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Poly(ether ketone)s by Fluoride Catalyst Systems

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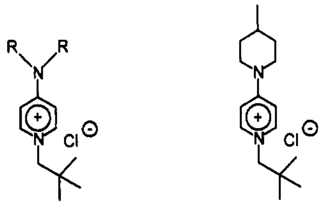
ABSTRACT: Potassium fluoride or a mixture of potassium fluoride and *N*-neopentyl-4-(dialkylamino)-pyridinium chlorides 7, 8, or 9 were used as catalysts to improve poly(ether ketone) syntheses of dichloroaryl monomers such as 1,4-bis(4-chlorobenzoyl)benzene (1) via nucleophilic displacement. Polymers of increased molecular weight within a significantly reduced reaction time can be obtained by this method, as demonstrated with condensations of 2,2-bis(4-hydroxyphenyl)pentane (4) or 2,2-bis(4-hydroxyphenyl)heptane (5) with 1. Furthermore, high molecular weight semicrystalline poly(ether ether ketone)s, commonly known as PEEKK, were synthesized by fluoride anion assisted polycondensation of 1. Under severe conditions, fluoride induced nucleophilic cleavage of the activated ether linkages of the polymers was found.

Introduction

Aromatic poly(aryl ether)s, such as poly(ether ketone)s or poly(ether sulfone)s, are useful as high performance thermoplastics and have been studies extensively.[1] Two types of reactions are currently employed for the perparation of these polymers. These are the electrophilic Friedel–Crafts reaction and the nucleophilic aromatic substitution.[1–12] The nucleophilic substitution reaction is currently the method of choice for the preparation of aromatic poly(ether sulfone)s and poly(ether ketone)s because the resulting polymers are linear well-defined chemical structures and, moreover, side reactions are minimal. The synthesis of semicrystalline poly(ether ketone)s via nucleophilic displacement reaction requires very reactive but expensive fluoroaryl ketone monomers, such as 4,4′-difluorobenzophenone (3) or 1,4-bis(4-fluorobenzoyl)benzene (2). The use of the cheaper dichloroaryl monomers is not feasible due to their low reactivity. Amorphous poly(ether ketone)s could be synthesized under milder reaction conditions by the use of dichloroaryl ketone monomers; but the rate of the reaction is slow and a long reaction time is therefore required.[13] It has been shown that *N*-alkyl-4-(dialkylamino)pyridinium chorides 7, 8, or 9 are efficient phase-transfer catalysts (PTC) in the synthesis of poly(ether ketone)s using 1.[14]

Although decomposition of (dialkylamino)pyridinium salts was demonstrated to occur in the presence of 50% NaOH solutions,[25] these catalysts were shown to be stable even to the basic conditions and the high temperatures encountered in poly(ether ketone) synthesis. The polymer forming nucleophilic displacement reaction of 1 was significantly accelerated due to the improved solubility of the anionic species. Furthermore, chloride/fluoride exchange of activated aromatic chlorides has also been achieved using 7 or, alternatively, 8 or 9,[15,16] implicating the possibility of generating very reactive fluorinated derivates of 1 during the polycondensation in the presence of fluoride and PTC. Since ionic fluorides have proven to be versatile proton abstractors in a variety of typically base-assisted reactions,[17] we expected the fluorides to activate the phenolic monomers by polarizing the OH bonds.

In the present paper the fluoride ion assisted polycondensation of 1,4-bis(4-chlorobenzoyl)benzene (1) to high molecular weight poly(ether ketone)s is reported, which involves the phase-transfer catalyzed chloride/fluoride exchange of 1. The accelerating effects of the catalytic systems and, on the other hand, the polymer degradation induced by excessive fluoride content are discussed.



7 R = n - C_4H_9

8 R = n - C_6H_{13}

9

Figure 1. Stable phase-transfer catalysts based on pyridinium salts.

