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Aromatic homopolymers obtained by precipitation polycondensation:
1. Synthesis of naphthalene-containing polyketones

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High molecular weight film-forming semicrystalline aromatic polyketones with a regular structure were obtained by precipitation electrophilic Friedel–Crafts polycondensation of 2,6-naphthalenedicarboxylic acid chloride with diphenyl ether, 1,4-bis(*p*-phenoxy)benzophenone and 1,4-bis(*p*-phenoxybenzoyl) benzene. Using ^{1}H and ^{13}C n.m.r. spectroscopy, the polyketones obtained were shown to be linear with *para*-substituted arylene fragments in the main chain. These polymers are soluble in strong protic acids and in common organic solvents, such as dichloroacetic acid and $CHCl_3/CF_3CO_2H$ mixtures. Depending on the chemical structure, these 'as-made' polyketones were found to show multiple melting behaviour on heating.

(**Keywords: poly(aryl ether ketone)s; synthesis; precipitation polycondensation**)

INTRODUCTION

Poly(aryl ether ketone)s (PAEKs) are a family of semicrystalline, high temperature, high performance engineering thermoplastics[1–3]. They display an excellent combination of physical, thermal and mechanical properties and solvent resistance characteristics. Intensive study of PAEKs was started at the beginning of the 1980s. Such work has been significantly enhanced since 1985 through the commercialization of poly(aryl ether ketone) (PEEK) by ICI and in the late 1980s through the commercialization of poly(ether ketone ether ketone ketone) (PEKEKK) (Ultrapek) and poly(ether ketone ketone) (PEKK) (Hostatek) by BASF and Hoechst, respectively. The poly(aryl ether ketone) Stilane has been produced since 1980 by Raychem.

Because of their high thermal stability and semicrystalline nature, PAEKs are a convenient and interesting subject for structural and morphological studies. The crystallization and melting behaviour of PAEKs have received special attention. The polyketones quenched from the melt and either annealed at a temperature between the glass transition (T_g) and the melting temperature (T_m) or cooled stepwise from the melt have been found to exhibit double melting peaks, as observed for other polymers[4,5]. The number of melting peaks observed has changed with the course of time. Thus, first it was two peaks[6–13], then four[14], five[15] and even 10 peaks[16] in the melting curve.

However, considerable controversy remains concerning the origin of the multiple melting endotherms in the melting curves of semicrystalline polymers. To some extent, the variations in the interpretation of multiple melting peaks can be attributed to the fact that the structure and, as a consequence, the melting behaviour are strongly affected by the sample history and especially its thermal treatment, which are not identical in the different published works. Nevertheless, the question of the origin of that multiple melting is left open. It should be noted that the investigations have mainly focused on PEEK, and to a lesser extent on other commercially available polyketones[14,17].

From this point of view, the synthesis and investigation of new polyketones would be very useful for a better understanding of the phenomenon and for a more rigorous structure–property correlation of this very interesting class of polymers. Taking into account that polyketones (e.g PEEK) suffer from poor creep behaviour above their relatively low glass transitions, the synthesis of semicrystalline polyketones with increased T_g is of high interest. For example, it is common knowledge that introduction of bulky groups in the main chain leads to an increase in the temperature of the glass transition. Also, the incorporation of side groups leads to an increase in T_g. However, in this case low crystallinity or (more often) amorphous polymers are obtained. Intensive study of amorphous polymers (called 'cardo') has been carried out by Russian scientists[18]. In the present study, naphthalene was chosen as the bulky group because it offers good advantages concerning the stability and thermal resistance of the resulting polymer.

Furthermore, a convenient synthetic method, called

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precipitation polycondensation[19,20], has recently been developed for the preparation of low solubility or even insoluble polymers, so that the synthesis of high molecular weight aromatic polyketones by this approach is possible.

The work presented here involves the preparation of the polyketones with the structures presented in *Figure 1*. Although wholly aromatic polyketones with naphthalenic groups have been mentioned in the patent literature[21,22], their study and properties have not been reported. The synthesis and characterization of these polyketones are the main topics of this report.

EXPERIMENTAL

Materials

1,2-Dichloroethane (DCE, Aldrich) and diphenyl ether (DPE, Aldrich) were distilled prior to use. 2,6-Naphthalenedicarboxylic acid, trifluoroacetic acid, thionyl chloride and chloroform were used as received. Aluminium trichloride was sublimed prior to use. 1,4-Bis(*p*-phenoxy)benzophenone was prepared by the reaction of DPE with phosgene in the presence of aluminium trichloride. The crude product was recrystallized from ethanol to afford 1,4-bis(*p*-phenoxy)benzophenone as white crystals (melting point 146°C, 74% yield). 1,4-bis(*p*-phenoxybenzoyl)benzene was prepared as described elsewhere[23]. The pure dichloroanhydride of 2,6-naphthalenedicarboxylic acid was obtained by the usual treatment of 2,6-naphthalenedicarboxylic acid with thionyl chloride followed by recrystallization of the crude product from DCE (melting point 189–190°C, 86% yield).

Polycondensation

A typical preparative procedure for polyketone **2** is described hereafter. Other polymers were also obtained in a similar manner.

