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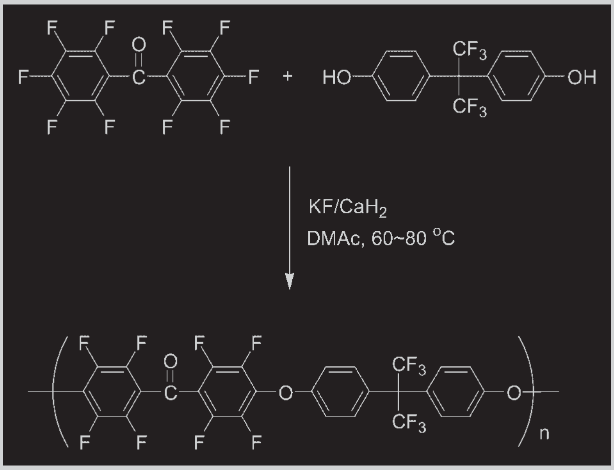
Summary: A new reaction procedure has been developed for the polycondensation of hexafluorobisphenol A (6F-BPA) with bis(pentafluorophenyl) ketone (BPK) in dimethylacetamide (DMAc). In this reaction, CaH_2 has been used as a base to facilitate the formation of the phenolate; an alkali metal fluoride was used as a catalyst. Unlike the conventional polycondensation reactions, this procedure avoided producing water during the reaction, and hence, azeotropic distillation with the assistant of a low-polar co-solvent is not required. This improvement maintains the high polarity of the reaction medium; consequently, the selectivity of the reaction at the *para*-position of BPK is significantly enhanced and polymers with high molecular weights ($\overline{M}_n$ ca. 30 000 Da) can be obtained with very low branching contents (less than 3 mol-%) and free of any cross-linked gel particles. In addition to avoiding the formation of water in the reaction, the use of CaH_2 also reduced the concentration of the fluoride ion in the solution. These effects minimize chain degradation reactions such as hydrolysis. The use of CaO instead of CaH_2 for this reaction produces similar effects. In the case of CaO, traces of water can be introduced into the reaction. The presence of trace amounts of water increases the polycondensation rate, probably due to the enhanced ionization of the phenolate. However, it also causes a hydrolysis of polymer chains, resulting in the elimination of the ketone group in the polymer backbone. Fortunately, this side reaction is highly water and temperature dependent, and can be efficiently prevented by using CaH_2 or conducting the reaction at a lower temperature (<65 °C).



CaH_2-mediated polycondensation for the preparation of highly fluorinated poly(arylene ether ketone).

Highly Fluorinated Poly(arylene ether ketone) Prepared by a CaH_2-Mediated Polycondensation Reaction

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Introduction

Fluorinated poly(arylene ether ketone)s (FPAEK)[1–5] are conventionally prepared by the polycondensation of the phenol groups of hexafluorobisphenol A (6F-BPA) with *para*-fluorines of bis(pentafluorophenyl) ketone (BPK) using a nucleophilic aromatic substitution reaction (S_NAr),[6–10] which has been traditionally used for the preparation of non-fluorinated poly(arylene ether)s.[11,12] The major problem of this reaction when applied to the preparation of FPAEK is the high tendency of a side reaction at the *ortho*-fluorines of BPK,[3,4] which are activated by the strong electron-withdrawing effect of the ketone group.[10] This side reaction leads to the formation of branched and eventually cross-linked structures. Initial work in our laboratory has shown that this side reaction produces a certain amount of branched and cross-linked structures in the final product when the conventional reaction conditions were used.[4–9] Even under mild reaction conditions (i.e., at 113 °C) when molecular sieves were used to dehydrate the solution, a shoulder peak associated with branched structures was observed in the GPC curves of the final products.[3,13] In addition, it was also noted that molecular weights obtained were always lower than the designed values due to this side reaction upsetting the

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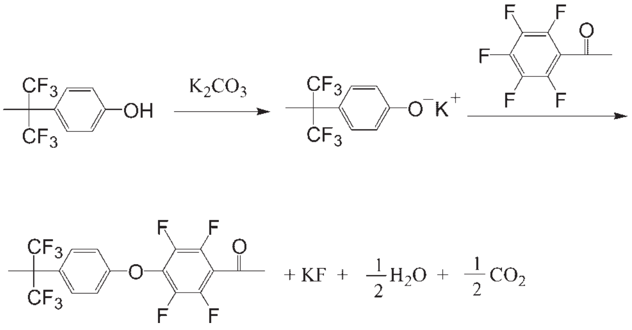
stoichiometric balance between the phenol groups and *para*-fluorines.[3] Therefore, in order to further reduce this side reaction, additional modifications to this reaction have been investigated in an attempt to improve the selectivity of the reaction at the *para*-fluorines.

The conventional polycondensation (shown in Scheme 1) involves the activation of the phenol group by a base such as K_2CO_3, the formation of a phenolate followed by the reaction with the fluorines on BPK to form an ether linkage. This reaction has been conducted in an aprotic, polar solvent such as DMAc.[14,15] The use of a highly polar solvent induces a higher polarity to BPK and, thereby, selectively promotes the reactivity of the *para*-fluorines. However, under these conventional reaction conditions with the use of K_2CO_3,[5–7] water is produced during the reaction and has to be removed due to the potential hydrolysis of the polymer.[16] Therefore, a low boiling, non-polar co-solvent such as toluene has been introduced into the reaction medium to facilitate the removal of water by azeotropic distillation[5–7] or by refluxing.[3,13] Unfortunately, this approach reduces the polarity of the polymerization medium and results in a lower selectivity of the reaction. In addition, the azeotropic distillation is not able to completely remove all the water from the reaction solution. The presence of trace amounts of water in association with fluoride ions produced during the reaction in the solution will cause serious polymer degradations by side reactions such as hydrolysis and chain scission.[17–20] It has been reported that the introduction of calcium or magnesium carbonates into the reaction associated with an alkali metal carbonate facilitates the polycondensation.[21–25] Very high molecular weight poly(arylene ether)s have been synthesized when a mixture of calcium carbonate and a small amount of potassium carbonate is used, whereas only low molecular weight polymers are produced using potassium carbonate alone.[21–23] This effect is attributed to the elimination of the equilibration by the effective removal of fluoride ion from the reaction solution due to the formation of insoluble calcium or magnesium fluoride.[24,25] By considering the advantages of an efficient removal of water and scavenging fluoride ion from the reaction, CaH_2 is investigated for the polycondensation reaction in this paper. CaH_2 is known to remove traces of water irreversibly and to act as a base without producing water. Although we observed that CaH_2 is not able to sufficiently activate the phenol to displace the *para*-fluorines in BPK, it has been found that, in association with a trace of KF or CsF as catalysts, CaH_2 can lead to a smooth polymerization reaction at low temperature in dimethyl acetamide (DMAc), Scheme 2. Furthermore, CaH_2 acts as a fluoride ion scavenger, readily reacting with the fluoride ion to form CaF_2, which has a very low solubility in anhydrous organic solvents. This is extremely advantageous since the presence of F^- in the reaction solution can attack the polymer and degrade the polymer chain in addition to hydrolysis and cyclization reactions.[14–20]