Experimental Section

General Methods. 1,4-Bis(4-chlorobenzoyl)benzene (1) and 1,4-bis(4-fluorobenzoyl)benzene (2) were gifts from Hoechst AG, Frankfurt/Main, and used without further purification. 1,4-Hydroquinone (6) (Aldrich) was purified by recrystallization from acetone. Tetramethylammonium fluoride (TMAF) and tetra-*n*-butylammonium fluoride (TBAF) were obtained from Aldrich Chemical Co. and used as received. Potassium carbonate and potassium fluoride (Aldrich) were dried by heating at 100 °C under vacuum for 48 h. *N,N*-Dimethylacetamide (DMAc) (Aldrich) and toluene (Aldrich) were distilled over CaH_2 prior to use. Other common solvents were obtained from Aldrich Chemical Co. and used as received. *N*-Neopentyl-4-(dibutylamino)pyridinium chloride (7), *N*-neopentyl-4-(dihexylamino)-pyridinium chloride (8), and *N*-neopentyl-4-(4-methylpiperidinyl)pyridinium chloride (9) were synthesized according to literature procedures.[16]

The ^1H and ^{13}C NMR spectra were recorded on either a Varian Gemini 200 or a Bruker AC-300 instrument. Melting points were taken on a Büchi melting apparatus and are uncorrected. EI mass spectra were obtained from a Varian CH 7 A. Inherent viscosities were measured in a 0.5 g/dL chloroform solution at 25 °C using an Ubbelohde dilution viscometer. Molecular weights were determined on a Spectra Physics GPC instrument relative to polystyrene standards using chloroform as an eluent at a flow rate of 1.0 mL/min; a UV detector was set at 254-nm wavelength. The glass transition temperatures were determined by differential scanning calorimetry (DSC) on either a Mettler TC 10 A or a Mettler TC 11 at a heating rate of 10 °C/min under nitrogen, taken as the midpoint of the change in slope of the baseline.

Monomer Synthesis. The bis(phenol)s 4 and 5 were synthesized according to an improved literature procedure.[24]

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2,2-Bis(4-hydroxyphenyl)pentane (4). A mixture of 50 mmol of 2-pentanone (43.08 g), 2 mol of phenol (188.2 g), and 5 mmol of mercaptoacetic acid (0.46 g) was saturated with hydrogen chloride gas. The mixture turned red and was stirred 24 h at room temperature in an argon atmosphere. The reaction mixture was poured into hot water and the remaining reactands were removed by steam distillation. Recrystallization of the residue from toluene afforded the product as a colorless solid in 90% yield (mp 149 °C, lit.[24] mp 147 °C).

2,2-Bis(4-hydroxyphenyl)heptane (5). It was prepared and purified analogously to 4. The yield of the colorless solid was 85% (mp 139 °C, lit.[24] mp 136 °C).

Halogen Exchange of 1. A 10-mmol sample of 1 (3.55 g) and 20 mmol of potassium fluoride (116.2 mg) or 20 mmol of TBAF or 20 mmol of TMAF were stirred at 160 °C in 50 mL of DMAc for 24 h. The reaction mixture was then poured into water. The precipitate was filtered off and subsequently washed with acetone and water to remove the salts and the solvent. As examined by ^{1}H NMR, the fluoride content of the product mixture varied in the range of 35% when using KF and 60% when using TBAF or, alternatively, TMAF. ^{1}H NMR (300 MHz, 150 °C, $C_2D_2Cl_4$, δ/ppm): 7.8, 7.6 (AB system), 7.15 (dd). ^{13}C NMR (125 MHz, 150 °C, $C_2D_2Cl_4$, δ/ppm): 194.1, 167.9 (d), 141.1, 139.7, 135.8, 132.7 (d), 131.3, 129.6, 115.8 (d). EI-MS: *m/e* 355.2, 338.3, 322.3.