Into a 250 ml flask equipped with magnetic stirrer, thermometer, nitrogen inlet and outlet tubes were placed 5.06 g of the dichloroanhydride of 2,6-naphthalenedicarboxylic acid (0.02 mol), 7.32 g of 1,4-bis(*p*-phenoxy) benzophenone (0.02 mol) and 135 ml of DCE. After the solution had been cooled to below −20°C, 10.13 g of $AlCl_3$ (0.076 mol) was added and the reaction mixture was stirred for 1 h. Thereafter, the temperature was raised to 20°C over 2 h and reaction was continued at this temperature for 20 h. The suspension obtained was filtered. The precipitate was washed with methanol and extracted with boiling methanol for 20 h and allowed to dry in air. The air-dried product was heated at 100°C overnight under vacuum to give 10.67 g of the polymer (91.5% yield). The intrinsic viscosity of the polymer, measured in concentrated sulfuric acid at 25°C (0.5 g per 100 ml), was 1.39 dl g^{-1}.

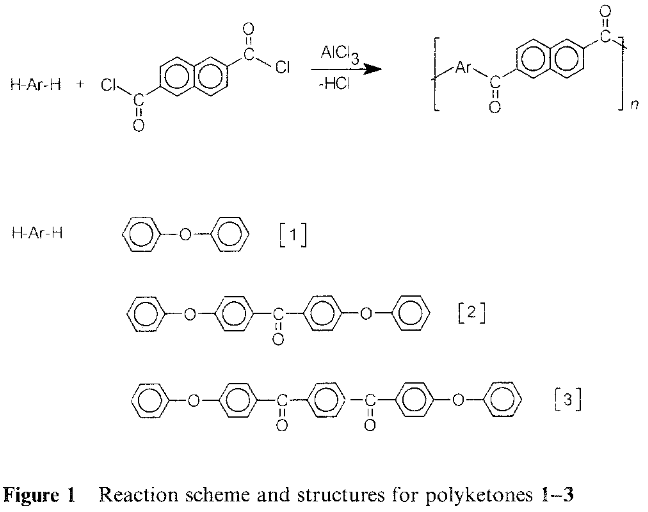


Figure 1 Reaction scheme and structures for polyketones 1–3

Measurements

^{13}C and ^{1}H n.m.r. spectra of the polymers were recorded using a Bruker AMX-300 operating at 75.47 MHz for ^{13}C. The polymers were dissolved in a $CDCl_3$/CF_3CO_2H mixture (50/50 v/v) to give 10% (w/v) solutions. We used a pulse width of 4.6 μs, an acquisition time of 1.376 s; a spectral width of 23 810 Hz, a pulse delay of 2.376 s and line broadening of 1 Hz. The number of accumulated scans was typically 3000, and an accumulation of 62k points was Fourier transformed.

Differential scanning calorimetry (d.s.c.) curves were run on a Perkin–Elmer DSC-4 device joined to a TADS workstation. The experiments were performed under N_2.

Thermogravimetric analysis (t.g.a.) was carried out on a Setaram TG-DSC-111. The heating rate was 5°C min^{-1} below 400°C and 10°C min^{-1} above 400°C. The samples were placed in platinum crucibles and the sample size was chosen in order to give a maximum weight loss of 5 mg.

I.r. spectra of polyketone films were recorded with a Bruker IFS 113 v Fourier transform i.r. spectrometer working under primary vacuum.

The crystalline aspect was examined by wide angle X-ray scattering (WAXS) on the 'as-made' and annealed samples. The X-ray data of unoriented samples were collected on the double-focusing monochromator mirror camera x33 of the European Molecular Biology Laboratory (EMBL)[24] on the storage ring DORIS of the Deutsche Elektronen Synchrotron (DESY), Hamburg, using a wavelength of 0.15 nm. The data were recorded using a CAMAC data acquisition system[25] and a linear position sensitive gas (Ar/CO_2 80/20 mixture) detector with delay line read-out. Small angle X-ray scattering (SAXS) experiments were also performed on an ultra-small angle scattering camera which can resolve superstructures up to 600 nm[26].

RESULTS AND DISCUSSION

The three polyketones[1–3] can be prepared via two routes involving nucleophilic or electrophilic polycondensation. We chose the electrophilic procedure based on the polycondensation of aromatic hydrocarbons with 2,6-naphthalenedicarboxylic acid chloride in the presence of aluminium trichloride according to *Figure 1*.

Polymer syntheses were carried out using the precipitation polycondensation method (PP method)[19,20]. The term refers to a category of polymer synthesis wherein polymer particles (or polymer/catalyst complexes) are formed from an initially homogeneous reaction mixture. The polymer-forming reaction proceeds in both the formed particles and solution. Although this kind of polymer synthesis involves the

Figure 2 Micrograph of 'as-made' particles of polyketone **2**

precipitation of polymer/$AlCl_3$ complexes during the reaction, the experimental conditions (e.g. molar ratio, change in viscosity of polymer with reaction time, monomer concentration) have similar effects as in the usual solution polycondensation. Because the polymer-forming reaction proceeds in both phases (in the precipitate and the solution), high molecular weight polymers are obtained. This is of great importance in the case of low solubility or even insoluble polymers.

