Nucleophilic cleavage of activated aryl ethers by a fluoride anion

V. Carlier*, B. Jambe, J. Devaux and R. Legras
Unité de Physique et de Chimie des Hauts Polymères, Université Catholique de Louvain, 1 Croix du Sud, 1348 Louvain-La-Neuve, Belgium

and P. T. McGrail
ICI Wilton Materials Research Centre, PO Box 90, Wilton, Middlesbrough TS6 8JE, UK

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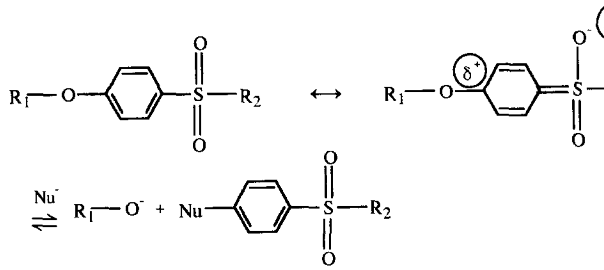
The nucleophilic cleavage of differently activated aryl ethers by a fluoride anion is studied. Two sulphone groups in *para* positions to the ether link appear to activate this sufficiently to allow its nucleophilic substitution by F^- to occur from 280°C upwards. No reaction is observed up to 300°C when two ketone links are *para* to the ether, whilst the reaction occurs from 300°C upwards in the case of a mixed sulphone–ketone activation.

(Keywords: nucleophilic cleavage; cleavage by fluoride anion; transetherification; poly(aryl ether ketones); poly(aryl ether sulphones))

INTRODUCTION

Because of their very low reactivity, ethers are often used as inert solvents in organic reactions. However, in severe conditions, when the ether link is electron-deficient as a result of a mesomeric effect, nucleophilic cleavage can be observed. For instance, the following reaction can be written for an aryl ether sulphone:



(1)

Among the nucleophiles able to induce this reaction are the phenates; such reactions lead to a so-called transetherification. With polymers such as poly(ether ether ketone) (PEEK)[1] and poly(ether sulphone) (PES)[2], the following reactions have been observed:

$$\sim\phi CO\phi O\phi O\phi CO\sim + {}^{-}OAr \longrightarrow \sim\phi CO\phi O\text{–}Ar + {}^{-}O\phi O\phi CO\sim \qquad (2)$$

$$\phi SO_2\phi O\phi SO_2\sim + {}^{-}OAr \longrightarrow \sim\phi SO_2\phi O\text{–}Ar + {}^{-}O\phi SO_2\sim \qquad (3)$$

The hydroxide anion[3–8] and the fluoride anion[2] have also been reported to cleave activated ether links:

$$\sim\phi O\phi\sim + OH^- \xrightarrow{300^\circ C} \sim\phi OH + \sim\phi O^- \qquad (4)$$

$$\sim\phi SO_2\phi O\phi\sim + F^- \longrightarrow \sim\phi SO_2\phi F + \sim\phi O^- \qquad (5)$$

Whilst reaction (4) above was only reported at high temperatures (above 300°C), reaction (5) was shown to occur in PES in sulpholane solution at 200°C[2]. This reaction of fluoride anion is mentioned in a Union Carbide patent[9] on a PEEK.

Finally, an analogous reaction has also been exploited by Kricheldorf[10] to form phenates in the presence of CsF:

$$\sim\phi OSi(Me)_3 + F^- \longrightarrow \sim\phi O^- + FSi(Me)_3 \qquad (6)$$

In this paper, a specific study of the nucleophilic reactivity of F^- is reported, which was undertaken in order to assist with the understanding of polyether syntheses involving fluorinated species[11,12].

This cleavage mechanism was studied on sulphone–sulphone (–S–S–), ketone–sulphone (–B–S–) and ketone–ketone (–B–B–) activated aryl ethers in order to follow the reaction of ether links in poly(ether sulphone) (PES) poly(aryl ether ketone-*co*-sulphone) and poly(ether ketone) (PEK). The structures of these links are given in *Table 1*, in order of their expected reactivity.