Polymer Synthesis. 11 and 12. A 50-mmol sample of 4 or 5, 50 mmol of 1, 150 mmol of anhydrous potassium carbonate, and 0–5 mmol of phase-transfer catalyst 7, 8, or 9 were placed in a 250-mL four-necked round-bottomed flask equipped with a mechanical stirrer, an argon inlet, a water separator, and an addition funnel. Evacuation of the reaction unit and flushing with high-purity argon were repeated several times. A 100–120-mL aliquot of DMAc and 40 mL of toluene were added, and the reaction mixture was stirred and heated in an argon atmosphere to 60 °C. The reaction unit was subsequently evacuated and flushed with argon, and finally, an argon stream was passed through. The mixture was then heated to 155 °C for 3 h while the toluene–water azeotrope was removed by distillation. The reaction temperature was kept constant until a very viscous solution was obtained. The polymer was then precipitated by pouring the hot solution slowly into a blender containing a water/acetic acid mixture. The resulting precipitate was subsequently washed with water and methanol and finally boiled in methanol. The polymers 11 and 12 were obtained in 95% yield. ^{1}H NMR (200 MHz, $CDCl_3$, δ/ppm) of 11: 7.84 (m, 8H, phenylene), 7.22 (s, 4H, phenylene), 7.03 (m, 8H, phenylene), 2.12 (m, 2H, methylene), 1.68 (s, 3H, methyl), 1.16 (m, 2H, methylene), 0.92 (t, 3H, methyl). ^{13}C NMR (125 MHz, $CDCl_3$, δ/ppm) of 11: 195.38, 162.87, 153.78, 146.92, 141.59, 133.15, 129.86, 129.48, 120.44, 117.73, 46.47, 45.15, 28.62, 18.77, 15.48. ^{1}H NMR (200 MHz, $CDCl_3$, δ/ppm) of 12: 7.84 (m, 8H, phenylene), 7.27 (s, 4H, phenylene), 7.04 (m, 8H, phenylene), 2.09 (m, 2H, methylene), 1.67 (s, 3H, methyl), 1.28 (m, 4H, methylene), 1.13 (m, 2H, methylene), 0.81 (t, 3H, methyl). ^{13}C NMR (125 MHz, $CDCl_3$, δ/ppm) of 12: 195.25, 162.85, 153.72, 147.05, 141.59, 133.27, 131.83, 130.15, 129.62, 120.35, 117.82, 46.33, 42.81, 33.22, 28.89, 25.18, 23.09, 14.88.

13. A 50-mmol amount of 1,4-bis(4-chlorobenzoyl)benzene (17.78 g), 55 mmol of anhydrous sodium carbonate (7.60 g), 0.125–0.175 mmol of anhydrous potassium fluoride (7.26–10.16 mg), and 60 g of diphenyl sulfone were placed in a 250-mL four-necked round-bottomed flask equipped with a mechanical stirrer, an argon inlet, an argon outlet, and a solid addition funnel. The reaction unit was evacuated and flushed with high-purity argon. This procedure was repeated several times. The reaction mixture was then heated with stirring to 200 °C in an argon atmosphere. Over a period of 1 h 0.48 mmol of hydroquinone was added. The water formed during the reaction was removed by an argon stream which was passed through. The reaction temperature was raised to 270–280 °C and kept there until a very viscous solution was formed. The reaction mixture was then poured into a metallic tub, cooled to room temperature, and ground to a powder. The product was subsequently washed with water and acetone to remove salts and the solvent. The inherent viscosity (0.1% solution in concentrated H_2SO_4) of the resulting polymer was 0.9 dL/g.

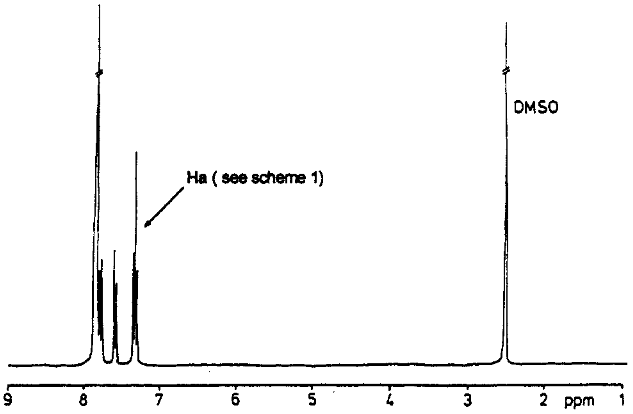
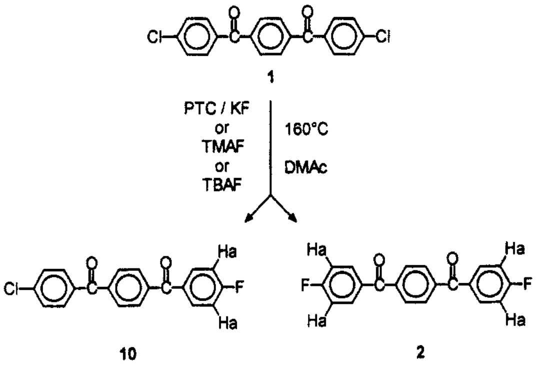


Figure 2. ^{1}H NMR (300 MHz, DMSO-d_6) of the product obtained by halogen exchange of 1 with TMAF.