Using the PP method, polyketones **1–3** were obtained as colourless particles. As can be seen from *Figure 2*, the particles of polyketone **2** are aggregates of smaller particles, characterized by a nearly equal size. Polyketones **1** and **3** give similar aggregates. It should be pointed out that the polymer synthesis occurs in the presence of a large amount of aluminium trichloride. Nevertheless, it is quite remarkable that the catalyst residues are easily removed from these aggregates by extraction with solvents. After such treatment, the polymer particles contain only a few parts per million of aluminium trichloride. The resulting polymers are soluble and their solubility behaviour is typical of semicrystalline PAEKs. They are insoluble in hot chlorinated solvents, tetrahydrofuran and a variety of dipolar aprotic solvents including dimethylacetamide (DMAc) and *N*-methylpyrrolidone. The polyketones are soluble in strong protic acids, such as aqueous sulfuric acid and dichloroacetic acid, and in $CHCl_3/CF_3CO_2H$ mixtures (*Table 1*). The high molecular weights of the polyketones were verified by inherent viscosity measurements in concentrated sulfuric acid. A $CDCl_3/CF_3CO_2H$ mixture was found to be a convenient solvent for n.m.r. measurements.

The solution ($CDCl_3/CF_3CO_2H$) ^{13}C n.m.r. spectrum of polyketone **2** is shown in *Figure 3a*. Except for the most downfield absorbances at 201.87 and 201.19 ppm which can be assigned to the carbonyl carbon atoms, an unambiguous assignment for the remaining absorbances of the carbon atoms of the benzene and naphthalene moieties is quite problematic. The reason is the unavailability of the necessary substituent chemical shift values in the $CDCl_3/CF_3CO_2H$ solvent system for various benzene and naphthalene ring substituents. However, using the known data for benzene rings some assignments can be made (*Table 2*).

Additional evidence concerning the structure of the linear polyketone was obtained by using n.m.r. spectroscopy with a polarization transfer sequence (DEPT 90). The technique allows one to distinguish the carbon atoms connected to one hydrogen atom. It is easy to calculate that polyketones containing *para*-substituted aromatic fragments in the main chain should possess seven signals in such a spectrum (C-2, C-6, C-22, C-24; C-3, C-5, C-21, C-25; C-8, C-12, C-16, C-18; C-9, C-11, C-15, C-19; C-31, C-36; C-28, C-33; and C-29, C-34). If the polymer was branched with *ortho* or *meta* substitution in the main chain, for example, additional signals would be observed. Because the spectrum reveals only seven signals (*Figure 3b*), it can be concluded that only *para* substitution occurs in the main chain.

The ^1H n.m.r. spectrum of polyketone **2** is shown in *Figure 3c*, and assignments for the observed signals are given. The singlet at 8.47 ppm arises from protons H-31 and H-36. The doublet at 7.34 ppm belongs to protons H-3, H-5, H-8, H-12, H-16, H-18, H-21 and H-25. The doublet at 8.21 ppm arises from protons H-33 and H-28. The remaining protons appear as overlapping doublets between 7.99 and 8.09 ppm. The small signal near 7.30 ppm is peculiar to impurities contained in $CDCl_3$.

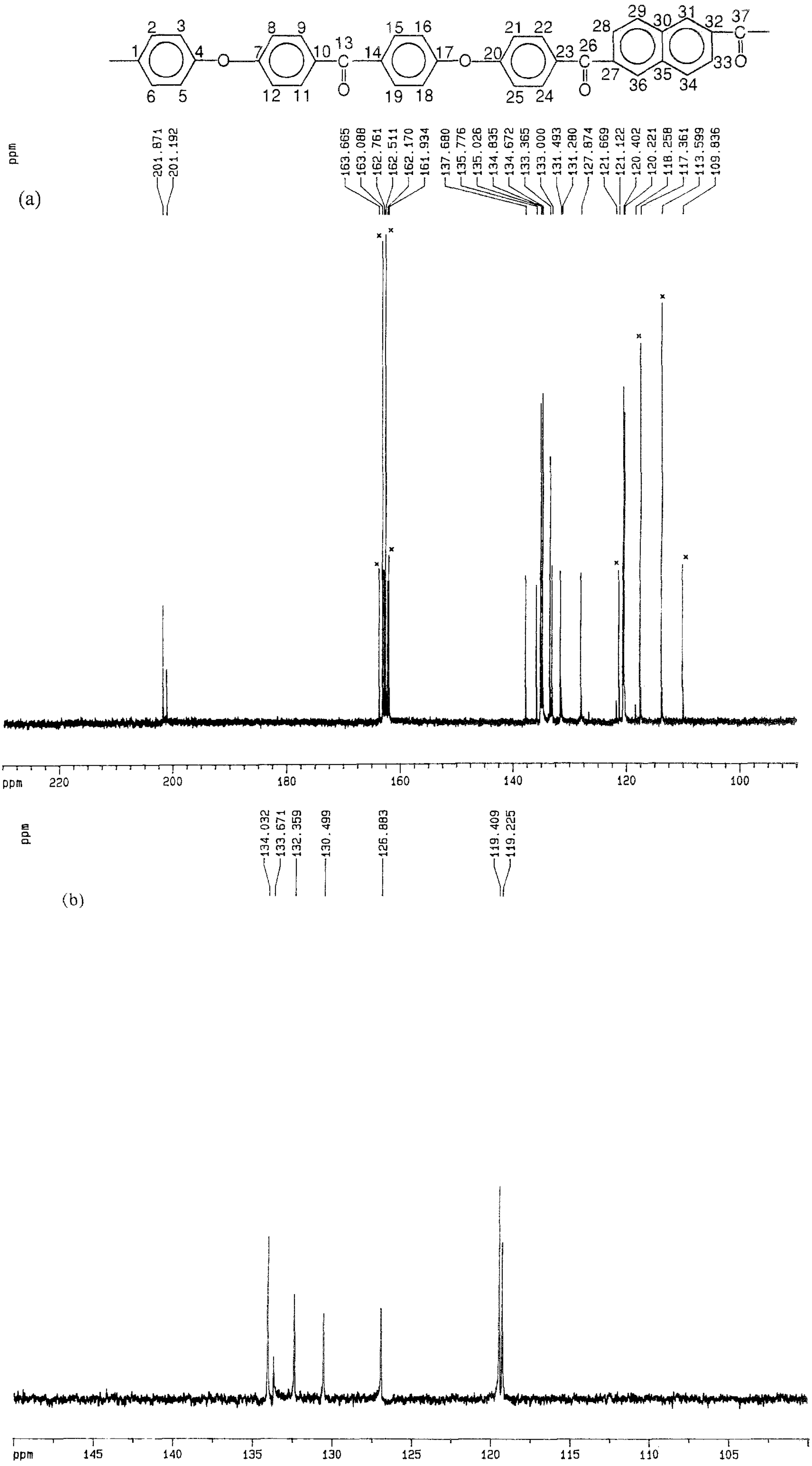
Table 1 Viscosities and solubilities of polyketones **1–3**

