective catalytic species for this purpose. This is because they are highly nucleophilic (unless solvated by hydrogen bonds), and because the Si-F bond is more stable than any other silicon bond. Thus, all anions which form insoluble caesium salts must be absent from the reaction mixture. For this reason the silylation of the bisphenols must be conducted in a way which avoids their contamination with chloride ions. This aspect is important because amine hydrochlorides, which result from silylation with chlorotrimethylsilane and tertiary amines, are volatile *in vacuo* and contaminate the silylated bisphenols even after distillation.

It was found that the initial reaction temperature of the syntheses of poly(ether sulphone)s depends on the nucleophilicity of the bisphenol and its anion. The lowest reaction temperature, i.e. 220°–230°C, was observed for condensations of bisphenols I and II. Only slightly higher temperatures (~250°C) were necessary for hydroquinone (V), 4,4'-dihydroxydiphenyl (VI) and 2,7-dihydroxynaphthalene (IX). A similar reactivity was observed for the 4,4'-dihydroxydiphenylsulphide (VII) whereas the less nucleophilic 4,4'-dihydroxydiphenylsulphone required reaction temperatures around 300°C. The order of



reactivities of the above discussed bisphenols depends mainly on the electron density of the phenolate group, but the lower reactivity of the tetramethyl bisphenol A (III) is due, of course, to a steric origin. In this case not only a higher initial reaction temperature (compared with I) was observed, but also a lower yield and molecular weight (No. 3, Table 1). A low conversion and formation of a small quantity of a precipitate was observed in the case of the tetrachlorobisphenol A (IV). The precipitate contained caesium and chloride ions, suggesting that the caesium fluoride had reacted with the chlorine substituents of the bisphenol. Whether this substitution is the result of direct nucleophilic attack or of an arene mechanism is a question that cannot at present be answered. The non-crystalline poly(ether ketone)s were dissolved in methylenechloride and precipitated from ethanol. The thorough solubility in methylenechloride proved the absence of crosslinking. The crystalline poly(ether ketone)s were dissolved in conc. sulphuric acid and filtered through a glass frit. Whereas the polymers obtained from the monomers V, VI and IX were thoroughly soluble, a substantial fraction of gel-like, insoluble particles was found in the case of the poly(ether sulphide) (prepared from VII). Since sulphide groups are considerably more nucleophilic than ethers and considering the high reaction temperature the crosslinking probably results from arylation of sulphide groups.

Finally, it is important to note that 'silyl method' has the advantage to allow the preparation of various copolymers. We attempted the syntheses of a random and a blockcopoly(ether) of identical monomer composition (formulas X and XI). The random copolymer was pre-

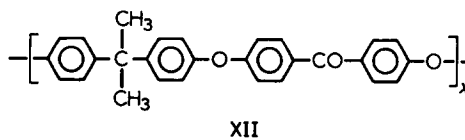


Preparation of poly(ether ketone)s: H. R. Kricheldorf and G. Bier

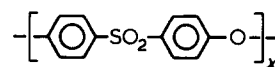
pared by the condensation of an equimolar mixture of the silylated bisphenols I; VIII; 4,4'-difluorobenzophenone and 4,4'-difluorodiphenyl sulphone. When the condensation was conducted at 270°C (0.5 h) and at 320°C (1.5 h), an amorphous copoly(ether ketone sulphone) which was entirely soluble in chloroform was obtained with a yield of 98%. The synthesis of the block copoly(ether) was carried out by first condensing silylated bisphenol-A and 4,4'-difluorobenzophenone at 230°C (0.5 h) and 300°C (0.5 h) until the evolution of fluorotrimethylsilane had nearly ceased. Then an equimolar mixture of silylated 4,4'-dihydroxydiphenyl sulphone and 4,4'-difluorodiphenyl sulphone, was added and a homogeneous melt prepared by stirring at 270°C. This was finally condensed at 340°C. An amorphous material soluble in chloroform was obtained with a yield of 96%. The d.s.c. curves of both copolyethers are discussed later.