Scheme 1. Halogen Exchange Reaction of 1



Results and Discussion

In order to explain the catalytic effect of fluoride on the polycondensation reaction, two different mechanisms can be envisioned. Activation can occur by generating very reactive fluorinated aryl ketone intermediates from reaction of fluorides with 1. Consequently, we were interested in methods to increase the generally low nucleophilicity of fluorides toward carbon[17] and to achieve the halogen exchange of 1. On the other hand, the fluoride can activate the phenolic monomers by polarizing the OH bond and thus increasing the nucleophilicity of this moiety. Such polarizing effects of fluorides on compounds with acidic functionalities have been studied by IR spectroscopy.[18] We therefore examined the influence of various fluorides on bis(phenol)s directly in polycondensation reactions of 1, which is discussed in the next chapter.

Halogen Exchange Reaction of 1. In a first reaction series we tried to accomplish a chloride/fluoride exchange of 1,4-bis(4-chlorobenzoyl)benzene (1) under conditions which are similar to those employed for the polycondensation reaction. However, when 1 was refluxed with an equimolar amount of KF in DMAc, no exchange products were detected by NMR and mass spectroscopy. Even when an excess of KF was used, no reaction occurred after 150 h. It has been shown that *N*-neopentyl-4-(dialkylamino)pyridinium chlorides 7–9 promote nucleophilic displacement reactions.[14–16] We therefore conducted the halogen exchange experiments in the presence of one of the above phase-transfer catalysts and found that, under these conditions, chloride/fluoride exchange of 1 does indeed occur. Fluorinated substitution products were formed in 35% yield with 10 mol % PTC 7, 8, or 9 after 24 h. The rate of the substitution reaction was calculated by ^{1}H NMR spectroscopy of the product mixture.

The intensity of the signal at 7.15 ppm, which is due to the protons (Ha in Scheme 1 and Figure 2) in the ortho

Table 1. Representative Results of Catalyzed Polycondensation of 1 with Bis(phenol)s

monomers dihalide/bis(phenol)[a]	catalyst[b]	amt of catalyst (mol %)[c]	reacn time (h)	M_w
1/4	uncatalyzed		17	~120 000
1/4	7	5	7	~175 000
1/4	7	10	4.5	~190 000
1/4	KF	0.3	8	~150 000
1/4	7 and KF	5 (7) and 0.3 (KF)	5	~180 000
1/4	7 and KF	10 (7) and 0.3 (KF)	3.5	~210 000
1/4	TBAF or TMAF	5–10	17	~115 000
2/4			2	~260 000

[a] Comparable results were obtained using 5 instead of 4 as the bis(phenol). [b] Comparable results were obtained using 8 or 9 instead of 7. [c] Relative to the amount of dihalide monomer.

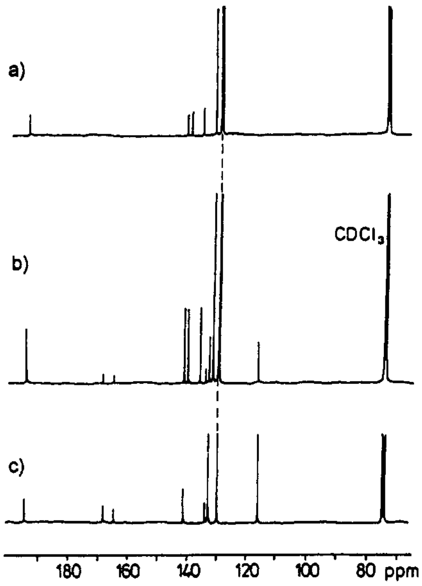


Figure 3. ^{13}C NMR (75 MHz, $CDCl_3$) of the product obtained by halogen exchange of 1 with TMAF in comparison with the dihalide spectra of 1 and 2: (a) ^{13}C NMR of 1; (b) ^{13}C NMR of the halogen exchange product of 1; (c) ^{13}C NMR of 2.