Polyketone	Yield (%)	η_{inh}^{a} (dl g^{-1})	Solubility^{b,c}					
			H_2SO_4	MSA	$CHCl_3/CF_3CO_2H$	DCAc	*o*-ClPh	*m*-Cr
1	90.7	2.23	++	+−	++	+	+−	+−
2	91.5	1.39	++	++	++	+	+−	+−
3	92.4	1.66	++	+−	++	+	+−	+−

[a] Measured at a concentration of 0.5 g dl^{-1} in 94.5% sulfuric acid at 25°C

[b] Solubility: ++, soluble at room temperature; +, soluble when heated: +−, partially soluble or swollen

[c] MSA, methanesulfonic acid; DCAc, dichloroacetic acid; *o*-ClPh, *o*-chlorophenol; *m*-Cr, *m*-cresol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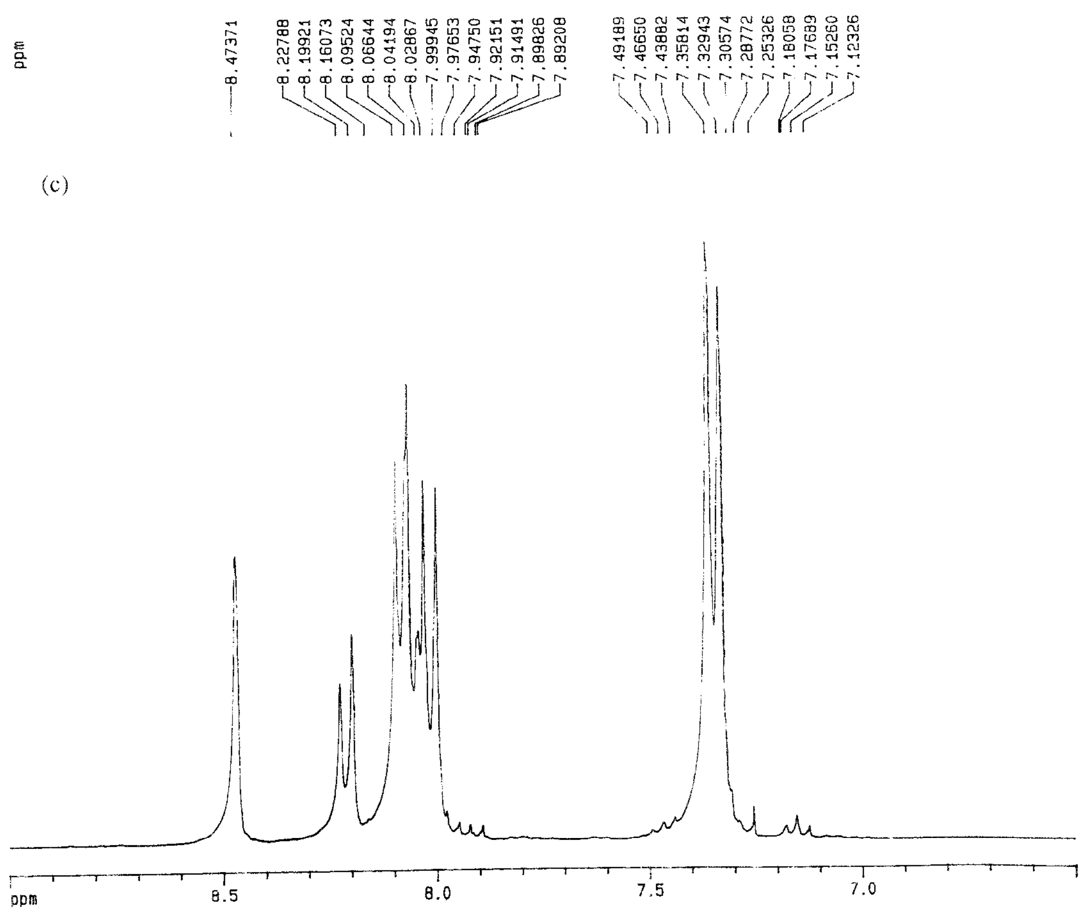