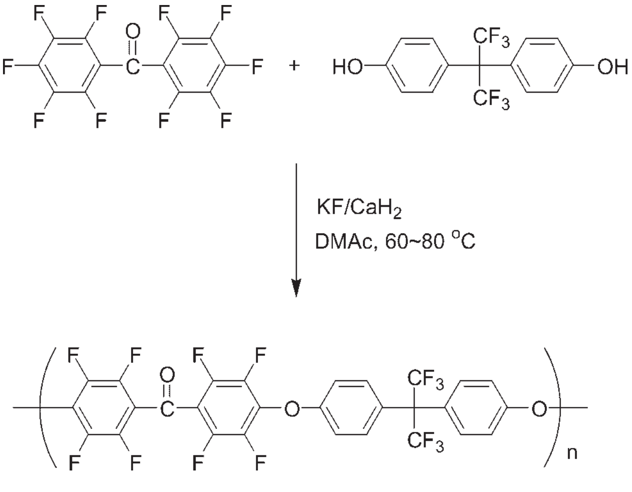


Scheme 1. Conventional polycondensation reaction.

Experimental Part

Instrumentation

Polymer molecular weights were determined by gel permeation chromatography (GPC) using a Waters 515 HPLC pump, coupled with a Waters 410 differential refractometer detector and a Waters 996 photodiode array detector, operating at a wavelength of 260 nm. A set of Microstyragel columns (10^3, 10^4, and 10^5 Å) were used and calibrated with polystyrene standards in THF. The values of polystyrene equivalent number average molecular weight ($\overline{M}_n$) are found very close to those determined from the end-group analysis by ^{19}F NMR. In this regard, see also the GPC analysis of the cyclic fraction in ref.[3] Typical GPC curves are shown in Figure 1 and 5. The small peak on the low molecular weight side at 30.5 min is attributed to the cyclic oligomers.[3] Consequently, in $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ calculations, this portion was eliminated from the GPC curve using a peak resolution technique. NMR spectra were recorded in $CDCl_3$ using a Varian Unity Inova spectrometer at a resonance frequency of 400 MHz for ^{1}H and 376 MHz for ^{19}F. $CFCl_3$ was used as an internal standard (0 ppm) for the ^{19}F NMR measurements. IR spectra were collected using a



Scheme 2. CaH_2-mediated polycondensation for the preparation of highly fluorinated poly(arylene ether ketone).

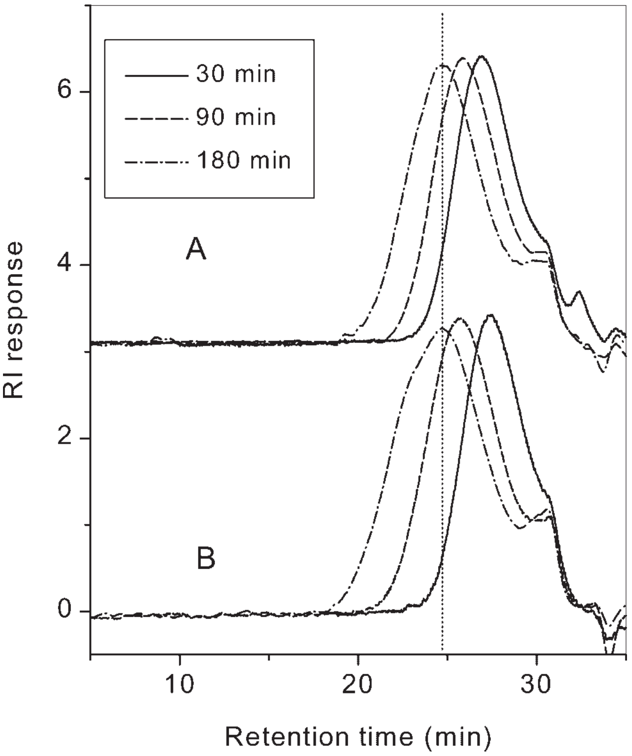


Figure 1. GPC curves of the samples taken at different reaction times from the CaH_2-mediated synthesis of FPAEK catalyzed by KF in DMAc at 80 °C. The molar ratio of 6F-BPA:BPK is (A) 59:60 and (B) 61:60.

MIDAC FT-IR spectrometer (Model, M1200-SP3) with a resolution of 2 cm^{-1}. The samples were prepared by coating THF solutions on NaCl disks. Thermogravimetric analysis (TGA) was performed in a nitrogen atmosphere (50 $mL \cdot min^{-1}$) at a heating rate of 10 $°C \cdot min^{-1}$, using TA Instruments TGA (Model 2950).

Materials

Hexafluorobisphenol A (6F-BPA) and bis(pentafluorophenyl) ketone (BPK) were purified by recrystallization in toluene and isopropanol, respectively. Anhydrous dimethyl acetamide (DMAc), KF, CsF, CaH_2, $Ca(OH)_2$ and CaO were purchased from Sigma-Aldrich Ltd. and used as received. Two other types of CaO samples were also used. One sample was flame baked at about 1 000 °C for 30 min in air. The other sample was dried at 300 °C under high vacuum (0.5 mm Hg) for 3 h (Table 1).

Polymerizations by the CaH_2-Mediated Reaction

This polymerization was conducted in DMAc at a temperature between 40 and 80 °C in the presence of a catalyst, KF or CsF, and a base, CaH_2. The following represents a typical polymerization procedure that gave the results shown in Figure 1–4. BPK (1.086 g, 3.000 mmol) and 6F-BPA (0.992 g, 2.950 mmol) were dissolved in 20 mL DMAc in a 50 mL flask. KF (0.035 g, 0.6 mmol) and CaH_2 (0.25 g, 6.0 mmol) were then added. The solution was purged and protected with argon, and stirred at 80 °C for 3 h. Small aliquots of the reaction solution (ca. 0.2 mL) were removed at intervals during the reaction for GPC and NMR analysis. The solutions were first filtered to remove insoluble salts and then dropped into an acidic water/methanol mixture (2:1 v:v) with agitation to precipitate the polymer. The resulting powder was then washed twice with water and dried under vacuum overnight prior to GPC and NMR measurements.