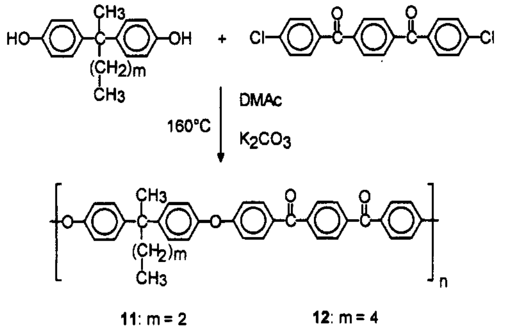
positions of the fluoride, was related to the intensity of the signal at 7.6 ppm, which arises from the AB system of the exclusively chloro substituted phenylene units. When ammonium fluorides such as TMAF or TBAF were used under analogous reaction conditions, fluoride substituted products of 1 were obtained in 56% (TMAF) and 62% (TBAF) yields within 24 h. In the ^{13}C NMR, the chemical shift of the aromatic carbons of the central phenylene unit at 129.55 ppm are independent of the different halogens (Figure 3).

Nevertheless the chloride/fluoride exchange of 1 was confirmed by ^{13}C NMR, since the signals at 167.8, 115.9, and 133.3 ppm are doublets as a result of C–F coupling. The product mixture was then further examined by mass spectroscopy and both monofluoro (*m/z* 338.11) and difluoro substituted products (*m/z* 322.13) of 1 were found. These results implicate an alternative route to high molecular weight poly(ether ketone)s by generating very reactive fluorinated aryl ketone monomers of 1 during polycondensation in the presence of the fluoride catalysts.

Catalyzed Polycondensation. Equimolar amounts of 2,2-bis(4-hydroxyphenyl)heptane (5) or 2,2-bis(4-hydroxyphenyl)pentane (4) and 1,4-bis(4-chlorobenzoyl)benzene (1) were used as a standard monomer mixture to optimize reaction conditions for the poly(ether ketone) synthesis.

These reactions, which yield very soluble, well characterizable amorphous polymers, were used as models for a kinetic study, since they allow us to examine the course of polycondensation, e.g., by correlation of reaction time and molecular weight (or viscosity). The condensations were conducted in close analogy to the solution polycondensation reported by Hergenrother[13]:DMAc was used as the solvent, and toluene was added to remove the water formed during the condensation. In order to obtain detailed information and comparable results of the catalyzed polycondensations, different bis(phenolic) monomers and catalysts were used. The separate experiments demonstrated, however, that comparable results were obtained using 4 or, alternatively, 5 as the bis(phenol)s and 7 or, alternatively, 8 or 9 as the phase-transfer catalyst.

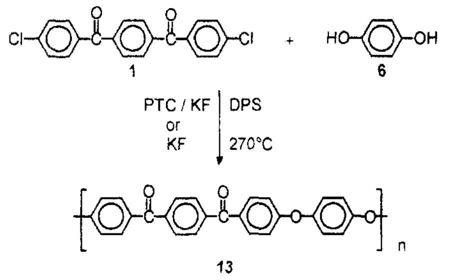
Scheme 2. Syntheses of the Polymers 11 and 12



In absence of a catalyst, a reaction time of 17 h was required to obtain polymers 11 and 12 (M_w > 100 000) using the dichloro monomer 1 and the bis(phenol) 4 or 5. If catalytic amounts of KF were added (0.25–0.35 mol % relative to the monomer), the condensation was accelerated significantly: a reaction time of 8 h was sufficient to obtain the high molecular weight polymers 11 and 12 (M_w > 150 000). This effect can be attributed exclusively to polarization and thereby activation of the OH bonds in the bis(phenol) monomers in the presence of KF, since halogen exchange of 1 can be excluded under these reaction conditions.