A poly(ester-ether-ketone) containing terephthalate groups was obtained, by a similar stepwise cocondensation. Initially, 4,4'-difluorobenzophenone was condensed at 230°C–300°C with a well defined excess of silylated bisphenol-A (I). After the evolution of fluorotrimethyl silane had ceased the resulting oligo ethers (formula XIV, DP = 3) were condensed with terephthaloyl chloride at 250°–300°C in the presence of a catalytical amount of triethylamine hydrochloride. The poly(ester-ether-ketone) XV was obtained with a yield of 97% as an amorphous material. The solubility of XV in chloroform enabled the measurement of both the molecular weight (Table 2) and a ¹³C n.m.r. spectrum (Figure 1). In order to prove the presence of ester groups in copolymer XV an i.r.-spectrum was measured in potassium bromide and compared with that of a pure poly(ether ketone).

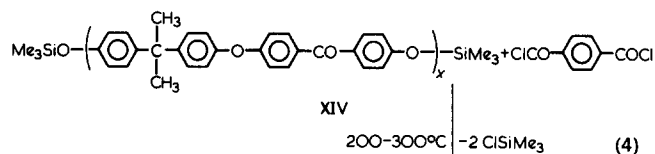
This spectrum shows the C=O stretch vibration of the ester group at 1740 cm⁻¹ which is clearly separated from the corresponding band of the keto group at 1650 cm⁻¹. Clear evidence for complete esterification of the terephthalyl units was also obtained from the ¹³C n.m.r. spectrum (Figure 1), because the carbon of the ester group absorbs 30 ppm upfield of the keto group. Free carboxyl groups which might have resulted from the hydrolysis of



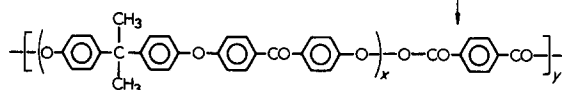
XII



XIII



XIV



XV

unreacted acid chloride groups were not detectable; although their chemical shifts differ by several ppm from those of ester groups¹². The present synthetic method, i.e. the esterification of silylated oligo ethers (equation (4)), is also applicable to the preparation of other poly(ester ether)s, such as poly(ester ether sulphone)s, because the condensation of silylated phenol groups with acid chlorides is very versatile¹³⁻¹⁶. Another route of synthesis of poly(ester ether sulphone)s, namely the polycondensation of silylated hydroxybenzoic acids with fluorobenzosulphones was previously described^{9,17}. However, this method is not useful for syntheses of poly(ester ether ketone)s because the reaction of silyl ester groups with fluorobenzophenones is too sluggish. A more detailed study of the syntheses and properties of various poly(ester ether)s will be published in a later part of this series of papers.

Characterization of the poly(ether ketone)s

With exception of the crosslinked polymer prepared from VII, the homopolymers listed in Table 1 and the

Table 2 Properties of some poly(ether ketone)s prepared from 4,4'-difluorobenzophenone and silylated diphenols

No. ^a	Diphenol	η_{rel}^b	η_{rel}^c	η_{spec}/c^c (cm ³ g ⁻¹)	\bar{M}_n^d	\bar{M}_w^e	T_g (°C) ^f	T_m (°C) ^f
1	Bisphenol-A	1.11	3.26	113	11.500	60 000	151–153	—
2	Bisphenol-A	1.10	3.03	101	10.000	45 000	152–154	—
3	3,3',5,5'-Tetramethylbisphenol-A	1.06	1.52	13	1.700	3 200	143–145	—
4	1,1-Bis(4-hydroxyphenyl)cyclohexane	1.09	2.95	96	9.000	40 000	173–175	—
6	4,4'-Dihydroxydiphenyl sulphone	1.21	1.52	25	3.600	8 300	168–170	—
7	4,4'-Dihydroxydiphenyl sulphone	1.46	2.40	70	7.000	insol.	184–186	—
8	2,7-Dihydroxynaphthalene	—	insol.	—	insol.	insol.	152–154 ^g	241–243 ^g
9	Hydroquinone	2.21	insol.	—	insol.	insol.	—	343–345 ^g
10	4,4'-Dihydroxydiphenyl	1.85	insol.	—	insol.	insol.	—	420–422 ^g
11	Random poly(ether-ketone sulphone) (X)	1.10	1.54	26	4.700	12 000	143–145	—
12	Blocky poly(ether-ketone-sulphone) (XI)	1.08	insol.	—	insol.	insol.	146–148 + 206–208	—
13	Poly(ester ketone) (XV)	1.08	2.35	65	6.800	32 000	153–155	—