Table 1. CaO samples used for the reaction and their water content.

Type	H_2O content[a)
	wt.-%
Flame dried	0.0
Vacuum dried[b)]	2.2
As-received	4.0
Hydrolyzed[c)]	24.0

[a)] Water content was measured by TGA and calculated from the weight loss of the sample at 450 °C.

[b)] Dried under high vacuum at 300 °C for 3 h.

[c)] Commercial $Ca(OH)_2$ was used.

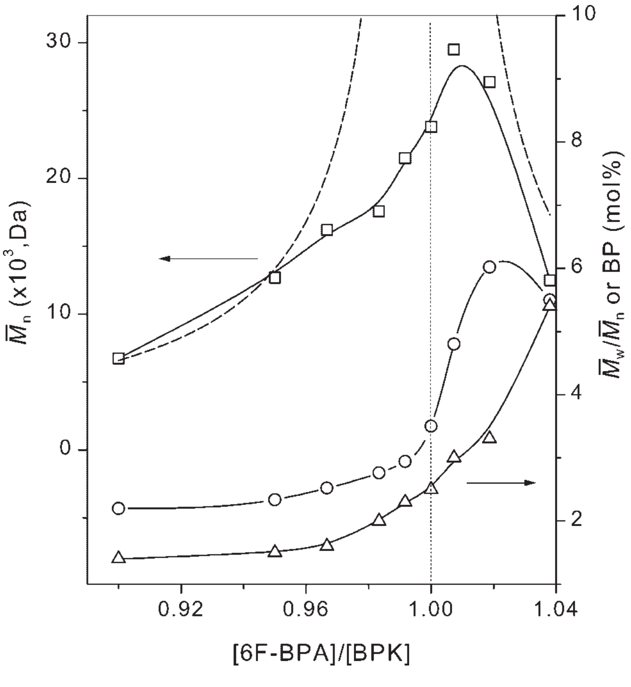


Figure 2. Feed ratio ([6F-BPA]:[BPK]) dependence of molecular weight ($\overline{M}_n$, square), polydispersity index ($\overline{M}_w/\overline{M}_n$, circle) and number of branch points (BP, triangle) of the samples from the CaH_2-mediated reaction of 6F-BPA with BPK catalyzed by KF in DMAc at 80 °C for 3 h. Dashed line represents the theoretical curve of Equation (1).

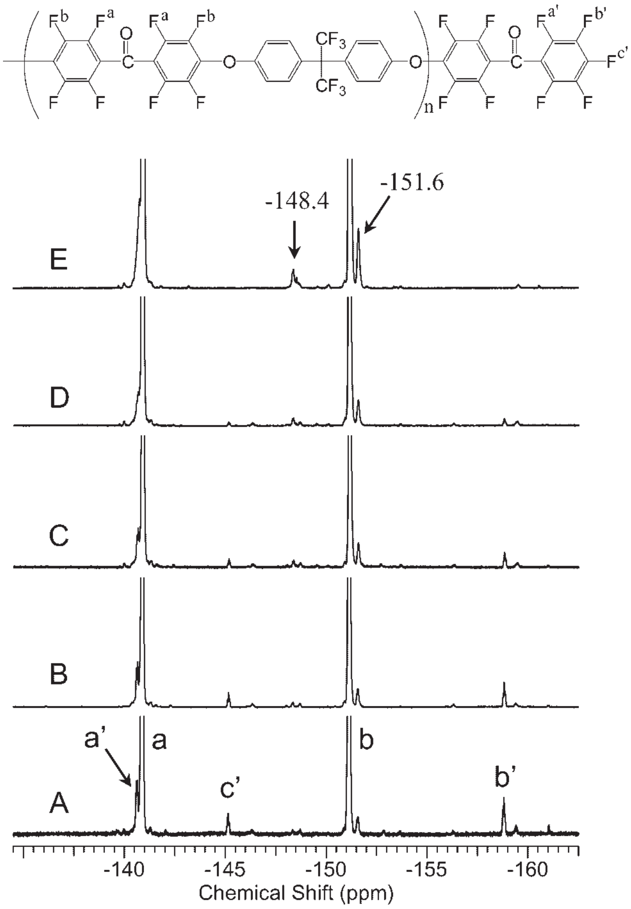


Figure 3. ^{19}F NMR spectra of FPAEK prepared by CaH$_2$-mediated polycondensation of BPK with 6F-BPA catalyzed by KF in DMAc at 80 °C for 3 h with the molar ratio of [6F-BPA]:[BPK] as (A) 0.967, (B) 0.983, (C) 1.000, (D) 1.017, and (E) 1.037. The peak intensities were normalized to the peak at −63.8 ppm of CF$_3$ group on 6F-BPA unit and the signals were magnified 20 times for the comparison of the peaks related to end-groups and branching units.

Polymerizations by the CaO-Mediated Reaction

This polymerization was conducted using the same reaction conditions as those used for the CaH$_2$-mediated reaction except that CaH$_2$ was replaced by CaO. In addition, the effect of water on the reaction kinetics was studied by GPC and ^{19}F NMR using four different CaO samples which contained different amounts of water in the form of Ca(OH)$_2$ (Table 1).

Degradation of FPAEK

The degradation of FPAEK with a high molecular weight ($\overline{M}_n = 28\,000$ Da, $\overline{M}_w/\overline{M}_n = 2.91$) was examined under conditions similar to those used for the polycondensation reactions. In this evaluation, Ca(OH)$_2$ was used instead of CaO or CaH$_2$ to provide water for the degradation. Typically, FPAEK (0.2 g, 0.3 mmol) was placed in 1.5 mL DMAc in a rubber-sealed test tube which also contained KF (0.005 g, 0.07 mmol), Ca(OH)$_2$ (0.07 g, 0.9 mmol), and a magnetic stirrer bar. The test tube was then heated in an oil bath at 80 °C under stirring. Aliquots of the solution (0.2 mL) were taken every 5 min for analysis. The solution was filtered to remove solids and was then mixed with CDCl$_3$ (0.5 mL) for ^{19}F NMR measurement. After 40 min, the reaction was stopped. The final solution was filtered to remove solids and then dropped into 10 mL acidic water. The aqueous solution was extracted three times with 20 mL ether. The combined ether solutions were washed twice with water and then vacuum evaporated to remove the ether. The resulting sticky solid was then dried under vacuum for 3 h prior to NMR and IR measurements.