Figure 3 The n.m.r. spectra of polyketone **2** in $CDCl_3/CF_3CO_2H$ at 25°C: (a) the ^{13}C n.m.r. spectrum (the two sets of quadruplets from CF_3CO_2H solvent are marked with crosses; a triplet for $CDCl_3$ is also detected at 76.9 ppm); (b) the DEPT 90 ^{13}C n.m.r. spectrum; (c) the ^1H n.m.r. spectrum

The absence of other (unassingnable) peaks should be taken as proof of the degree of purity achieved in the polyketone synthesis. Therefore, within the sensitivity of this method, the n.m.r. data point to *para* substitution of the main-chain arylene fragments. It should be noted that *para* substitution in the main chain does not exclude the possibility of macrocycles. Indeed, the formation of cyclic tetramers during the homopolycondensation of *p*-phenoxybenzoyl chloride at low monomer concentration has been observed[27]. Taking into account that cyclic (macrocyclic) molecules should possess different solubility in comparison with linear polymers, polyketone **2** was dissolved in a $CDCl_3/CF_3CO_2H$ mixture (concentration of 6% w/v) and the solution was poured into methanol. The precipitated polymer was then successively extracted with hot methanol, benzene and acetone. The polymer was then dried and analysed. The yield of the polymer was 97.5% and the inherent viscosity was 1.31 $dl\,g^{-1}$. The ^{13}C n.m.r. spectrum of the so-obtained polymer was the same as the spectrum of the initial product.

Table 2 Chemical shifts and multiplicities of the peaks in the ^{13}C n.m.r. spectrum of polyketone **2** in $CDCl_3/CF_3CO_2H$

Assignment	δ (ppm)
C-26, C-37	201.87 s
C-13	201.19 s
C-4, C-20	162.76 s
C-7, C-17	162.17 s
C-27, C-32	137.68 s
C-30, C-35	135.77 s
C-9, C-11, C-15, C-19	135.03 d
C-22, C-24, C-2, C-6	134.83 d
C-23, C-1	134.67 s
C-10, C-14	133.36 s
C-31, C-36	133.00 d
C-28, C-33	131.49 d
C-29, C-34	127.84 d
C-8, C-12, C-16, C-18	120.40 d
C-3, C-5, C-21, C-25	120.22 d

The i.r. spectra of the 'as-made' and reprecipitated polyketones are almost identical (*Figure 4*). The slight differences at 1603, 1286, 1200 and 934 cm^{-1} cannot be attributed, in our opinion, to any significant structural changes. Hence, polyketone **2** consists of strictly alternating sequences of hydrocarbon and naphthalenic components. A similar procedure was applied to confirm the structures of polyketones **1** and **3**, where linear structures were also established.

As stated by many authors[28-31], PAEKs have very similar structures involving a two-chain zigzag orthorhombic packing, the ether linkages and ketone groups being crystallographically equivalent. Accordingly, PAEKs maintain the space group of poly(*p*-phenylene oxide)(PPO), namely *Pbcn*. The presence of a proportion of ketone links leads to a slight variation of the *b* and *c* parameters[30]. From this point of view, the sequence of ether and ketone linkages correlates polymer **2** with PEKEKK ($a = 0.774$ nm, $b = 0.604$ nm, $c = 1.027$ nm) and polymers **1** and **3** with PEKK ($a = 0.769$ nm, $b = 0.606$ nm, $c = 1.005$ nm). Let us note that PEKK under appropriate conditions exhibits

