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Synthesis of a soluble poly(ether ketone) prepolymer

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The synthesis of a soluble poly(ether ketone) (PEK) precursor via a ketimine route is described. The synthesis is realized by using a halogenophenol monomer, i.e. *N*-(4-fluoro-4′-hydroxydiphenylmethylene) imine. First we describe the synthesis of the monomer and its characterization by infra-red and ^{13}C nuclear magnetic resonance spectroscopies. Subsequently, the polymerization of the monomer is reported and the factors influencing the polymerization reaction are considered. The ketimine PEK prepolymer is soluble in common organic solvents. The rate of the ketimine PEK condensation is decreased compared with that of the equivalent ketimine poly(ether ether ketone) condensation due to the deactivation of the reactive intermediate (Meisenheimer's complex). The poly(ether ketimine) can be readily hydrolysed to the poly(ether ketone). Copyright © 1996 Elsevier Science Ltd.

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Introduction

During the last two decades, aromatic poly(aryl ether ketone)s (PAEKs) have given rise to much interest. They are high-performance thermoplastics with excellent environmental resistance and good mechanical properties. They are semicrystalline polymers having a melting temperature (T_m) around 340–360°C and a glass transition temperature (T_g) around 140–160°C. Among them, poly(ether ketone) (PEK, **1**) and poly(ether ether ketone) (PEEK, **2**) (*Figure 1*) have achieved significant commercial importance as matrices for carbon fibre composites and as dielectrics in the microelectronics field.

However, due to their semicrystalline structure, they are insoluble in most organic solvents. At room temperature, they dissolve only in some concentrated acids. At temperature close to the melting point (> 300°C), they dissolve in polar aprotic solvents like benzophenone and diphenylsulfone.

For this reason, PAEKs must be synthesized at high temperature[1] (around 300°C) in order to avoid premature crystallization and precipitation in the reaction mixture. Moreover, the impregnation process for making composites must also be performed using a high-boiling-point solvent, and elimination of the solvent requires temperatures up to 400°C. This makes the impregnation process very expensive.

In order to facilitate the synthesis and impregnation, use of a low-boiling-point solvent would be advantageous. Others have already described the synthesis of amorphous PAEK prepolymers in sulfolane, dimethyl acetamide (DMAc) or *N*-methylpyrrolidone (NMP). These PAEK prepolymers contained removable tert-butyl[2], ketal[3] or ketimine[4–7] substituents along the chain, making them soluble in the more common polar aprotic solvents like dimethyl sulfoxide (DMSO), tetrahydrofuran (THF) and DMAc.

The aim of this communication is to describe the synthesis of a soluble PEK precursor via a ketimine route. The synthesis is realized by using a halogenophenol monomer, i.e. *N*-(4-fluoro-4′-hydroxydiphenylmethylene) imine. First we describe the synthesis of the monomer and its characterization. Subsequently, the polymerization of the monomer is reported and the factors influencing the polymerization reaction are considered.

Experimental

Reagents. 4-Fluoro-4′-hydroxybenzophenone (Aldrich) was washed through charcoal and recrystallized twice from ethanol. Aniline (Janssen) was distilled from CaH_2 before use. Toluene (p.a., Janssen), *p*-toluenesulfonic acid (Aldrich) and hexane (p.a., Janssen) were used as received. 1-Hexanol (Merck) was distilled on Mg before use. Potassium carbonate (Janssen) was finely sieved and dried at 120°C for 2 h before use. NMP (ISP) was distilled from CaH_2 under vacuum. Methanolic potassium methylate solution (Merck, 25%) was used as received.