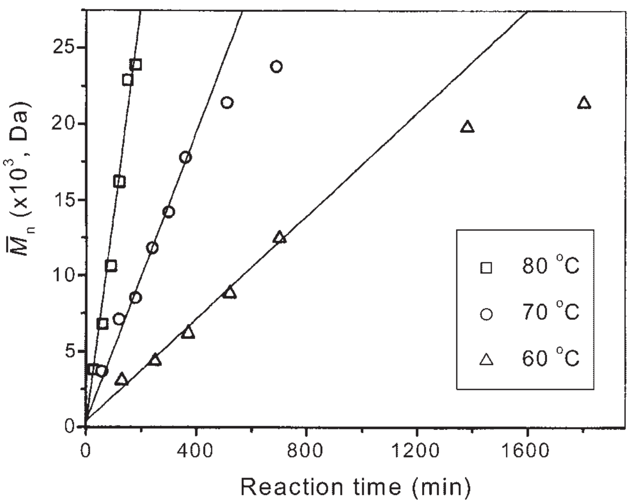


Figure 4. Reaction time dependence of the molecular weight of FPAEK prepared from CaH$_2$-mediated synthesis catalyzed by KF with feed ratio of [6F-BPA]:[BPK] = 59:60 at 60 (triangle), 70 (circle), and 80 °C (square). The solid lines are the fitting curves of Equation (2) in ref.[27]

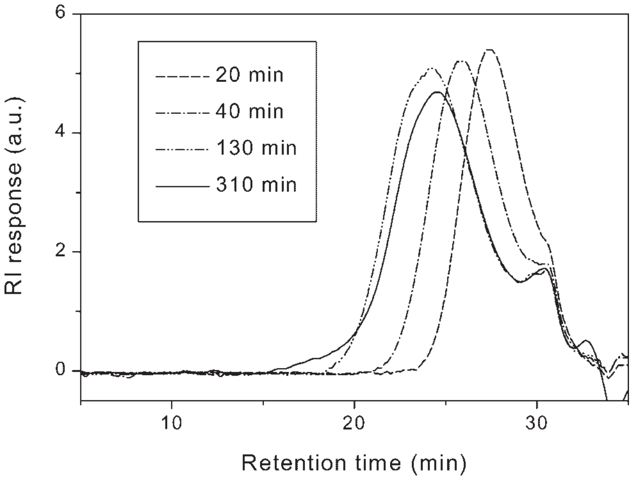


Figure 5. GPC curves of the samples taken at different reaction times from the CaO (as-received)-mediated synthesis of FPAEK catalyzed by KF at 70 °C with a feed ratio of [6F-BPA]:[BPK] = 119:120.

Results and Discussion

CaH_2-Mediated Reaction

The polycondensation of 6F-BPA with BPK has been modified by suspending CaH_2 and trace amount of KF in the reaction medium. In the reaction, CaH_2 acts as a drying agent as well as a base and KF acts as a catalyst. The GPC results obtained under these conditions are shown in Figure 1. It should be noted that the specimens used to obtain this data were recovered by dropping the reaction solution into a mixture of acidic water/methanol (2:1 v:v), so that both the polymer and the low molecular weight cyclic oligomers were collected. The presence of about 10 wt.-% cyclic oligomers can be clearly seen as a small peak in the low molecular weight region at 30.5 min of the GPC curves.[3] When the BPK is in a 1:60 excess over the 6F-BPA (Curves 1A), as the molecular weight increases with the reaction time, the GPC curves show a very similar pattern (i.e., a narrow polymer peak along with a cyclic oligomer peak) until the reaction reaches completion. No peak in the high molecular weight region associated with the branched polymers is apparent. At the completion of the reaction after 180 min, the value of $\overline{M}_w/\overline{M}_n$ is less than 3.0. A more detailed investigation has revealed that the reaction is complete in about 120 min at 80 °C and that the GPC curves remain practically unchanged during the last hour (from 120 to 180 min). This high stability of the polymer structures during the extended reaction time is in contrast to the continuing branching observed in the modified conventional polycondensation, in which molecular sieves are used for dehydrating.[3] Even when excess 6F-BPA (1:60 mol) is used, the GPC peak only slightly broadens as shown in the extended reaction time (Figure 1B) after the reaction is close to completion. At this moment, the excess phenol groups have no choice but to react with the *ortho*-fluorines because almost all of the *para*-fluorines have been consumed. This result provides evidence that under these new conditions, the branching side reaction has been effectively retarded, and high molecular weight polymers with mostly linear structures are easily produced.

The extent of the branching reaction during the polymerization has been further examined by systematically varying the feed ratio ($r = [6F\text{-}BPA]:[BPK]$) from 0.90:1.00 to 1.04:1.00 as shown in Figure 2. For an ideal polycondensation of A-A and B-B monomers, the number average molecular weight, $\overline{M}_n$, of the final polymer can be estimated from the feed ratio (r) according to the equation:

$$\overline{M}_n = M_0/|1-r| \tag{1}$$

where M_0 is the molar mass of the repeat unit. Based upon the data presented in Figure 2, it appears that when BPK is in a large excess, i.e., $r = 0.90$ and 0.95, the value of $\overline{M}_n$ is very close to the calculated value (dashed line in Figure 2). Notable deviations of $\overline{M}_n$ from the calculated value only appear when r becomes larger than 0.96. Obviously this deviation was caused by the side reaction at *ortho*-positions, which consumed extra phenol group of 6F-BPA and caused a change in r. Equation (1) indicates that close to $r = 1$ a small variation in r causes a large change in the molecular weight. The fact that the molecular weight deviation is observed only when r is very close to 1 indicates that the extent of the side reaction at the *ortho*-positions is minor under this reaction condition. In this regard, it is interesting to note in Figure 2 that polycondensation with a small excess of phenol groups leads to the highest apparent $\overline{M}_n$ but at the expense of a broader MW distribution.