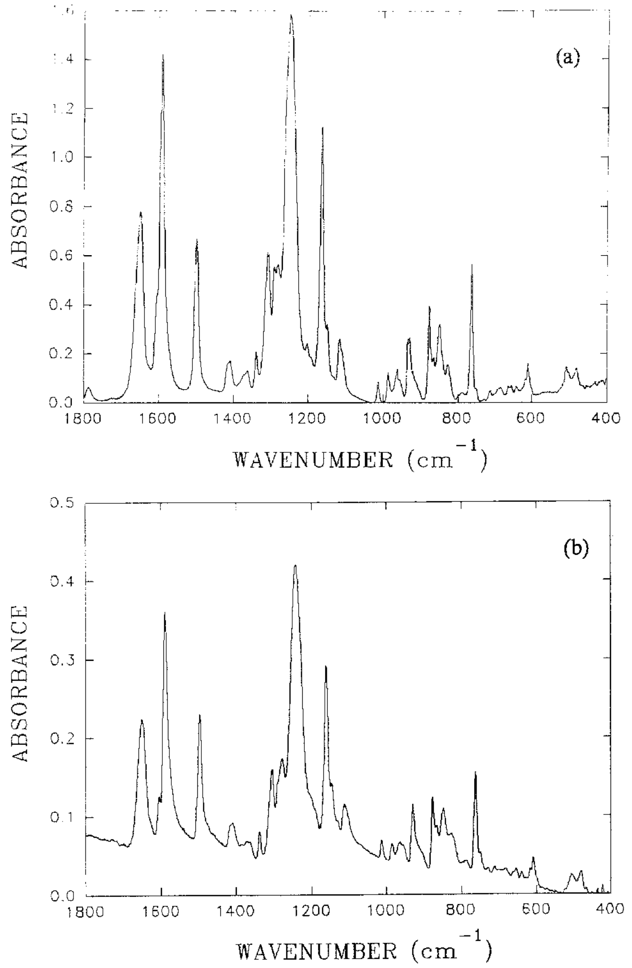

Figure 4 Fourier transform i.r. spectra of films of polyketone **2**: (a) 'as-made'; (b) reprecipitated

polymorphism[30,32], mainly characterized by a different packing of the chains and thus by a different unit cell ($a = 0.417$ nm, $b = 1.134$ nm, $c = 1.008$ nm). The WAXS patterns of polyketones **1–3** are presented in *Figure 5* and compared to the WAXS pattern of a PEEK sample annealed at 320°C ($a = 0.777$ nm, $b = 0.591$ nm, $c = 0.999$ nm, 36% weight crystallinity[33]). It is clear that the 'as-made' precipitated particles are partially crystalline, with a crystallinity somewhat lower than that of the reference PEEK sample. With the hypothesis that the polyketones **1–3** could also adopt a structure close to that of PPO, possible unit cell dimensions were evaluated which are close to the actual values for the three samples ($a = 0.76$ nm, $b = 0.61$ nm, $c = 1.08$ nm). The quite high value for c could be the result of the greater size effect of the naphthalenic substituent compared to the phenyl group. These proposals must be supported by a structural study on oriented samples. SAXS experiments were also performed on the particles, but no superstructure was detected in this manner, even at a scale of 100 nm. This could be related to the fact that these particles are directly obtained during the chemical synthesis, thus implying an unusual 'growth' mechanism. The morphology of these polyketones should be studied using various semicrystalline samples obtained either from the glassy state or from the melt.

The synthesized polyketones were investigated with respect to their thermal degradation behaviour using t.g.a. The results of these analyses are summarized in *Figure 6*. They prove the generally excellent thermal stability of these aromatic polyketones. The thermograms obtained in air for the three synthesized polyketones are shown in *Figure 6a*. The weight loss of polyketones **1** and **3** starts at almost the same temperature, i.e. around 450°C, while the weight loss of polyketone **2** begins at a temperature higher by about 25°C. The weight loss is of the order of 2% per 10°C around 550°C. At 800°C, the char yield is 52% for polyketone **2**, the most stable product, whereas the loss is 10–15% higher for polyketones **1** and **3**. The same tendency appears from the t.g.a. curves recorded when the polyketones are under vacuum (*Figure 6b*). However, the weight loss starts at higher temperatures (about 500°C for **1** and **3** and 525°C for **2**). The losses are especially important around 550°C (5% for each 10°C), but we observe final weight losses of 40–45% at 800°C. This study shows that the thermal stability of the 'as-made' polyketones is better for polyketone **2** than for samples **1** and **3**. It is very important to emphasize that t.g.a. curves do not reveal weight losses which could be attributed to the presence of solvent in the polymers.

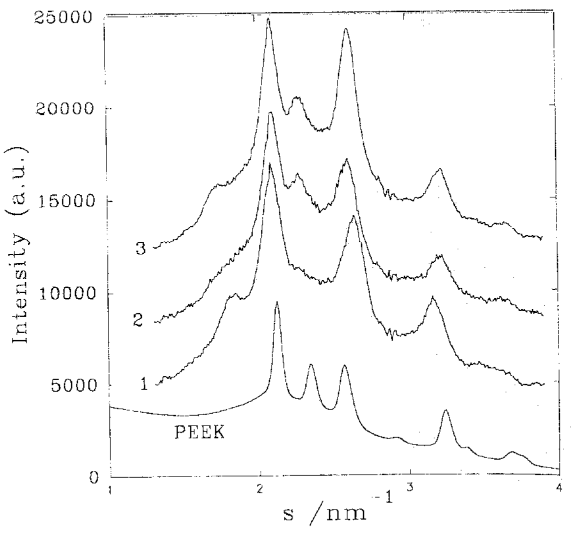

Figure 5 WAXS patterns of polyketones **1–3** compared to the pattern for a PEEK sample annealed at 320°C