Synthesis of N-*phenyl (4-fluoro-4′-hydroxydiphenylmethylene) imine.* A three-necked round-bottomed flask, fitted with a Dean–Stark trap with condenser, an N_2 inlet and a thermoregulated electrical heating mantle, was charged with aniline (85.6 g, 0.92 mol), 4-fluoro-4′-hydroxybenzophenone (100 g, 0.46 mol) and *p*-toluenesulfonic acid (0.5 g) and the contents dissolved

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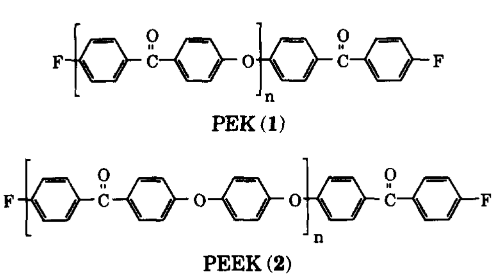

PEK (1)

PEEK (2)

Figure 1 Molecular structures of PEK (1) and PEEK (2)

in 400 ml toluene. The solution was heated to 120°C under magnetic stirring and water was removed as a toluene azeotrope over a 24 h period. The toluene was then evaporated and the crude product was recovered as small crystals. These crystals were washed twice with hexane/1-hexanol (80/20) to remove the excess of aniline. Finally, the purified product (79 g, 63%) was dried at room temperature under vacuum.

Synthesis of the PEK precursor—K_2CO_3 route. A three-necked round-bottomed flask, fitted with a Dean–Stark trap with condenser, a N_2 inlet and a thermoregulated electrical heating mantle, was charged with *N*-phenyl (4-fluoro-4′-hydroxydiphenylmethylene) imine (13.65 g, 0.05 mol) and K_2CO_3 (5 g) and the solids were dissolved in a mixture of 110 ml of NMP and 50 ml of toluene. The solution was slowly heated to 140°C, at which point the toluene azeotrope began to reflux. The temperature was raised to 170°C and maintained for a 4 h period. Finally the temperature was raised to 175°C and maintained for 18 h. The solution was cooled to room temperature and filtered to remove the carbonate.

Synthesis of the PEK precursor—potassium methylate route. The *N*-phenyl (4-fluoro-4′-hydroxydiphenylmethylene) imine (1.1415 g, 4.18×10^{-3} mol) was dissolved in a methanolic potassium methylate solution (1.1009 g, 3.93×10^{-3} mol). The methanol was removed with a Rotavapor and the potassium salt dried at room temperature under vacuum. In a three-necked round-bottomed flask fitted with a N_2 inlet and a condenser, the potassium phenate was dissolved in 25 ml of NMP. The temperature was raised to 160°C using a silicone oil bath and maintained for a 24 h period. At 160°C, the polymer was completely dissolved in NMP but, upon cooling of the solution, the polymer began to precipitate. The high-molecular-weight fraction was removed by filtration under Ar.

Hydrolysis of the prepolymer. The prepolymer prepared above (1 g) was dissolved in 200 ml of NMP, and the solution was heated and refluxed for 1 h. The solution was then cooled down to room temperature, and 25 ml HCl (UCB, 37%) added. After 5 min of reaction, the solution was filtered; the polymer was then washed several times with methanol and acetone before finally being dried at 120°C under vacuum.

Infra-red (i.r.) characterization. The i.r. spectra were recorded on a Perkin–Elmer FT-IR 1760X spectrometer coupled with an IBM PS2 data station provided with the 'IR Data Manager' Program from Perkin–Elmer.

^{13}C nuclear magnetic resonance (n.m.r.). The ^{13}C n.m.r. spectra were taken on a Brüker AM 500 spectrometer at 125.76 MHz. The *N*-phenyl (4-fluoro-4′-hydroxydiphenylmethylene) imine spectrum was obtained at room temperature using deuterated acetone (Fluka) as solvent.

^{19}F n.m.r. The ^{19}F n.m.r. spectra were recorded on a Brücker WM 250 spectrometer at 235.34 MHz. The samples were dissolved in deuterated acetone (Fluka).