The results of ^{19}F NMR analysis of the same samples as for the GPC measurements are shown in Figure 3. In this figure, only the aromatic region of the spectra is displayed, and all the spectra have been normalized to the CF_3 peak at −63.8 ppm. The signals have been magnified 20-fold to monitor effectively any changes in the small peaks associated with the end groups and branched units. The peak assignment is based on a theoretical chemical shift analysis.[26] The peaks at −140.9 (a) and −151.1 ppm (b) can be attributed to the fluorine atoms of the BPK units in the polymer backbone, whereas the small peaks at −140.6 (a′), −145.1 (c′), and −158.8 ppm (b′) arise from the fluorine atoms of the BPK end groups. Close examination of Figure 3 reveals that as the feed ratio r approaches 1.00 (from spectra A to C), the intensities of the peaks related to the BPK end groups gradually become lower, corresponding to the increase in the molecular weight observed by GPC as shown in Figure 2. Furthermore, as the feed ratio continues to increase over 1.00 (spectra C to E), a new peak at −148.4 ppm becomes evident. In addition, the intensities of the peak at −151.6 ppm as well as the shoulder on the left side of the tall peak at −140.8 ppm also increase. These changes are possible evidence of the formation of branched structures by the reaction of the phenol groups with the *ortho*-fluorines of BPK units in the polymer. Provided this assumption is correct, the number of branch points (BP) in the polymer can be estimated by comparing the integral intensity of the peak at −148.4 ppm with that of the CF_3 peaks at −63.8 ppm. The results of this calculation are presented in Figure 2 and suggest that the values of BP are less than 2.5 mol-% when the feed ratio r is below 1.00. Based upon the fact that the polymers are composed of around 30 repeat units ($\overline{M}_n$ ca. 20 000 Da), it can be estimated that the average number of branch point is less than 1 in each polymer chain. Even when the feed ratio r is increased to 1.04, the BP value is only about double that of the reaction with a feed ratio of 1.00. On the other hand, as the feed ratio increases above 1.00 (Figure 3, spectra C to E), the peaks associated with BPK end groups (a′, b′, and c′) start to disappear despite the molecular weight of these polymers remaining around 20 000 Da. This suggests that under these conditions, the polymers are mostly end-capped with phenol groups of 6F-BPA units. In contrast, any excess of phenol groups in the conventional reaction for the attempt to produce polymer with phenol end group only yields cross-linked polymer gels. This result indicates that the reactivity of *ortho*-fluorines has been significantly reduced in the CaH_2-mediated polymerization reactions, and thus, phenol end groups can survive during the reaction.

The influence of reaction temperatures on the CaH_2-mediated polycondensation has also been investigated and the results are shown in Figure 4. It can be clearly seen that the molecular weight increases linearly with reaction time when the reaction was conducted at a temperature between 60 and 80 °C. This is consistent with a second-order reaction [Equation (2) in ref.[27]]. The results in Figure 4 indicate that a 10 °C rise in reaction temperature results in approximately a threefold increase in reaction rate. Similar reaction kinetics, but with increased rates, have been found when KF was replaced by CsF as the catalyst. As an example, the CsF-catalyzed reaction at 50 °C exhibits a rate similar to that of the KF-catalyzed reaction at 70 °C. Both reactions are complete within 10 h and produce similar products ($\overline{M}_n$ around 25 000 Da and $\overline{M}_w/\overline{M}_n = 2.7$). The effects of temperature and the heavier alkali metal on the reaction rate are similar to those found in the synthesis of fluorinated poly(arylene ether sulfone).[27] It was found that the cesium phenolate reacts about 8 times fast than the potassium phenolate at the same temperature and the activation energy for the CsF-catalyzed reaction is 83 $kJ \cdot mol^{-1}$. Consequently, with a heavier alkali metal catalyst, such as CsF, a lower polymerization temperature can be used.

CaO-Mediated Reaction

It is clear from the foregoing discussions that the major functions of CaH_2 in this reaction are as a drying agent, a base and a fluoride ion scavenger. In principle, these functions can also be performed by a safer reagent, CaO. Therefore, CaO has been tested as a substitute for CaH_2 in the polycondensation reaction. The GPC results obtained for the CaO (as-received) mediated reaction are presented in Figure 5. From these results, it can clearly be seen that polymerization behavior is similar to that observed with CaH_2 (Figure 1A). The molecular weight ($\overline{M}_n$) increases at a similar rate as that for Figure 1A to reach a value of 25 000 Da within 130 min at 70 °C, which is 10 °C lower, indicating a higher polymerization rate of the reaction with CaO. On the other hand, in comparison with Figure 1A, the peak of the sample with the highest molecular weight in Figure 5 appears slightly wider. More importantly, as the reaction time is extended beyond 130 min, the molecular weight starts to decrease along with an increased peak broadening (see 310 min curve, Figure 5). These observations suggest that after 130 min, chain degradation and branching begin to dominate the reaction. These phenomena are not found in the CaH_2mediated reaction. The only obvious difference between the use of CaO and CaH_2 in the reaction is related to water. It is important to note that the commercial CaO product usually contains a trace amount of water in the form of $Ca(OH)_2$. Therefore, hydrolytic chain degradation becomes possible due to the presence of traces of H_2O or OH^- or both, which are released from the commercial CaO sample.

This hydrolytic effect has been verified by using four CaO samples with different water contents as listed in Table 1. The GPC results obtained for the polymerizations at 70 °C using these four different CaO samples are summarized in Figure 6. All reactions showed some similarity in that the molecular weights all increased linearly with reaction time in the initial stages. In addition, all samples had a narrow molecular weight distribution ($\overline{M}_w/\overline{M}_n$ of about 2.5) in this linear region. These results are similar to those obtained from the CaH_2-mediated reactions. However, in the case where the CaO samples with a high water content (as received and hydrolyzed) are used, a reduction in molecular weight has been found after the molecular weight reached a certain value, indicating the hydrolytic degradation eventually dominates over the polycondensation reaction. This effect became more significant when a CaO sample with higher water content was used. It resulted in a much lower maximum $\overline{M}_n$ value. Figure 6 also clearly shows that the initial polymerization rate increases strongly with the water content in the CaO samples. Whereas this may be due to a variety of different surface effects of the four CaO samples, it is believed that trace quantities of water released from the base into the reaction medium enhance the ionization of potassium phenolate and thereby increasing its nucleophilicity.

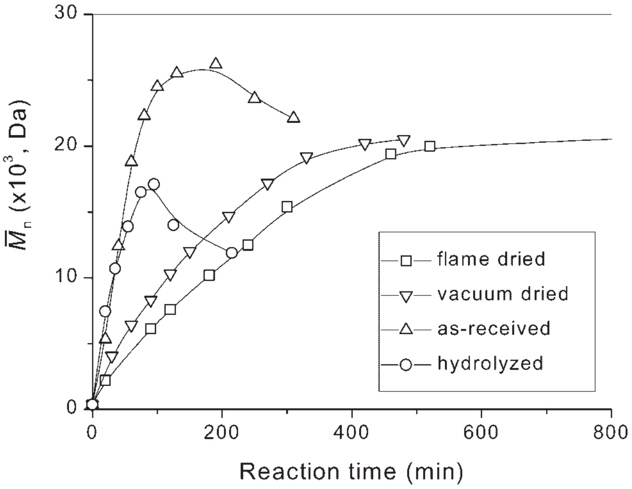


Figure 6. Reaction time dependence of $\overline{M}_n$ for the preparation of FPAEK on the feed ratio of [6F-BPA]:[BPK] = 119:120 mediated by different CaO samples containing different amounts of water. (Temperature: 70 °C).