The d.s.c. analysis of particles of polyketone **1** indicates a melting point of 391°C (*Figure 7*, curves A and B; *Table 3*). From the d.s.c. curve for the quenched sample, we see a glass transition at 199°C, a cold crystallization peak at 276°C and a melting peak at 385°C. The enthalpy of the exothermic process is nearly equal to the enthalpy of the endotherm (*Table 3*). Because of the large difference in temperature between the cold crystallization and the melting of stiff-chain semicrystalline polymers, the enthalpy of the transition cannot be taken as a constant as is usually assumed. The phase transition enthalpy involved in melting is basically temperature dependent, because the heat capacities of the crystalline and liquid phases do not follow the same dependence on temperature. Therefore, the given values of these variations in enthalpy can only be used as a crude estimate. The d.s.c. analysis of polyketones **2** and **3** (*Figure 7*, curves C–F) reveals unexpected results. It is seen that polyketone **2** has two melting peaks in the first heating stage. The melting curve (D) of the quenched sample shows a glass transition at 180°C, a cold

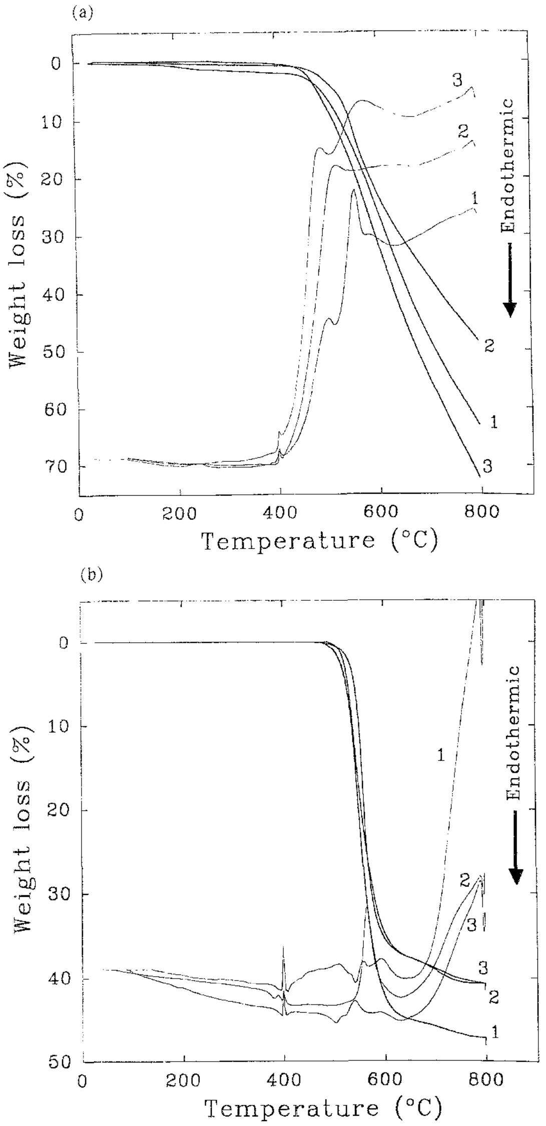

Figure 6 T.g.a. curves of polyketones **1–3**: (a) in air; (b) under vacuum

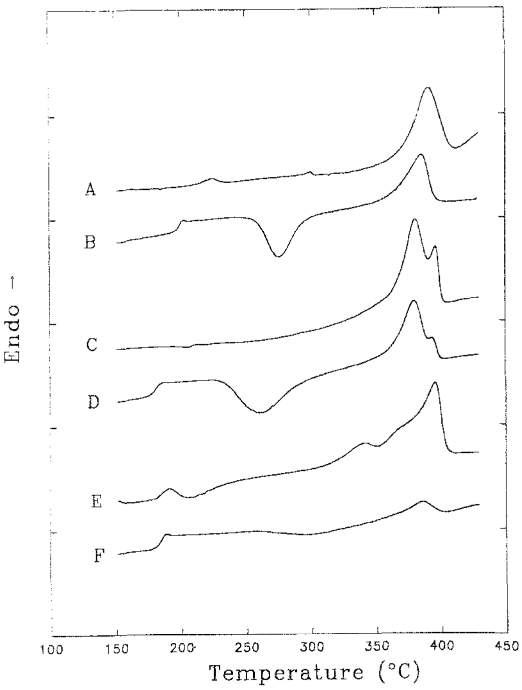

Figure 7 First (heating rate 20°C min^{-1}) and second d.s.c. scans of the three 'as-made' polyketones: **1**, curves A and B; **2**, curves C and D; **3**, curves E and F. The samples were quenched after the first melting stage

crystallization at 260°C and two well-resolved melting peaks at 380 and 393°C. The enthalpies of cold crystallization and melting are nearly equal. The melting behaviour of polyketone **3** is much more complicated. The first heating stage (E) exhibits an endotherm followed by a small exotherm at 190°C, and three melting peaks at 341, 369 and 395°C. The second heating stage (F) reveals a glass transition at 184°C, a broad peak of cold crystallization and a melting peak at 385°C. The d.s.c. curves were recorded several times on different samples of each polymer in order to be quite sure of the reproducibility of the data.

It is well known that 'as-made' aromatic copolyketones (or poly(ether ketone-*co*-sulfone)s) often show double melting behaviour[34]. But, as stated above, the three polyketones **1–3** are polymers with well-defined, regular structures. Multiple melting behaviour has been reported for aromatic polymers prepared from diphenyl ether, terephthalic acid and isophthalic acid[35,36]. It is believed that a polymer containing terephthalic acid and isophthalic fragments in a 50/50 ratio represents a homopolymer. Indeed, such a polymer with a regular structure can be obtained in at least two different ways using the electrophilic route. Unfortunately, there is no information about the conditions of synthesis or the polyketone spectral characteristics in the literature[35,36]. Furthermore, polyketones with naphthalenic groups have been obtained by nucleophilic polycondensation of bisphenols with appropriate dihalide monomers[37,38]. Such polyketones are mostly amorphous (or exhibit a low temperature single melting peak).