Differential scanning calorimetry (d.s.c.). The d.s.c. analyses were carried out on a Perkin–Elmer differential scanning calorimeter (DSC 7) calibrated with indium and zinc, and operating under nitrogen. From 7 to 15 mg of the sample was weighed and analysed in an open aluminium d.s.c. pan.

Size exclusion chromatography (s.e.c.). The s.e.c. chromatograph consisted of a Millipore–Waters 600A pump, an automatic injector (Millipore–Waters WISP 712), a set of three PL gel columns from Polymer Laboratories (500 Å, 100 Å and 50 Å) and a u.v. detector (Perkin–Elmer LC 55) set at 254 nm. The solvent was unstabilized THF (Lab Scan). All analyses were carried out at 25°C. The flow rate was 0.6 ml min^{-1} and the sample concentration 0.1 g l^{-1}. The calibration was carried out with isomolecular PS standards from 37 200 to 580 Dalton and with low-molecular-weight compounds such as ethylbenzene, toluene, etc. down to 96 Dalton.

MOPAC calculations. The heats of formation were calculated for both the *cis* and *trans* isomers of the imine (*Figure 3*) using a Silicon Graphics Personal Iris 4D/35 Workstation. The initial structures were set up, and converted to data files via the INSIGHT II package of Biosym Corporation. The calculations were run using the MOPAC 6 package using the PM3 Hamiltonian[8] and the default convergence criteria. Geometry optimization