^a These numbers correspond to those of Table 1

^b Measured with c = 1% (w/v) in conc. H₂SO₄ at 25°C

^c Measured with c = 2% (w/v) in 1,1,2,2-tetrachloroethane at 30°C

^d Vapour pressure osmometry in chloroform

^e G.p.c. in tetrahydrofuran, calibrated with polystyrene

^f D.s.c. measurements, heating rate 20 K/min

^g Crude reaction products

copolymers X and XI were characterized with respect to their molecular weights, crystallinity and thermal stability. Because absolute molecular weights have not yet been reported in literature, we have attempted to determine the number molecular weights (\bar{M}_n) of the non-crystalline polymers by means of vapour pressure osmometry. The data obtained by this method (Table 2) indicate that in most cases molecular weights were achieved which were sufficient for the preparation of films and for other technical applications. Furthermore, it is confirmed that only oligomers were formed with tetramethyl bisphenol-A due to the steric hindrance of two substituents in *ortho* positions (with respect to the siloxy group). They also confirm, that condensations of the less nucleophilic 4,4'-dihydroxydiphenyl sulphone (VIII) require reaction temperatures up to 340°C to produce satisfactory molecular weights.

In order to compare the \bar{M}_n 's of the amorphous poly(ether ketone)s with the crystalline compounds the relative viscosities of most samples were measured in concentrated sulphuric acid at a concentration of 1% weight per volume. These conditions were chosen to allow a comparison with the viscosity data of Attwood⁹. Interestingly the poly(ether ketone)s prepared from silylated hydroquinone (V) and 4,4'-dihydroxydiphenyl (VI) yield relatively high viscosities (although they began to crystallize at an early stage of the polycondensation). In contrast to the \bar{M}_n values; low viscosities were found for the amorphous poly(ether ketone)s. Repetition of the viscosity measurements themselves were conducted correctly. In order to decide which method gave the more reliable information in this case, viscosities of the amorphous poly(ether ketone)s were measured in 1,1,2,2-tetrachloroethane (Table 2). This second series of viscosity data not only confirmed that most of the amorphous poly(ether ketone)s possessed high molecular weights, but they also parallel the differences between the \bar{M}_n 's of the individual samples. This is in contrast to the relative viscosities found in sulphuric acid. Furthermore, viscosities measured in methylene chloride (not listed in Table 2) confirm the data obtained with tetrachloroethane. Finally, the samples which were soluble in tetrahydrofuran were subjected to gel permeation chromatography (g.p.c.). The weight average molecular weights (\bar{M}_w) obtained after calibration with polystyrene (Table 2) confirm that the poly(ether ketone)s prepared from the silylated bisphenols I and II possess fairly high molecular weights. When the \bar{M}_w values obtained by g.p.c. are compared with the \bar{M}_n values obtained from vapour phase osmometry (v.p.o.) measurements, two corrections must be taken into account. First, the most probable molecular weight distribution (*MWD*) required (for normal polycondensations) an \bar{M}_w/\bar{M}_n ratio of 2. Secondly, the relatively stiff chains of the aromatic poly(ether ketone)s effect a higher hydrodynamic volume than polystyrene; so that calibration with the latter 'M_w-standard' yields \bar{M}_w values which are too high.

Differential scanning calorimetry (d.s.c.) studies confirmed the results from the solubility studies. These results suggested the existence of two classes of poly(ether ketone)s; 'amorphous' and 'crystalline' poly(ether ketone)s. The labelling 'amorphous' and 'crystalline' is only justified because, the latter class crystallizes rapidly under the conditions of their synthesis regardless which condensation procedure⁹ is used. The former class, however, is difficult to crystallize and it was not possible

to prepare crystalline samples. On the basis of our results and those of Attwood⁹ we can conclude that the 'amorphous class' of poly(ether ketone)s is characterized by bisphenols which possess an *sp*³ hybridized atom between both phenol groups. This two-class system was not obvious from literature data because Glendinning *et al.* reported a melting point of 248°C from the poly(ether ketone) of bisphenol-A. The poly(ether ketone) of 4,4'-dihydroxy diphenyl sulphone was the only amorphous polymer described by Attwood *et al.*⁹

