# Aromatic polymers obtained by precipitation polycondensation, 2[a]

# Synthesis of poly(ether ketone ether ketone ketone) (PEKEKK)[b]

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SUMMARY:
   A high molecular weight, linear aromatic poly(ether ketone ether ketone ketone) (PEKEKK) has been synthesized by electrophilic Friedel-Crafts acylation condensation of 1,4-diphenoxybenzophenone with terephthaloyl chloride. The syntheses were performed as precipitation polycondensations, and the polyketones were obtained in particle form. The viscosity (molecular weight), shape and size of these particles were found to be strongly dependent on the reaction conditions. For low monomer concentration, highly ordered needle-like particles were also obtained. The chemical structure of the polymers obtained was confirmed by $^1$H and $^{13}$C NMR spectroscopy, and *para*-substitution in aryl fragments of the main chain was identified. Analysis of the expanded $^1$H NMR spectra for the ring proton resonances reveals defect *meta*- and *ortho*-structures. The amount and isomer ratio of these defect structures depend on the monomer concentration used.

## Introduction

   Aromatic poly(ether ketone)s are an emerging family of materials that are currently attracting technical interest on account of their impressive thermal and mechanical properties and their chemical resistance[2,3]. At present, several aromatic poly(ether ketone)s have been commercialised. Among them are Victrex PEEK and PEK (ICI), Hostatek PEEKK (Hoechst), Ultrapek PEKEKK (BASF) and Declar PEKK (Du Pont). The commercial utility of these polymers is based on a combination of properties, among which toughness and crystallinity are crucial. To obtain tough polymers, high molecular weights are required.

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[a]   Part 1: cf. ref.[1].
[b]   Structure-based name: Poly(oxy-1,4-phenylenecarbonyl-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylenecarbonyl-1,4-phenylene).

The synthesis of these polymers is usually performed by Friedel-Crafts acylation or nucleophilic aromatic displacement. It is believed that the only way to obtain high molecular weight semicrystalline aromatic polyketones is to keep the polymers in solution during synthesis, and that premature polymer precipitation prevents further macromolecular chain growth[2, 3].

This is why nucleophilic synthesis is conducted at 300°C and even higher temperatures, using solvents like diphenyl sulfone. For the electrophilic reaction, good results can be achieved by working in strongly acidic medium (i.e., HF-BF$_3$ system), or in a mixture composed of catalyst (AlCl$_3$ in a large excess) and a Lewis base (dimethylformamide or lithium chloride) in a chlorinated organic solvent (methylene chloride or dichloroethane). Under these conditions, the polymer can be maintained in solution or, to be more precise, in a reactive gel state.

While, in general, it is thought that polymer precipitation from initially homogeneous solution in polycondensation syntheses terminates chain growth, there are reports that polymer forming reactions can occur in precipitates, i.e., after phase separation[4, 5]. Recently, we have shown[6–8] that electrophilic precipitation polycondensation can be performed in such a way that the polymer precipitates as quite uniform small particles. More recently still, this finding was confirmed in the course of electrophilic polycondensation of isophthaloyl chloride with diphenyl ether[9]. It is clear that the preparation of polyketones in particle form has unquestionable technological advantages, since pure polymer is straightforwardly obtained by filtration followed by washing with organic solvents and drying. Another very important advantage is that the polyketone particles obtained can be subjected to further processing without traditional post synthesis operations like granulation. The application of the precipitation polycondensation method for the preparation of both novel and traditional polymers is very promising. In a preceding publication the synthesis and properties of aromatic polyketones containing napthalene groups have been reported[1].

This paper (Part 2) concerns the preparation of aromatic poly(ether ketone ether ketone ketone) (PEKEKK) by the electrophilic precipitation polycondensation method.
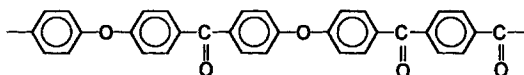


The influence of the reaction conditions on the viscosity and shape of polymer particles is highlighted. Formation of highly ordered needle-like particles is reported. The use of a high-field NMR spectrometer working at 600 MHz (for the protons) has allowed, for the first time, a detailed characterization of the chain structure as well as determination of the defect structures and their ratio. The influence of molecular weight and amount of defect structures on the thermal behaviour and microstructure of the polymers has been discussed in a companion paper (Part 3[10]).