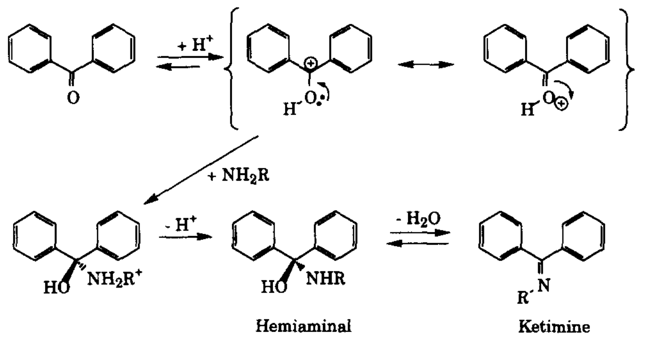

Figure 2 Synthesis of the ketimine monomer

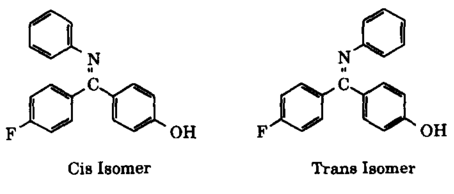

Figure 3 *Cis* and *trans* isomers of the ketimine monomer

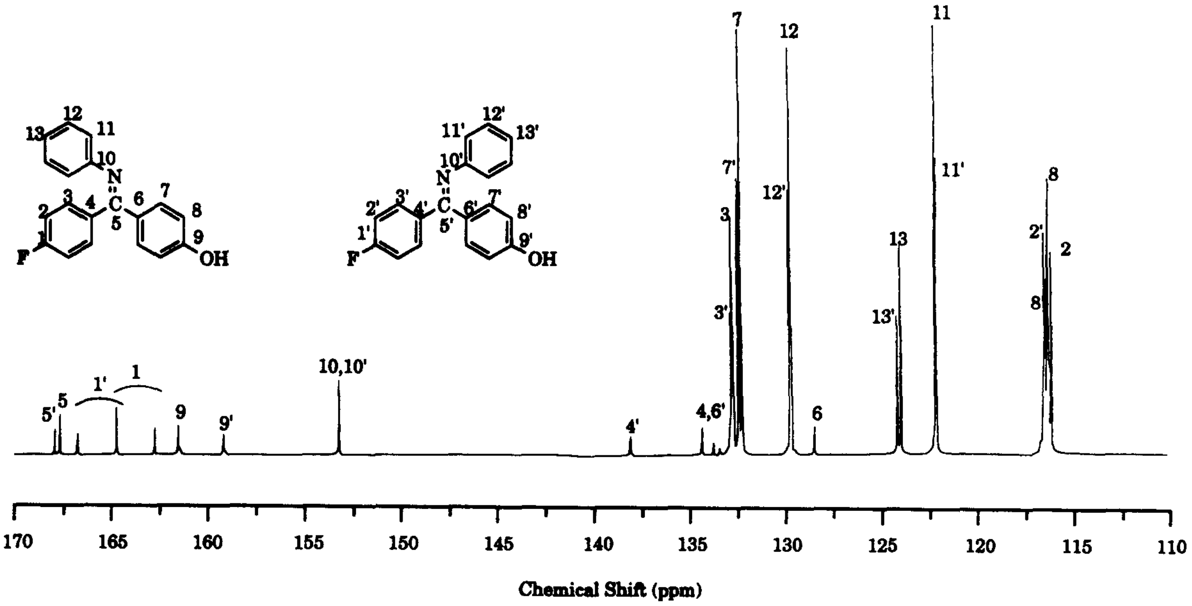

Figure 4 ^{13}C n.m.r. spectrum of the ketimine monomer

Table 1 Chemical shift assignments of the ketimine monomer

Atom no.	Chemical shift (ppm)	
	Cis isomer	*Trans* isomer
1	164.85 and 162.84	166.8 and 164.85
2	116.4 and 116.2	116.5 and 116.3
3	133.0 and 132.9	133.1 and 133.0
4	134.5	138.2
5	167.7	168.0
6	134.5	128.6
7	132.5	132.7
8	116.4	116.6
9	161.64	159.33
10	153.43	153.43
11	122.24	122.20
12	129.87	129.93
13	124.05	124.24

was unconstrained, and the Newton–Raphson minimization routine was selected. Converged geometries were checked using the steepest descent algorithm.

Results and discussion

Synthesis and characterization of the monomer. The synthesis of the ketimine monomer proceeds through a nucleophilic substitution where the primary amine reacts first with the carbonyl compound to form the hemiaminal (or carbinolamine)[9] (*Figure 2*). The hemiaminal undergoes the elimination of water to form the ketimine compound. This overall reaction is acid catalysed. When the ketone compound is asymmetric, the synthesis leads to the formation of *cis* and *trans* isomers[10] (*Figure 3*).

Low-molecular-weight s.e.c. was used to verify the purity of the monomer. The purified monomer gives only one peak, at elution volumes lower than 4-fluoro-4′-