Table 1 Links studied

Ether links	Abbreviation
$-\phi CO\phi\text{–}O\text{–}\phi CO\phi-$	–B–B–
$-\phi SO_2\phi\text{–}O\text{–}\phi CO\phi-$	–S–B–
$-\phi SO_2\phi\text{–}O\text{–}\phi SO_2\phi-$	–S–S–

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* To whom correspondence should be addressed

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First, the cleavage reaction was studied directly on PES and PEK polymers by ^{19}F n.m.r. and g.p.c.; secondly, nucleophilic cleavage was studied on model compounds by ^{19}F n.m.r. only.

EXPERIMENTAL

Starting materials

Samples of PES and PEK polymers and diphenylsulphone (DPS), which was used as a reaction solvent, were kindly provided by ICI plc. Dimethylsulphoxide (DMSO) (Janssen product) was redistilled over CaH_2 under vacuum. Toluene (Merck p.a.) was used without further purification. Potassium carbonate and sodium carbonate (UCB p.a.) were finely ground and then vacuum dried at 120°C before use. Potassium fluoride (Janssen product, 99%) was used as received. 4-Hydroxybenzophenone, 4-fluorobenzophenone and 4-chlorophenylsulphone (Aldrich products) were used as received. Sodium hydroxide and potassium hydroxide were commercial products (Merck p.a.).

Model compound syntheses

$\phi CO\phi O\phi CO\phi$. In a three-necked round-bottomed 500 ml flask, fitted with a temperature probe, a Dean and Stark attachment and an argon inlet, 180 ml DMSO and 30 ml toluene were heated to 115°C. 4-Hydroxybenzophenone (11.5 g), 4-fluorobenzophenone (10.66 g) (stoichiometric ratio) and K_2CO_3 (1.4 M excess) were then introduced. After the azeotropic elimination of water by toluene distillation, the temperature was raised to 160°C and held at this level for 16 h. After cooling, the mixture was poured into a 10^{-2} M NaOH aqueous solution. The solid precipitate was filtered off, washed with MeOH and recrystallized from absolute ethanol. The chemical structure was assessed by ^{13}C n.m.r. Yield, 78%; melting temperature, 163–164°C.

$\phi CO\phi O\phi SO_2\phi$. To synthesize this model compound, a similar procedure to that described above was adopted, but 4-chlorophenylsulphone (12.62 g) and 4-hydroxyphenylsulphone (10.89 g) in stoichiometric ratio, and Na_2CO_3 (7.632 g) in 1.4 M excess, were used as the reactants. The reaction was carried out at 160°C for 7 h. Yield, 40%; melting temperature, 177–178°C.

$\phi SO_2\phi O\phi SO_2\phi$. As one of the starting materials, $\phi SO_2\phi OH$ was required; in order to obtain this, $\phi SO_2\phi Cl$ (85.9 g) (recrystallized from ethanol) and KOH (62.7 g) were first dissolved in a mixture of 394 ml DMSO and H_2O (98 ml), then refluxed for 4 h. The solution was poured into 1 litre of 0.01 M aqueous HCl, then extracted with ether. The organic phase was separated and dried over anhydrous Na_2SO_4. The solvent was evaporated, yielding $\phi SO_2\phi OH$.

$\phi SO_2\phi OH$ (10.5 g) and KOH (3.95 g) were dissolved in 150 ml EtOH; on evaporating the solvent, $\phi SO_2\phi OK$ (17.78 g) (pale yellow) was recovered. This phenate was dissolved in 30 ml DMSO together with $\phi SO_2\phi Cl$ (17.10 g) and then refluxed with stirring for 3 h. After completion of the reaction, the mixture was poured into 250 ml water and the solid precipitate filtered off. A first purification step involved its dissolution in 100 ml acetone and reprecipitation in 500 ml water. After filtration, the product was finally recrystallized from ethanol. The chemical nature of the product was assessed by ^{13}C n.m.r. Its melting temperature was 175°C.