## Experimental part

### Materials

1,2-Dichloroethane, terephthaloyl chloride, diphenyl ether, all from Aldrich, were distilled prior to use. Aluminium chloride was sublimed prior to use. 1,4-Diphenoxybenzophenone was obtained by condensation of excess of diphenyl ether with phosgene in presence of aluminium chloride in methylene chloride. Purification by refluxing in ethanol containing activated charcoal, followed by filtration, recrystallization (2 ×) from ethanol and drying at 100 °C gave colourless plates, m.p. = 146–146.5 °C.

### Methods

A typical procedure of polyketone synthesis was as follows. A 300 mL three-necked flask equipped with a magnetic stirrer, nitrogen inlet, thermometer, solids addition funnel and gas outlet was purged with dry nitrogen and charged with 3.66 g of diphenoxybenzophenone (0.01 mol), 2.03 g of terephthaloyl chloride (0.01 mol) and 120 mL of 1,2-dichloroethane. The addition funnel was charged with 5.00 g of high purity aluminium chloride (0.037 mol). The transparent, colourless solution was cooled to –15 °C, aluminium chloride was added to the solution and the resulting orange reaction mixture was stirred for 30 min. 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 was allowed to dry in air. The air-dried product was heated at 100 °C over night under vacuum. Yield after drying in vacuum: 4.60 g (93%), inherent viscosity $\eta$ = 2.42 dL/g.

### Measurements

The viscosity of polymer solutions in 94.5% sulfuric acid was measured at 25 °C in a viscometer of the Ubbelohde type. The $^1$H and $^{13}$C NMR spectra were recorded at room temperature on a Bruker AMX-600 spectrometer operating at 600.13 and 150.92 MHz (for $^1$H and $^{13}$C frequencies, respectively) using 5% (samples P1 and P2) and 3% (sample P3) (w/v) solutions in a $CF_3COOH$—$CDCl_3$ (50 : 50 v/v) mixture. DEPT[11] and APT[12] sequences were used to obtain the subspectra of CH and quaternary carbons, respectively. A polarizing optical microscope was used for the polymer particles characterization.

## Results

### Polymer synthesis

In our study we obtained PEKEKK by polycondensation of 1,4-diphenoxybenzophenone with terephthaloyl chloride by the following scheme:



$$(1)$$

The syntheses were conducted using the precipitation polycondensation method. The essential features of the precipitation polycondensation are the following:
a)  formation of a homogeneous solution at the very beginning of synthesis,

b) precipitation of polymer/catalyst complex during polycondensation,
c) existence of polymer-forming reactions in the precipitate.

In general, the syntheses proceeded in the same way as in other precipitation poly-ketone preparations. $AlCl_3$ was added to a cooled mixture of monomers in 1,2-dichloroethane. While stirring, the temperature of the reaction mixture was slowly raised from $-20\,°C$ to room temperature for the first 2 hours. When the reaction has proceeded for 1 hour, precipitation took place, and thereafter the amount of precipi-tate gradually increased. In contrast to polycondensation of terephthaloyl chloride (or isophthaloyl chloride) with diphenyl ether[7], the reaction of terephthaloyl chlor-ide with 1,4-diphenoxybenzophenone proceeds with less pronounced colour changes. After completion of the reaction, the particles formed were isolated from the reaction medium by filtration. Pure polyketone particles were recovered by washing with methanol and acetone followed by drying. After extraction with methanol and acetone, the polyketone particles contained about 50 ppm of alumi-nium. Additional treatment of the particles by continuous solvent extraction reduced the amount of catalyst residue to a few ppm. It is to be noted that washing and extraction of the particles does not change their shape.

The polyketone particles obtained were completely soluble in sulfuric acid and in $CF_3COOH/CDCl_3$ mixture. The high solubility of the polyketones synthesized allowed us to characterize them by viscosity and NMR measurements.