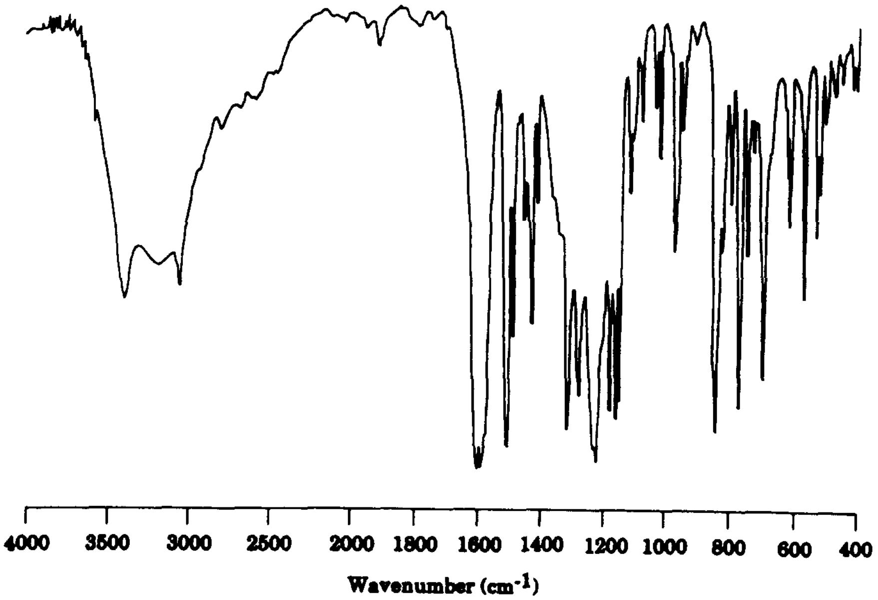

Figure 5 I.r. spectrum of the ketimine monomer

hydroxybenzophenone and aniline. From d.s.c. results, the monomer exhibits one narrow melting endotherm located at 196°C. However, the ^{19}F n.m.r. analysis of the monomer exhibits two peaks, showing that the amounts of the two isomers are in the ratio 60 : 40.

In order to determine which of the isomers is favoured, the heat of formation was calculated for each of them using the MOPAC program with the PM3 Hamiltonian. The calculated heats of formation are 8.41038 kcal mol^{-1} for the *trans* isomer and 8.16583 kcal mol^{-1} for the *cis* isomer. Thus, the PM3 calculations predict a difference in heats of formation of 0.25545 kcal mol^{-1} and hence a distribution of about 60 : 40 in favour of the *cis* isomer. Thus the calculations confirm qualitatively and quantitatively the ^{19}F n.m.r. observations, in the event that the isomer ratio is thermodynamically determined (i.e. product stability dominates any kinetic control). This is very reasonable in the present case, since the final dehydration step in the imine formation is reversible, favouring the thermodynamic outcome.

Furthermore, the calculations are very helpful in the attribution of the ^{13}C n.m.r. spectrum of the monomer since the peaks of both isomers are also in the ratio 60 : 40. The spectrum of the mixed *cis* and *trans* isomers is reported in *Figure 4* and *Table 1* presents the assignments of the chemical shifts for the different C atoms of each isomer.

I.r. analysis of the monomer was also performed and the spectrum is presented in *Figure 5*. A large absorption band is observed between 3700 and 2300 cm^{-1}. This band is due to hydrogen bonding between the hydroxyl group and either the nitrogen atom of the ketimine bond or the fluorine atom. The C=N stretching band is located at 1590 cm^{-1} (ref. 11). The purity of the monomer is also verified by the absence of any observable C=O stretching band around 1650 cm^{-1} (ref. 12).

Synthesis and characterization of the PEK prepolymer—K_2CO_3 route. The synthesis of ketimine PEEK prepolymer is widely described in the literature. All synthesis procedures involve the reaction of *N*-phenyl-(4-fluoro-4′-hydroxydiphenylmethylene) imine and hydroquinone in the presence of finely ground K_2CO_3.

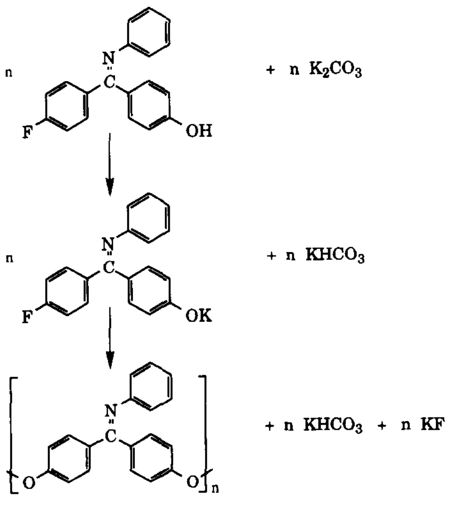

Figure 6 Synthesis of the PEK prepolymer

Therefore, the synthesis of ketimine PEK prepolymer was first attempted in NMP at 170°C in the presence of K_2CO_3. The reaction scheme is outlined in *Figure 6*. The change in the molecular weights was followed during the polycondensation reaction. After 24 h, only the trimer was obtained in the reaction solution. Some hypotheses can be put forward in order to explain this low conversion level.