Nucleophilic substitutions by F^-

Polymers. PES or PEK (10 g) was mixed with potassium fluoride in a small amount of methanol. This 'slurry' was then dried at 140°C under vacuum for a few hours. In a three-necked round-bottomed 150 ml flask, fitted with a temperature probe, an argon inlet and a glass mechanical stirrer, DPS (75 g) was heated to the desired temperature. The polymer/potassium fluoride mixture was then introduced to the heated DPS with stirring. Sampling was performed with the help of disposable 10 mm diameter PTFE tubes. These filled tubes were immersed in methanol. The recovered solid phase was crushed, refluxed in methanol, then filtered. The powder was vacuum dried at 140°C for several hours.

Model compounds. DPS (20 g) was heated to the desired temperature in a three-necked round-bottomed 150 ml flask fitted with an argon inlet, a temperature probe, a condenser and magnetic stirrer. Model compound (1 g) and potassium fluoride (0.1 g) were then introduced. Sampling was performed with small glass tubes. The samples (DPS, polymer, potassium fluoride) were cooled in air and ground up before further analysis.

Analysis techniques

^{19}F nuclear magnetic resonance. ^{19}F n.m.r. spectra were obtained on a Bruker WM250 spectrometer operating at 235.24 MHz for ^{19}F. The polymers were dissolved in conc. sulphuric acid (99%) at 3% w/w for PEK and 6% w/w for PES. Sodium trifluoroacetate was used as internal standard. The spectral width was 2000 Hz and pulse 13 μs (90°). The procedure used was similar to the one previously published[13].

For the model compounds, $CDCl_3$ and $CF_3CO\phi$ (0.2% w/w) were used as solvent and internal standard respectively. Concentration of the model compound was adjusted to ca. 0.6% w/v.

Gel permeation chromatography. G.p.c. analyses of PES samples were performed on a g.p.c. chromatograph made from two Shodex AD/80 MS columns, a Waters m 6000 pump, and a Perkin–Elmer LC55 UV detector. The automatic injector was a Gilson model 251. Data handling was performed on a Trivector computer. The solvent was *N*-methylpyrrolidone (NMP) containing 0.1 M LiCl. Molecular-weight values were calibrated for PES[14].

G.p.c. analyses of PEK samples were attempted following a procedure previously published for PEEK[15]. As the samples were not fully soluble in the 50/50 phenol/1,2,4-trichlorobenzene solvent, results may only be used in a qualitative way.

RESULTS AND DISCUSSION

Polymers

Poly(ether sulphone). PES samples were analysed by ^{19}F n.m.r. after increasing periods of time in DPS in the presence of potassium fluoride at high temperatures (250, 280 and 320°C). The level of fluorine introduction resulting from reaction (5) was, therefore, easily followed quantitatively.

Fluorine end-groups were detected at a negative chemical shift of 24.2 ppm from CF_3COOH. Since any fluorine end-groups correspond to a chain cleavage (equation (5)), a parallel g.p.c. analysis was undertaken in order to obtain M_n values of PES. The n.m.r. and g.p.c. results may be compared using equation (7):

$$\frac{1}{M_n} - \frac{1}{M_n^\circ} = \frac{[F]}{19 \times 10^6} \qquad (7)$$

where M_n and M_n° are the number-average molecular weights of degraded and original PES, respectively, and [F] is the fluorine concentration in ppm, introduced into the polymer. Using equation (7), data from n.m.r. and g.p.c. can be compared as M_n decreases (*Figures 1* and *2*) for reaction temperatures of 320 and 280°C respectively. A similar experiment at 250°C did not reveal any significant reaction.

Poly(ether ketone). Experiments were undertaken using PEK in a similar way to those reported above for PES. In this case, since fluorine end-groups already exist on the polymer chain, an increase in fluoride content would be expected. Surprisingly, no such increase was revealed by the ^{19}F n.m.r. analyses; in fact, there was a decrease at the highest temperatures. This decrease was not observed with a control experiment containing no potassium fluoride (*Table 2*). Since PEK has poor solubility in the eluting solvent, no conclusive results could be drawn from g.p.c. analysis, except for a possible tendency towards a decrease of the retention times (increase in molecular weight), which is in qualitative agreement with the loss of fluorine observed by ^{19}F n.m.r.