The glass transitions (T_g 's) of the 'amorphous' polymers show the expected dependence on the \bar{M}_n . The low molecular weight poly(ether ketone sulphone) No. 6 (Table 1), possesses a $T_g \sim 15$ degrees below that of sample No. 7 (Table 1). Furthermore, the poly(ether ketone) of tetramethyl bisphenol-A is expected to possess a less mobile chain than that of bisphenol-A; yet, the T_g of the oligomers is 10°C below that of the high molecular weight bisphenol-A poly(ether ketone). It is also reasonable that the polymer of the cyclohexane derivative II shows a higher T_g than the polymer of I, whereas the highest T_g is found for the poly(ether ketone) prepared from the sulphone VIII. A comparison of the random copolymer X, block copolymer XI and a blend of the corresponding homopolymers (e.g. XII) was of particular interest. As expected for a random sequence, only one T_g was found for X (Figure 2(C)) and this T_g is slightly lower than the lowest T_g of the block copolymer XI. The two T_g 's of copolymer XI (Figure 2(B)) demonstrate that this copolymer does not possess a random sequence. This indicates that the fluoride ions did not cause transesterification reactions during the course of the polycondensation. Furthermore, both T_g 's appear at slightly lower temperatures than the T_g 's of the corresponding homopolyethers (Figure 2(A)). This suggests that a blockcopolymer and not a blend of homopolymer was formed.

Since Clendinning *et al.*⁸ reported a melting point for the poly(ether ketone) of bisphenol-A (248°C) it was attempted to crystallize this polymer and all other 'amorphous' poly(ether ketone)s by annealing them at 30° or 60°C above their T_g 's. However, we were not able to detect an endotherm in the d.s.c. curves. A similar behaviour is known from corresponding polycarbonates and from poly(*m*-hydroxybenzoate)¹⁵. Yet in the latter case rapid crystallization may occur when the polyester is brought in contact with various solvents or nonsolvents.

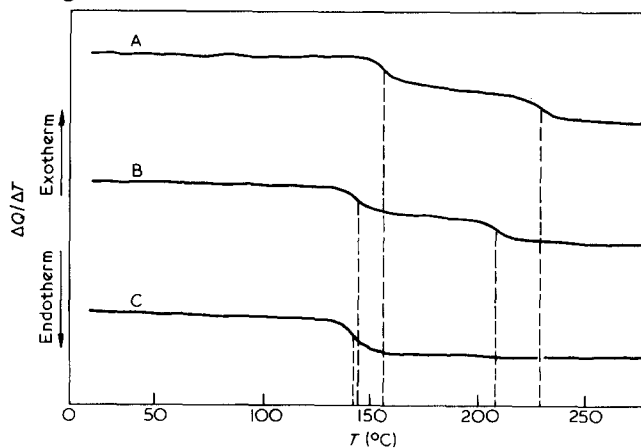


Figure 2 Differential scanning calorimetry measurements (heating rate 20 K/min) of: (A) blend of poly(ether sulphone) XIII and poly(ether ketone) of bisphenol-A; XII; (B) block-copoly(ether-ketone-sulfone) XI; (C) copoly(ether-ketone-sulphone) X

For this reason we dissolved the poly(ether ketone) of bisphenol-A in chloroform and added ~20 vol. % of other (non)solvents such as pyridine, toluene, *N,N*-dimethylamine, dimethylsulphoxide, dimethylformamide, *n*-butanol etc. However, over the course of 8 days crystallization was not observed, and this observation led us to label these poly(ether ketone)s as 'amorphous' materials.