The hydrolytic degradation noted above has further been investigated by conducting the polycondensation reaction at different temperatures. The results of this investigation using the as-received CaO sample which contained 4.0 wt.-% of water are shown in Figure 7. It appears that the decrease in molecular weight is only significant when the higher reaction temperatures are used. When the reaction was conducted at a lower temperature (65 °C), the molecular weight of the polymer continued to increase with time for the whole reaction period, reaching an apparent $\overline{M}_n$ of 35 000 Da after 420 min. However, once $\overline{M}_n$ exceeded 27 000 Da, the polydispersity index, $\overline{M}_w/\overline{M}_n$, increased rapidly reaching a value of 6.1 at 420 min (as shown in Figure 7). This increase is due to the appearance of a shoulder peak on the high molecular weight side of the GPC trace. In contrast for the reaction at 75 °C, $\overline{M}_w/\overline{M}_n$ reaches its maximum very quickly at a low value of 3.1 when the highest molecular weight is also achieved. At longer times $\overline{M}_w/\overline{M}_n$ decreases to 2.7 at 180 min. This indicates that the chain degradation narrows the molecular weight distribution. From these observations it is clear that, besides chain degradation, the presence of water also promotes chain branching as well as the polymerization discussed above. At high temperature (i.e., 75 °C), the hydrolytic degradation dominates the side reaction and the branching reaction becomes less prominent. However, the hydrolytic degradation is effectively depressed when the reaction is conducted at lower temperatures (i.e., 65 °C), at which the branching reaction becomes dominant, and high molecular weight polymers with a broad molecular weight distribution are obtained.

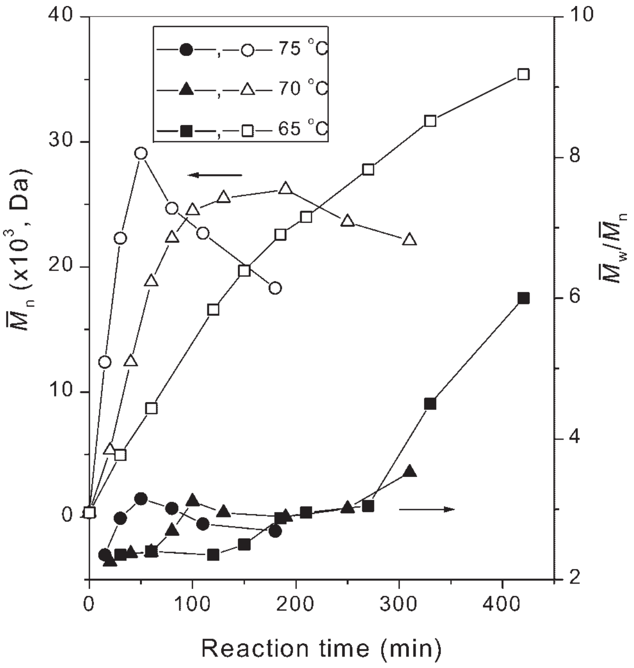


Figure 7. Reaction time dependence of $\overline{M}_n$ for the preparation of FPAEK with the feed ratio of [6F-BPA]:[BPK] = 119:120 mediated by the as-received CaO sample at different temperatures.

The mechanism of the hydrolytic degradation reaction was investigated by subjecting a FPAEK sample ($\overline{M}_n$ = 28 000 Da) to the reaction conditions similar to those for polymerization (i.e., 20 mol-% of KF vs polymer repeat units along with $Ca(OH)_2$ as a base in DMAc). This reaction was conducted at 80 °C and was monitored by taking samples at 5 min intervals for NMR and IR analysis. The results of the ^{19}F NMR analysis are shown in Figure 8. It can be seen from the four stacked spectra that the two peaks associated with the aromatic fluorines of the BPK units of the polymer at −140.9 (a) and −151.1 ppm (b) are quickly replaced by two new peaks at −137.9 (a′) and −153.4 ppm (b′) during the reaction, which increase in intensity at the same rate as the intensity of the other two peaks decreases. Using the same theoretical chemical shift predictive approach as before,[26] these new peaks have been assigned to the aromatic fluorine atoms (a′) and (b′) of tetrafluorophenyl-degraded species as indicated in the same figure. The final product related to Spectrum D has also been investigated by ^{1}H NMR, and the resulting spectrum has confirmed the results from ^{19}F NMR. In ^{1}H NMR spectrum (not shown), the original polymer shows two doublet signals with $J_{H\text{-}H}$ coupling constant of 8 Hz at 7.38 and 7.01 ppm in the aromatic region, which are attributed to the *ortho*- and *meta*-hydrogen atoms of 6F-BPA units. After the reaction, these two doublet peaks are replaced by two new doublet peaks at 7.34 and 6.95 ppm with the same aromatic coupling. At the same time, a new signal showing a complex coupling pattern emerges at 7.00 ppm. This new signal has been assigned to the *para*-hydrogen of the tetrafluorophenyl-degraded species and is heavily coupled with the fluorine atoms of the phenyl ring. The intensity of this new peak is half of that of the hydrogen peaks from 6F-BPA units as expected from the structure (2H:4H:4H). A possible reaction mechanism to account for this type of structure is presented in Scheme 3. Basically, the degradation is induced by the nucleophilic addition of OH^- ions on the ketone groups in the polymer backbone followed by cleavage, leading to the formation of a 2,3,5,6,-tetrafluorophenyl terminal group, along with a 2,3,5,6-tetrafluorobenzoic acid terminal group as a reaction intermediate. This process is very similar to a reported nucleophilic cleavage reaction of ketone groups which are adjacent to strong electron-withdrawing groups.[28] However, because the carboxylic acid group is detected neither by NMR, nor by IR analysis, it must be assumed that the tetrafluorobenzoic acid group readily undergoes decarboxylation to produce the 2,3,5,6-tetrafluorophenyl groups. Decarboxylation of fluorobenzoic acid is a well-known phenomenon, which is catalyzed by a strong base in a polar solvent.[29] Therefore, compound A becomes the only degradation product of this reaction as shown in Scheme 3. This structure explains the results obtained from ^{19}F as well as the ^{1}H NMR spectra.