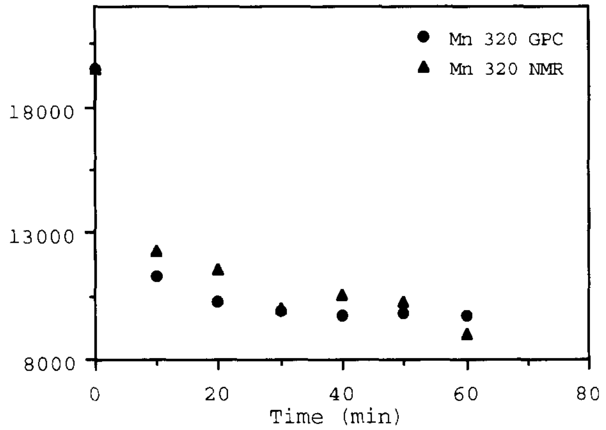

Figure 1 M_n decrease of PES heated with potassium fluoride in DPS at 320°C. Comparison between g.p.c. and n.m.r. results

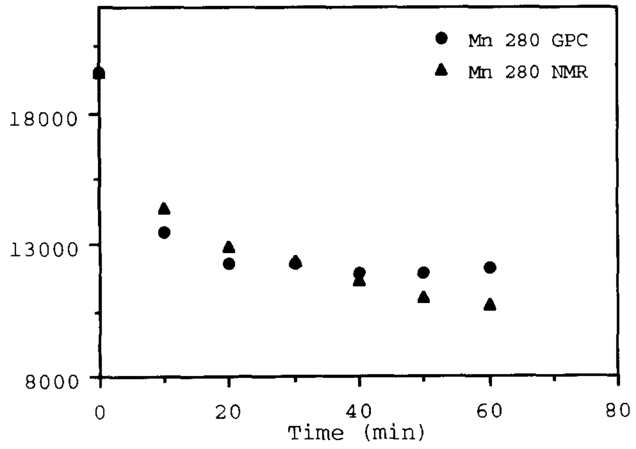

Figure 2 M_n decrease of PES heated with potassium fluoride in DPS at 280°C. Comparison between g.p.c. and n.m.r. results

Table 2 ^{19}F n.m.r. analyses of PEK after reaction with potassium fluoride at different temperatures

Samples	Reaction time (min)	Fluorine content (in ppm) assessed by n.m.r.
Control at 320°C (no potassium fluoride)	30	5920
	60	6092
Potassium fluoride (2%) at 320°C	10	5716
	20	5313
	30	5296
	40	5953
	50	4399
	60	2753
Potassium fluoride (2%) at 300°C	10	5580
	20	5473
	30	4575
	40	5089
	50	4869
	60	5176
Potassium fluoride (2%) at 280°C	10	5476
	30	5460
	60	5248
Sodium carbonate (10%) at 320°C	180	4643

Table 3 Synthesized model compounds

Model compounds		Abbreviation
MC1	$\phi CO\phi O\phi CO\phi$	B–B
MC2	$\phi CO\phi O\phi SO_2\phi$	B–S
MC3	$\phi SO_2\phi O\phi SO_2\phi$	S–S

In fact, a chain lengthening due to the reaction of residual –OH end-groups with fluorinated ends in the presence of potassium fluoride was expected to occur:

$$\text{PEK}\sim\sim\text{CO–}\phi\text{–OH} + \text{F–}\phi\text{–CO–}\phi\text{–O}\sim\sim\text{PEK}$$
$$\xrightarrow[T]{KF} \text{PEK}\sim\sim\text{CO–}\phi\text{–O–}\phi\text{–CO–}\phi\text{–O}\sim\sim\text{PEK} \qquad (8)$$

This chain extension was partially confirmed by similar behaviour of the same sample of PEK in the presence of sodium carbonate (*Table 2*). Therefore, the effectiveness of PEK chain cleavage by potassium fluoride could not be conclusively proved here.