The most interesting case of the crystalline polymers is the poly(ether ketone) prepared from 2,7-dihydroxynaphthalene IX. The molecular dimensions of this polymer do not fit into the characteristic crystal lattice described by Attwood *et al.*^{9,18} for various other poly(ether ketone)s. It possessed the lowest melting point ($T_m = 241^\circ\text{--}243^\circ\text{C}$) of poly(ether ketone)s described so far, and thus, we were able to dissolve it in boiling 1-chloronaphthalene (b.p. $\sim 260^\circ\text{C}$). However, it crystallized from this solution so rapidly that we were not able to filter the hot solution at temperatures below 240°C . The degree of crystallinity of the crude product was so high, that a glass transition was not detectable (Figure 3(A)). However, by cooling with liquid nitrogen we were able to quench the crystallization, so that a T_g but not a T_m was detected (Figure 3(B)). After annealing at 200°C (30 min) the d.s.c. displayed a melting endotherm, whereas the glass transition had disappeared (Figure 3(C)). These observations confirm that the low segmental mobility and the high melt viscosity of the poly(ether ketone)s are not a principal hindrance of rapid crystallization. This finding suggests in turn, that the lack of crystallization of the amorphous poly(ether ketone)s must have another origin. This may be unfavourable conformations or a T_m only a few degrees above T_g .

Finally, we have studied the thermal stability of various samples under conditions that allow a comparison with the poly(ether sulphone)s¹¹ and poly(hydroxybenzoate)s^{15,16} described previously. The data in Table 3 show for the poly(ether ketone)s prepared from the sulphone VIII that the thermal stability strongly depends on the molecular weight for \bar{M}_n 's < 5000 . The low molecular weight is also the reason why the poly(ether ketone) of tetramethylbisphenol-A (III) displays the lowest thermal stability of all our samples. Of course, an increasing number of aliphatic substituents also decreases the stability in air above 300°C and for this reason the

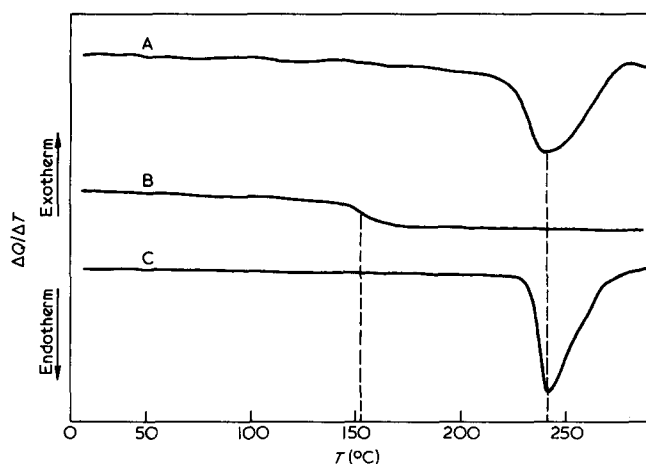


Figure 3 Differential scanning calorimetry measurements (heating rate 20 K/min) of: (A) crude poly(ether-ketone) prepared from silylated 2,7-dihydroxynaphthalene IX; (B) the same sample after quenching with liquid air; (C) the quenched sample after annealing at 200°C for 15 min

Table 3 Thermogravimetric analyses^a of some poly(ether-ketone)s prepared from 4,4'-difluorobenzophenone and silylated bisphenols

Silylated bisphenol used as monomer	loss of weight at the following temperatures			
	1%	5%	10%	20%
3,3'-5,5'-Tetramethylbisphenol-A	308	391	422	448
	312	393	425	447
Bisphenol-A	394	483	505	522
	396	486	508	520
1,1-Bis(4-hydroxyphenyl)cyclohexane	377	479	496	512
	374	475	492	509
4,4'-Dihydroxydiphenyl-sulphone (No. 6, Table 1)	300	433	484	530
	304	438	488	534
4,4'-Dihydroxydiphenyl sulphone (No. 7, Table 1)	411	482	517	551
	414	485	520	552
Hydroquinone	400	519	540	556
	406	525	544	556

^a Heating rate 8 K/min in air

polymers prepared from the cyclohexane derivative II possess a lower thermal stability than analogous polymers derived from bisphenol-A (I). The two poly(ether ketone)s with the highest stabilities are comparable with the best samples of poly(4-hydroxybenzoate)¹⁶, this is because they are only slightly less stable than poly(ether sulphone) XII which showed 1% degradation at 430°C when measured under identical conditions. Thus, from the view-point of short-term thermal stability poly(ether ketone)s are not inferior to poly(ether sulphone)s; yet due to the keto group their long-term stability against a combination of u.v.-light, oxygen and heat should be lower.

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