In another reaction series we studied the polycondensations of 1 in the presence of KF and the phase-transfer catalyst 7, 8, or 9. As demonstrated in polycondensation reactions of 1 and 4 or 5, the best results in terms of molecular weight and reaction time were obtained with KF (0.2–0.6 mol % based on the reactants) and 5–10 mol % PTC 7, 8, or 9 (Table 1). The reaction time was reduced up to 5-fold compared to the uncatalyzed reaction. On the one hand, this can be attributed to the polarizing influence of the fluorides on the bis(phenol)s. On the other hand, the improved solubility and nucleophilicity of anionic species in the presence of 7, 8, or 9[14] and the in situ formed very reactive fluorinated substitution products of 1 by the phase-transfer catalyzed halogen exchange of 1 can be pointed out as activating factors. Although fluoride substituted oligomeric end groups are not detectable, it can be confirmed by comparison of the different catalyzing methods (Table 1) that they are indeed formed during condensation. Moreover, the isolated polymers were of a significantly higher molecular weight (M_w >

Scheme 3. Catalyzed Synthesis of Polymer 13



190 000). This suggests that chain terminating reactions such as reductive elimination of chlorine from chloride substituted oligomeric end groups[19] become less important due to the decrease in reaction time.

In contrast to the above described accelerating influence of pyridinium salts, the course of polycondensation was not affected by the addition of TBAF or TMAF, although chloride/fluoride exchange of 1 was also observed in the presence of these fluorides. Obviously, the ammonium fluorides are not stable under the basic conditions and high reaction temperatures encountered in poly(ether ketone) synthesis.[15,16]

Our experience with both the fluoride assisted and the phase-transfer catalyzed poly(ether ketone) syntheses of amorphous polymers encouraged us to apply this procedure to the preparation of high molecular weight semicrystalline polymers of the general PEEKK structure from the dichloroaryl ketone monomer 1 and 1,4-hydroquinone (6). Since semicrystalline poly(ether ketone)s exhibit only low solubility, high reaction temperatures are necessary to avoid premature precipitation of the polymer. We used diphenyl sulfone (DPS, bp 379 °C) as an inert, high boiling solvent.

1,4-Hydroquinone (6) was thus treated at 270–280 °C with a slight excess of 1 in the presence of 0.3 mol % of potassium fluoride or of a potassium fluoride/PTC mixture. Sodium carbonate was used as the base, and toluene was added to remove the water formed during the reaction. We isolated a high molecular weight polymer (η_{inh} = 0.9 dL/g, 0.1% solution in sulfuric acid, 25 °C) which exhibited a good solubility in concentrated sulfuric acid and trifluoromethanesulfonic acid. Demonstrating the efficiency and the stability of the used catalysts even at high temperatures and the basic conditions, the uncatalyzed polycondensation of 1 and 6, however, yielded only a low molecular weight material (η_{inh} < 0.3 dL/g, 0.1% solution, sulfuric acid, 25 °C).

Polymer Degradation Reactions. In the context of the above described catalysis of poly(ether ketone) synthesis with fluoride or fluoride catalyst systems, we found that the maximum molecular weight correlates with the amount of fluoride used. We assume that the ether linkages of the polymers are broken by nucleophilic attack of fluoride, representing a process which is opposite the polymer forming nucleophilic displacement reaction.

It has been shown that under severe conditions, nucleophilic cleavage of activated aryl ethers can occur.[20] Among the nucleophiles able to induce this reaction are the phenolates. Such reactions lead to the so-called transetherification.[21] The fluoride anion has also been reported to cleave activated ether links of PEEK or PES.[22,23]

While ether cleavage of poly(ether ketone)s was observed only in the field of semicrystalline polymers at elevated temperatures (above 300 °C) (Scheme 5), the analogous reaction (Scheme 6) was shown to occur in poly(ether sulfone)s (PES) in sulfolane solution at 200 °C. However, for the synthesis of amorphous poly(ether ketone)s, which are prepared at reaction temperatures below 200 °C, such side reactions have not been mentioned so far.