Model compounds

Three model compounds were synthesized in order to represent the differently activated aryl ethers of interest (*Table 3*). The three model compounds of *Table 3* were reacted with potassium fluoride at different temperatures in DPS. No purification procedure was used for the samples, which were analysed as such (DPS + potassium fluoride + model compound) by ^{19}F n.m.r.

Even for the most severe conditions (300°C–60 min) no reaction was observed for the B–B model compound (MC1).

For MC2 and MC3, ^{19}F n.m.r. analyses revealed that significant amounts of fluorine were introduced by the reaction with potassium fluoride (*Tables 4* (B–S) and *5* (S–S)). However, owing to the very small amounts sampled during the high-temperature reactions, these results are affected by a too large experimental error in

Table 4 ^{19}F n.m.r. results of the analyses of MC2 samples after reaction with potassium fluoride in DPS

Reaction temperature (°C)	Reaction time (min)	Chemical shift (ppm)	Fluorine content (in ppm) assessed by n.m.r.
280	30 to 180		–
300	150	32.8	23
		34.5	23
320	120	32.8	10
		34.5	10
	150	32.8	16
		34.5	16

Table 5 ^{19}F n.m.r. results of the analyses of MC3 samples after reaction with potassium fluoride in DPS

Reaction temperature (°C)	Reaction time (min)	Chemical shift (ppm)	Fluorine content (in ppm) assessed by n.m.r.
280	30	32.8	40
	120	32.8	30
	150	32.8	33
	180	32.8	65
320	30	32.8	39
	60	32.8	48
	90	32.8	31
	120	32.8	66
	150	32.8	45

fluorine content assessment (10–20 ppm) to be considered for a kinetic analysis. This error seems to be partly due to some instability of the n.m.r. standard ($CF_3CO\phi$) in the analysis conditions.

Nevertheless, it can be concluded from the results reported in *Tables 4* and *5* that B–S and S–S links can effectively be cleaved by a fluoride anion in DPS. That cleavage significantly occurs from 300°C upwards for B–S and from 280°C upwards for S–S. Therefore, owing to its lower reactivity, the B–B link would be expected to be cleaved at temperatures $>300°C$.

A comparison between the chemical shifts reported in *Tables 4* and *5* leads unambiguously to the attribution of the peak at 32.8 ppm chemical shift from $CF_3CO\phi$ to 4-fluorophenylsulphone and the peak at 34.5 ppm chemical shift to 4-fluorobenzophenone.

Finally, from the results in *Table 4*, it should be noted that cleavage of both kinds (9) and (10) below seem equally probable for the B–S compound (MC2):

$$\phi CO\phi O\phi SO_2\phi + \text{potassium fluoride}$$

$$\leftrightarrows \phi CO\phi OK + F\phi SO_2\phi \qquad (9)$$

$$\leftrightarrows \phi CO\phi F + KO\phi SO_2\phi \qquad (10)$$

This behaviour was unexpected since the more powerful electron-attracting sulphone group should favour reaction (9). It seems that this is not the case here.

CONCLUSIONS

This work was aimed at studying the nucleophilic reactivity of a fluoride anion with ether linkages in DPS solution at high temperatures. The experiments on the nucleophilic substitution of differently activated aryl ether links has led to a better understanding of the experimental conditions under which this reaction can affect the polycondensation of poly(aryl ether ketones) and poly(aryl ether sulphones). It has been shown on both PES and its model compound that the S–S link is significantly cleaved from 280°C upwards whilst, for the PEK model compound, no reaction of the B–B link is observed up to 300°C. Intermediate results were obtained for the B–S link, which was found to be cleaved from 300°C upwards. Moreover, this unsymmetrical aryl ether link appears to undergo cleavage on both sides with equal probability.

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