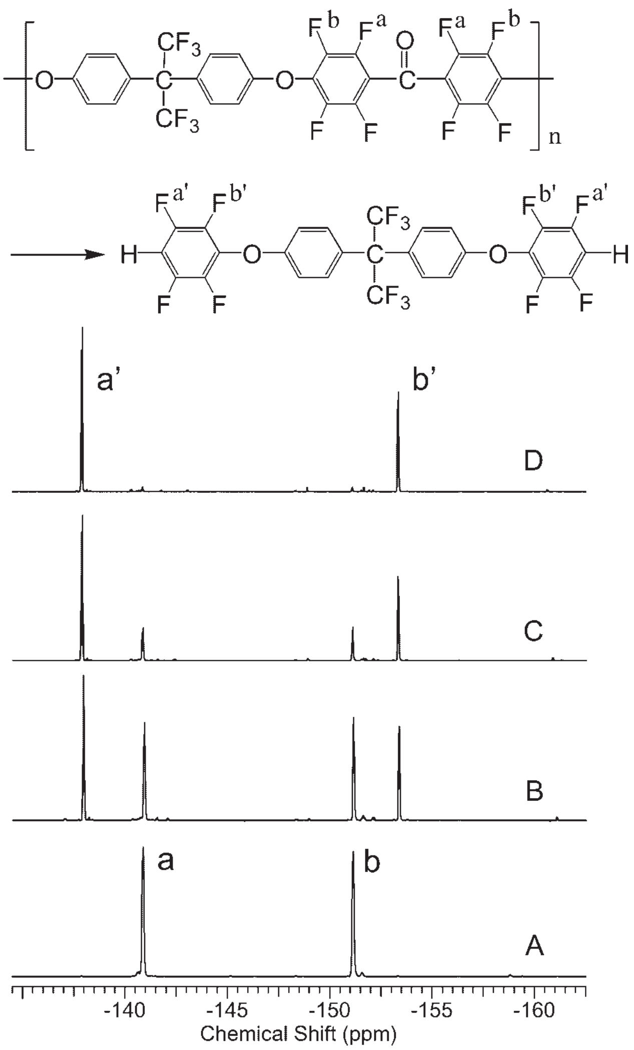


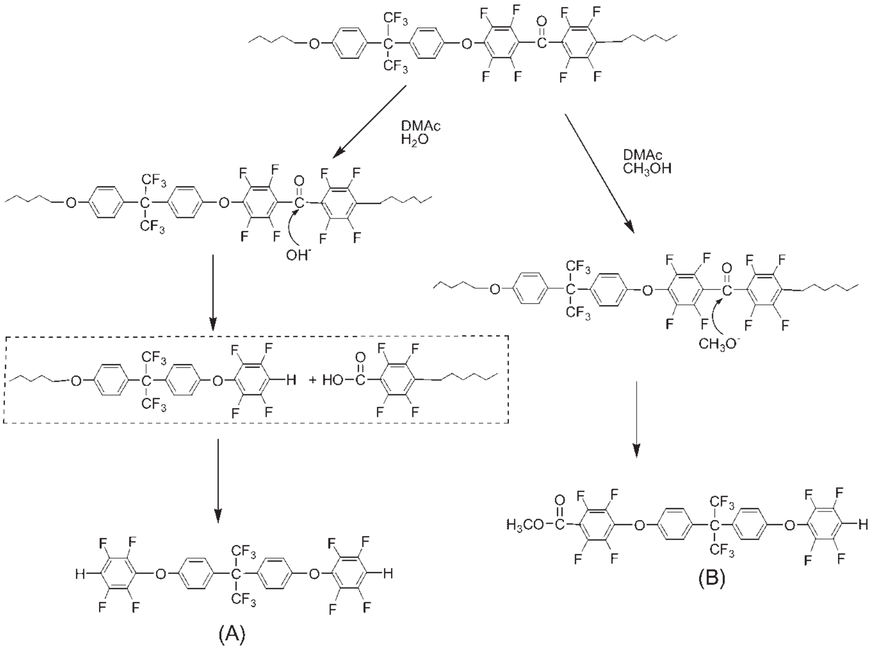
Figure 8. Aromatic ^{19}F NMR spectra of FPAEK (A) and its degradation products after heating in DMAc in the presence of KF and $Ca(OH)_2$ at 80 °C for the reaction times of (B) 5 min, (C) 15 min, and (D) 30 min.

This reaction mechanism involving the benzoic acid intermediate has been verified by performing the degradation in the presence of methanol at 80 °C for 12 h, in which the flame-dried CaO instead of $Ca(OH)_2$ along with methanol (0.2 wt.-% vs solvent) were added. In this case, the benzoic intermediate is possibly trapped by methanol to form methyl benzoate. The ^{19}F NMR spectra of the polymer (A) and the degradation product (B) are compared in Figure 9. Examination of Spectrum B clearly indicates the presence of two different types of tetrafluorophenyl species with a ratio of about 3:2. The larger resonance peaks (a′ and b′) are at the same position as the peaks from Species A (Figure 8D). The smaller peaks (a″ and b″) which are close to the peaks of the original polymer are assigned to fluorine atoms of tetrafluorophenyl group adjacent to the ester group of Species B in Scheme 3. The ^1H NMR of the final product of this reaction shows indeed a peak at 4.00 ppm, which is attributed to the methyl benzoate group. All of these results would appear to confirm that degradation follows the carboxylic acid route. However, based on the NMR analysis, only about 80% of the product carries a methyl benzoate group. The other 20% has the same structure as Species A carrying two hydrogen atoms, suggesting that this fraction has been formed by the simultaneous hydrolysis reaction probably due to the presence of traces of water introduced with the feed.

The structures of the degradation products have also been confirmed by IR analysis shown in Figure 10. From these spectra, it can be clearly seen that the band associated with the ketone group in the polymer backbone at 1 691 cm^{-1} completely disappears on reaction with water or methanol. In the case of treatment with methanol, a new band at 1 744 cm^{-1} appears due to the formation of the ester group.

Based upon these observations, it can be concluded that under basic reaction conditions, strongly nucleophilic species such as OH^- and CH_3O^- are capable of attacking bis(tetrafluorophenyl) ketone units in the polymer resulting in chain scissions. This reaction represents a completely different mechanism to that associated with the chain degradation of non-fluorinated polyether ketones and sulfones,[14–20] where the center of the degradation is the ether group. Clearly in the case of the fluorinated polymers, the ketone groups are more sensitive to nucleophilic attack than ether groups. This behavior is explained by the strong electron-withdrawing effect of the fluorine atoms on the phenyl rings adjacent to the ketone groups as demonstrated in Scheme 4.