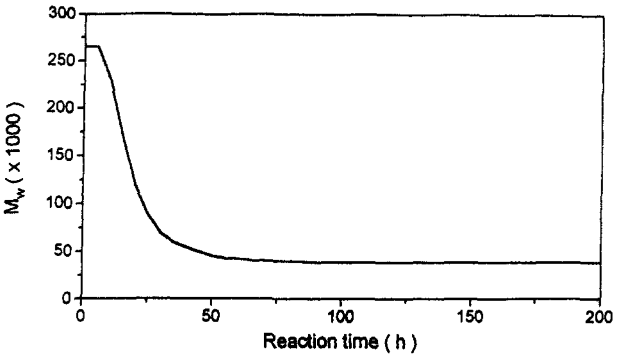
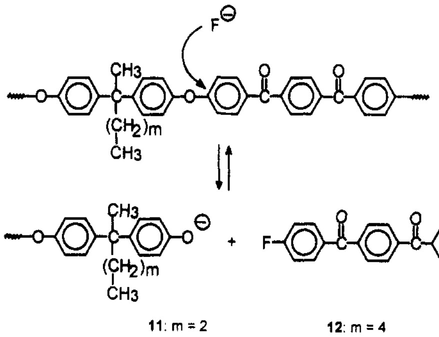
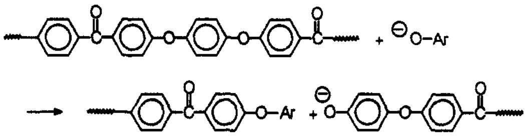


Figure 4. Polymer degradation of the polymers 11 and 12 induced by fluoride.

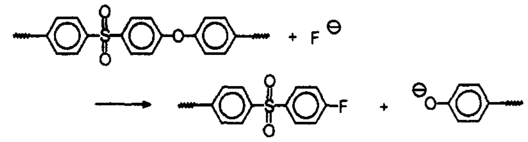
Scheme 4. Fluoride Induced Ether Cleavage of Amorphous Poly(ether ketone)s



Scheme 5. Ether Cleavage of Semicrystalline Poly(ether ketone)s by Phenolates



Scheme 6. Nucleophilic Ether Cleavage of PES by Fluoride



The catalyzed condensations of the bis(phenolate)s 4–6 with 1 result in high molecular weight amorphous or semicrystalline products when the fluoride content is kept below 0.5 mol % based on the reactants. Otherwise, the molecular weights (weight average) were decreased to 30 000–50 000, implying that polymer degradation can occur by nucleophilic ether cleavage in the presence of excess fluoride (Scheme 4). This hypothesis is supported by the following observations:

(1) The polycondensation of 1,4-bis(fluorobenzoyl)benzene (2) and 4 or 5 resulted in the formation of a high molecular weight polymer (M_w > 250 000), and equimolar amounts of potassium fluoride are formed during the reaction. The viscous reaction mixture, which was currently formed within 2 h, was stirred for 200 h at 160 °C. The molecular weight of the resulting product was significantly decreased to at least M_w = 26 000. The course of this degradation reaction was monitored by following the molecular weight as a function of the reaction time (Figure 4).

(2) This polymer degradation reaction, however, does not occur when the polymers **11** and **12** were stirred in DMAc at 160 °C for 200 h in the absence of fluoride, since the molecular weights of the polymers were not changed by this procedure.

It can be assumed that the use of fluoride anion in the synthesis of poly(ether ketone)s is followed by competing effects: activation by polarization of the OH bonds of the bis(phenolic) monomers and depolymerization by ether cleavage.

Conclusions

We have shown that potassium fluoride or a mixture of potassium fluoride and the *N*-neopentyl-4-(dialkylamino)pyridinium chlorides **7**, **8**, or **9** are suitable catalysts to promote the polymer forming nucleophilic displacement reaction in poly(ether ketone) synthesis. Although 1,4-bis(4-chlorobenzoyl)benzene (**1**) is considerably less reactive than the corresponding difluoro monomer **2**, this difference in reactivity can nearly be compensated for by the above described catalytic systems. The molecular weights of the resulting polymers **11** and **12** are considerably higher, presumably due to shorter reaction times. Moreover, these methods are also suitable for the synthesis of high molecular weight semicrystalline poly(ether ketone)s by reaction of hydroquinone **6** and **1**. Ether cleavage induced by excess potassium fluoride, however, causes polymer degradation, as shown for the amorphous polymers **11** and **12**.

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