1. Due to the reduced temperature (170°C instead of 300°C), the rate of formation of the phenate or of the substitution reaction itself might be reduced.
2. Due to decomposition of the bicarbonate at 170°C, water might be present within the reaction medium. This water could partly hydrolyse the ketimine bonds and ketone groups may be re-formed. The partial hydrolysis of the prepolymer could then lead to premature precipitation.
3. Due to acid/base equilibrium between $KHCO_3$ and K_2CO_3, some hydroxyl ions will be formed. These hydroxyl ions are good nucleophiles and the substitution of the fluorine chain ends might thus occur, limiting the molecular weight of the prepolymer.

—potassium methylate route. In order to prevent the problems due to the possible presence of water, another route was considered. This route involves the synthesis of the phenate by reaction between the phenol and potassium methylate in methanol prior to the dissolution of the monomer in NMP.

The polymer obtained after 24 h of reaction presents a wide molecular weight distribution ($H = 2.4$) with a peak molecular weight of 7000 Dalton. However, some unreacted monomer remains in the reaction solution.

Although the conversion level for the methylate route is much higher than for the K_2CO_3 route, the polycondensation reaction is still very slow in comparison with the results obtained for the PEEK prepolymer.

—factors influencing the polycondensation reaction. In general, an electron-withdrawing ring substituent is required to induce the nucleophilic aromatic substitution of halogen by a phenoxide ion[13]. The substitution mechanism is a bimolecular process (S_N2) involving an intermediate where the carbon has an sp^3 hybridization. This intermediate is known as the Meisenheimer complex.

In the case of polycondensation of PEK or PEEK prepolymer, the fluoride atom is sufficiently activated by the ketimine bond to undergo a nucleophilic aromatic substitution[14]. The structure of the relevant Meisenheimer complex is given in *Figure 7*.

However, the presence of an electron-withdrawing group on the phenoxide ring slows down the substitution[13]. Thus in the case of *N*-phenyl (4-fluoro-4′-hydroxydiphenylmethylene) imine, the ketimine bond

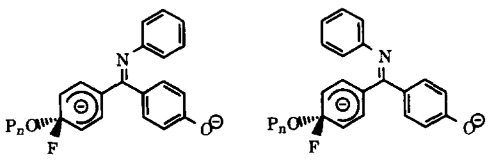

Figure 7 Structure of the Meisenheimer complex

also plays the role of a deactivating group *vis-à-vis* the phenoxide ion. This could explain the decreased rate of the polycondensation reaction compared with the PEEK prepolymer where the diphenol (i.e. hydroquinone) is not deactivated.

Characterization of the PEK prepolymer. I.r. analysis of the prepolymer was performed and the spectrum is presented in *Figure 8*. A large peak due to C=N stretching is observed at $1590\,cm^{-1}$. The C–O peak characteristic of ether linkages formed during the polycondensation reaction is located at $1240\,cm^{-1}$. However, the prepolymer seems to be partially hydrolysed, as a peak due to C=O stretching is observed at $1650\,cm^{-1}$.

Hydrolysis of the PEK prepolymer. After hydrolysis, the polymer was again analysed by i.r. (*Figure 9*). The vanishing of the C=N peak and the appearance of a large C=O stretching peak at $1650\,cm^{-1}$ confirm the hydrolysis of the polymer. The i.r. spectrum of the hydrolysed polymer (*Figure 9*, spectrum A) is similar to that of a PEK polymer made by the conventional high-temperature route (*Figure 9*, spectrum B).