The chemical structures of the polyketones and their conditions of synthesis seem to be important factors which must affect the polymer morphology. The melting behaviour of the polyketones is strongly dependent on

Table 3 Melting data[a] for polyketones **1–3**

Polyketone	Scan	T_g (°C)	T_c (°C)	T_m (°C)			$-\Delta H_c$ (J g^{-1})	ΔH_m (J g^{-1})
1	A			391				29.4
	B	199	276	385			−18.3	22.4
2	C			381	396			48.9
	D	180	260	380	393		−28.6	29.9
3	E			341	369	395		50.4
	F	184	277	385			−5.6	6.2

[a] T_g, T_c and T_m are the glass transition temperature, the crystallization temperature (maximum of the endotherm) and the melting temperature, respectively. ΔH_c and ΔH_m are the heats of crystallization and melting, respectively

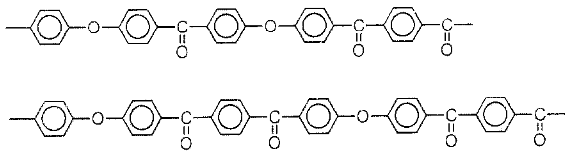

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Figure 8 Structures of polyketones **4** and **5**

the polymer structure. Thus, an increase in the length of the hydrocarbon component leads to multiple melting peaks. On the other hand, polyketone **4** (*Figure 8*), obtained by reaction of terephthaloyl chloride with 1,4-bis(*p*-phenoxy)benzophenone using the PP method, is representative of such melting behaviour. Moreover, the d.s.c. trace of polyketone **5**, made from terephthaloyl chloride and 1,4-bis(*p*-phenoxybenzoyl)benzene (*Figure 8*), reveals only one melting peak. Therefore, the multiple melting peaks of polyketones **2** and **3** could be the result of the presence of naphthalenic fragments in the repeat unit, or more exactly the result of a combination of naphthalenic fragments and hydrocarbon components.

In addition to the chemical structure, reaction conditions may also play a significant role. Thus, it is logical to suggest that precipitation of the particles consisting of polymer/$AlCl_3$ complexes at the beginning of the synthesis is caused by the low solubility of the complexes in the reaction medium. The polymer synthesis therefore occurs in a two-phase system and the precipitation of particles can be influenced by already preformed ones. In fact, this synthetic stage can be considered to some extent as a template (replica or matrix) polymerization. The outstanding characteristics of the template polymerization are (1) that interaction (or complex formation) can occur between two polymers, (2) that the polymerization rate is influenced by the template concentration and (3) that the structural and conformational features of the daughter polymers are affected by the template. Typically, template polymerizations occur in the presence of polymers which are expected to serve as templates by hydrogen bonding, electrostatic, charge transfer and hydrophilic interactions. These so-called template polymerizations, however, seem hitherto not to be strictly controlled, because the interaction between the monomers and the template polymer might be realized not so specifically. Nevertheless, it might be expected that electrostatic and charge transfer interactions would dominate in the electrophilic precipitation polycondensation. Furthermore, the polymerization rate is usually accelerated by the template. In the present case it is difficult to make conclusions about any reaction rate change. However, the reaction rate in precipitation polycondensation is evidently rather high because of the high local concentration of functional groups in the precipitated particles.

Finally, apart from an association between polymer and template, an additional controlling factor may come into play when polyketone synthesis is carried out in chlorinated aliphatic solvents. It is well known that aromatic polyketones (e.g. PEEK) interact very strongly with methylene chloride and chloroform[39]. The main effects of solvent absorption are usually plasticization, crystallization and, sometimes, chemical attack. For example, crystallization takes place in solid samples of amorphous PEEK through the influence of sorbed CH_2Cl_2[40]. As the d.s.c heating traces of polyketones **1** and **2** do not show any crystallization exotherms, it can be concluded that these two polyketones were already crystallized during the polycondensation. Therefore, solvent-induced crystallization takes place in the PP polyketone synthesis. The melting curve of polyketone **3** is more complicated and it is difficult to give definite conclusions in this case.

CONCLUSION

The analysis of the precipitation polycondensation method has allowed us to distinguish the following factors which can affect the conformations and packing of polymer chains in crystals: (1) the initial crystallization (precipitation) of polymer chains from homogeneous solution (unfortunately we have no morphological information about the initial stage of the precipitation); (2) the crystallization of polymer from homogeneous solution induced by preformed polymer complexes; (3) template effects; and (4) crystallization induced by nucleating heterogeneities from undissolved or unreactive $AlCl_3$. Obviously, all these processes can be influenced by the chlorinated solvent used. It is very likely that a combination of all the above-mentioned factors affects the chain conformations.

Studies of other aspects of these polyketones such as crystallization during heating, crystal structure, morphology and thermal behaviour are now in progress.

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