It should be noted that the above degradation might also be initiated by the phenolate of 6F-BPA and of the polymer end groups since these materials themselves are nucleophilic reagents. If this were to occur it would lead to the formation of benzoate linkages in the polymer chain. This reaction could then compete with the polycondensation reaction of 6F-BPA with BPK to consume extra phenol groups and upset the stoichiometric balance between 6F-BPA and BPF resulting in a low molecular weight polymer. Based on NMR, IR and GPC analysis, there appears to be no obvious evidence to support the occurrence of this side reaction during the polymerizations studied in the temperature range from 40 to 80 °C. Based on the data presented in Figure 7, it is clear that the attack of nucleophilic reagents on the ketone groups in the polymer is highly temperature dependent, and in the case of water as the nucleophilic reagent, the reaction is significantly depressed when the reaction temperature is decreased from 75 to 65 °C. Furthermore, the rate of reaction with CH_3OH is much lower than that with water (the reaction with methanol at 80 °C was completed within 12 h, while only 30 min were required for the reaction with water). Consequently, a similar reaction involving the phenol group is highly unlikely under these polymerization conditions due to the low nucleophilicity of the phenolate group.



Scheme 3. Reaction mechanism for the polymer degradation initiated by trace of water or methanol in the presence of CaO and KF in DMAc at 80 °C.

Conclusions

The preparation of fluorinated poly(arylene ether ketone)s by the polycondensation of 6F-BPA with BPK has been modified by the use of CaH_2 or CaO in the solution as a base, along with KF, or CsF (20 mol-% to monomer) as a catalyst. CaH_2 or CaO in the reaction serves the following roles: 1) It acts as dehydrating agents ensuring a water free reaction

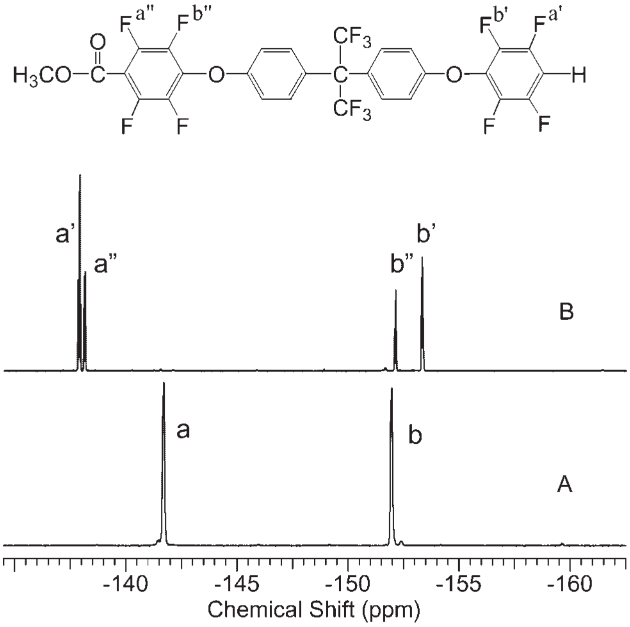


Figure 9. Comparison of the aromatic ^{19}F NMR spectra of FPAEK (A) and its final degradation product after the polymer was heated in DMAc in the presence of KF, CaO and a trace amount of CH_3OH at 80 °C for 12 h.

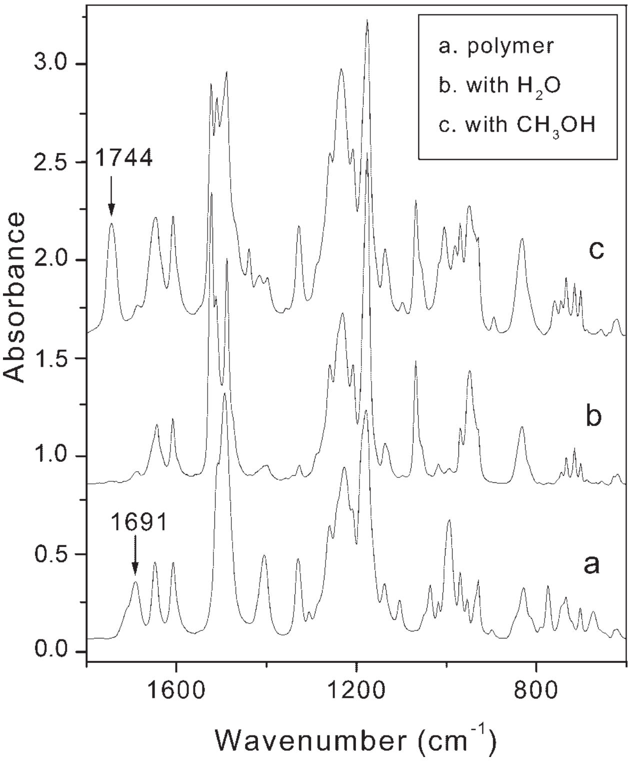
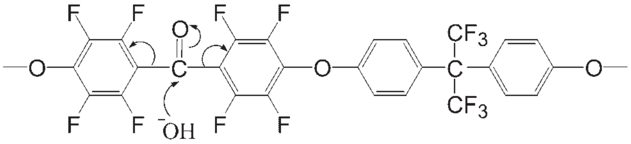


Figure 10. IR spectra of FPAEK (a) and its degradation products by reacting with trace amount of H_2O (b) and CH_3OH (c).



Scheme 4. Ketone is activated for the nucleophilic attack by the electron-withdrawing effect of tetrafluorophenyl ring in the polymer.

system. 2) It acts as a base in the reaction to facilitate the formation of the phenolate. Because this procedure does not produce water, the use of a co-solvent such as toluene to achieve azeotropic distillation is not required. This means that high polar solvents such as DMAc can be used, promoting the selectivity at the *para*-positions. 3) It controls the concentration of F^- ions in solution at a very low level because of the insolubility of CaF_2. These factors promote the formation of polymers with high molecular weights by reducing the opportunity for side reactions such as branching, chain scission and hydrolysis. Consequently, polymers with low branch content and high molecular weight can be prepared by using CaH_2 or CaO as a base suspended in the reaction solution. However, significant degradation of the polymer chains was observed when CaO containing trace amounts of water was used. This degradation has been attributed to the hydrolysis of the ketone linkages in the polymer backbone involving the nucleophilic attack of OH^- ions to form a carboxylic acid intermediate followed by subsequent decarboxylation to release CO_2. This reaction mechanism has been confirmed by reacting the polymer with trace amounts of methanol, which resulted in the formation of tetrafluorobenzoate terminal groups. Fortunately, this undesirable degradation can be prevented by the use of CaH_2 or anhydrous CaO, or by conducting the polymerization at low temperatures when a partially hydrolyzed CaO sample was used.

The CaH_2-mediated polymerization reaction in DMAc follows second-order reaction kinetics with the reaction rate increasing by a factor of 3 for each 10 °C rise in the range between 60 and 80 °C, which was found to be an ideal temperature range for this reaction. Increased reaction rates can be achieved by using a heavier alkali ion catalyst, such as Cs^-, or by using water-containing CaO as the base.

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