Conclusions

The synthesis of a poly(aryl ether ketimine) oligomer is reported. Presumably due to its amorphous character, the ketimine PEK prepolymer was soluble in common organic solvents. The poly(aryl ether ketimine) can be readily hydrolysed to the poly(aryl ether ketone). However, the rate of the ketimine PEK condensation is decreased compared with that of the equivalent ketimine PEEK condensation due to the deactivation of the

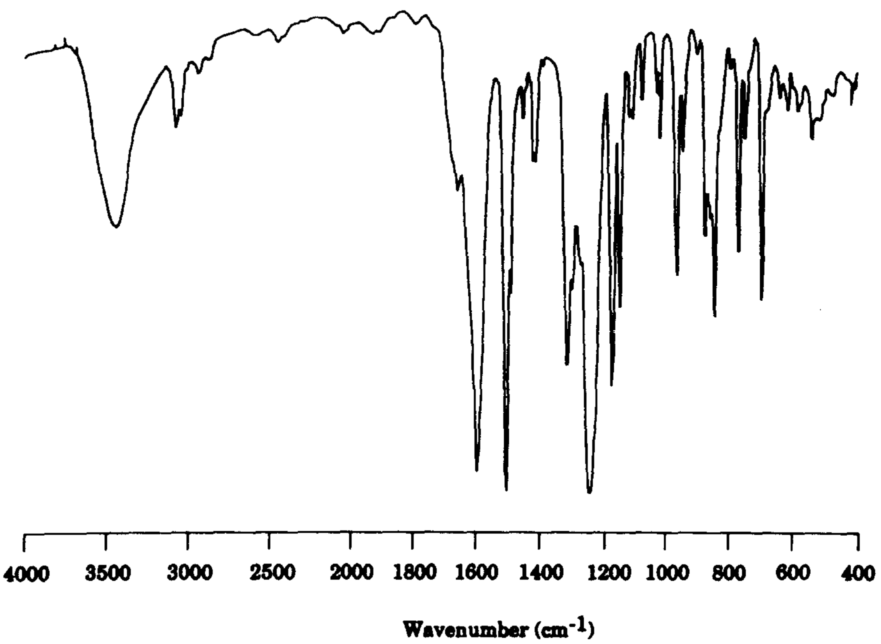

Figure 8 I.r. spectrum of the PEK prepolymer

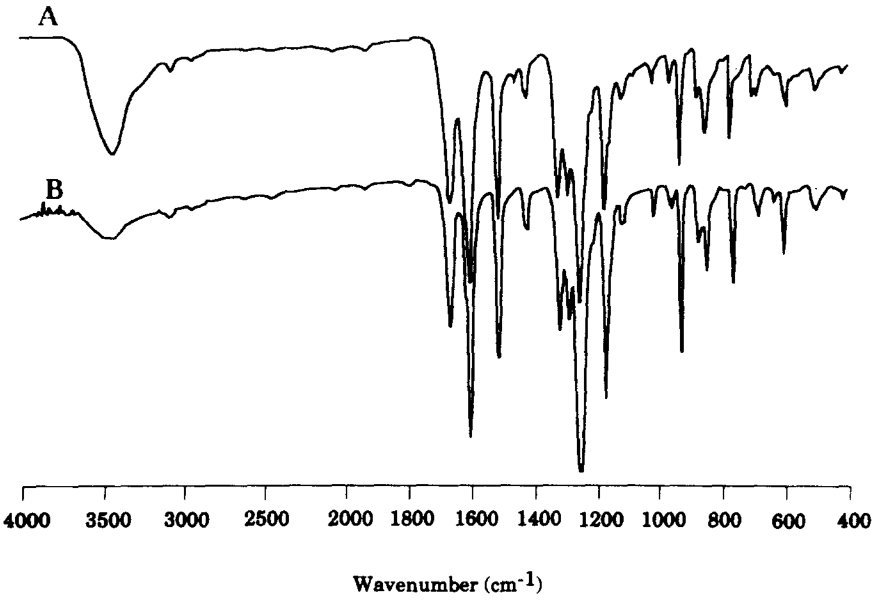

Figure 9 I.r. spectra of the PEK polymer after hydrolysis (A) and a PEK polymer made by a conventional high-temperature route (B)

reactive intermediate (Meisenheimer's complex). Therefore, the procedure described here cannot be used to synthesize PEK polymer of high molecular weight.

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