In order to demonstate the occurrence of a polymer-forming reaction in the preci-pitate during the polycondensation, a set of polymer syntheses was started under similar reaction conditions and stopped at different reaction times. The results obtained (Fig. 1) correspond to changes of the reaction medium during the synthesis.
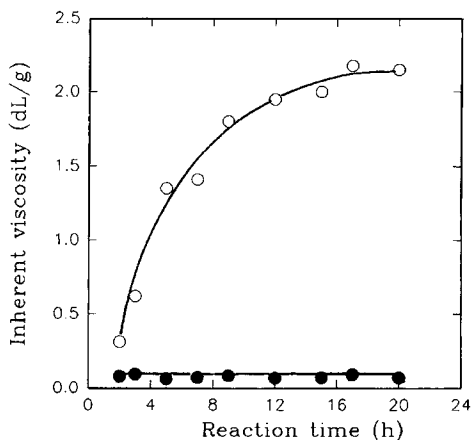


Fig. 1. Dependence of the poly-mer viscosity on the reaction time in polycondensation of terephtha-loyl chloride with diphenoxyben-zophenone; $C_M = 0.1$ mol/L; (o) precipitated polymer, (•) polymer in solution

Taking into account that, in polycondensation reactions, properties of the poly-mers obtained are strongly dependent on the monomer concentrations, three polymer syntheses were performed at different monomer concentrations: 0.2, 0.15 and 0.083 mol/L.

Tab. 1.  Characteristics of the polyketones "as obtained"

| Sample | Monomer conc. in mol/L | Yield[a] in % | Viscosity[b] $\eta_{inh}/(dL/g)$ |
|---|---|---|---|
| P1 | 0.20 | 91 | 1.46 |
| P2 | 0.15 | 89 | 1.85 |
| P3 | 0.083 | 93 | 2.42 |

[a] Reaction time 20 h.
[b] Measured with a concentration of 0.05 g/L in 94,5% sulfuric acid at 25 °C.

Yields of three polyketone preparations and some properties of the products are presented in Tab. 1. As can be seen, the polymers were obtained with good yields which are similar for all of the syntheses. However, a high dependence of polymer viscosity on the initial monomer concentration was observed. Lowering the initial monomer concentration resulted in a dramatic increase of polymer viscosity.

*Particle morphology*

Both the shape and the size of the particles were found to be governed by reaction conditions. Figs. 2a–c show micrographs of the three polyketone preparations produced using different initial monomer concentrations (Tab. 1). The difference in shape and morphology observed is remarkable. For P1 sample (Fig. 2a), rather smooth, elliptical particles are observed. The particles sizes are in the range of 0.4– 0.7 mm. In the case of sample P2 (Fig. 2b), very smooth, spherical particles of about 0.1 mm diameter in the form of elongated aggregates (less than 1 mm long) were found. For the lowest initial monomer concentration, sample P3 (Fig. 2c), rough, elongated particles which are thinner than those of P1 are observed. In addition to the larger particles isolated, small needle-like particles were also observed in the case of P3. SEM micrograph (Fig. 2c) shows that these large particles consist of both spherical and needle-like particles. While spherical particles seem to be aggregated one another, the needle-like particles should be more free, and consequently
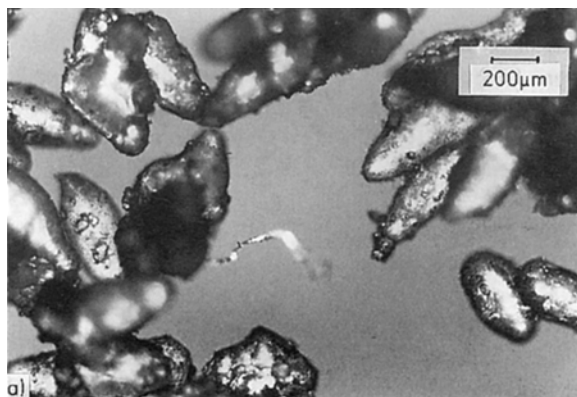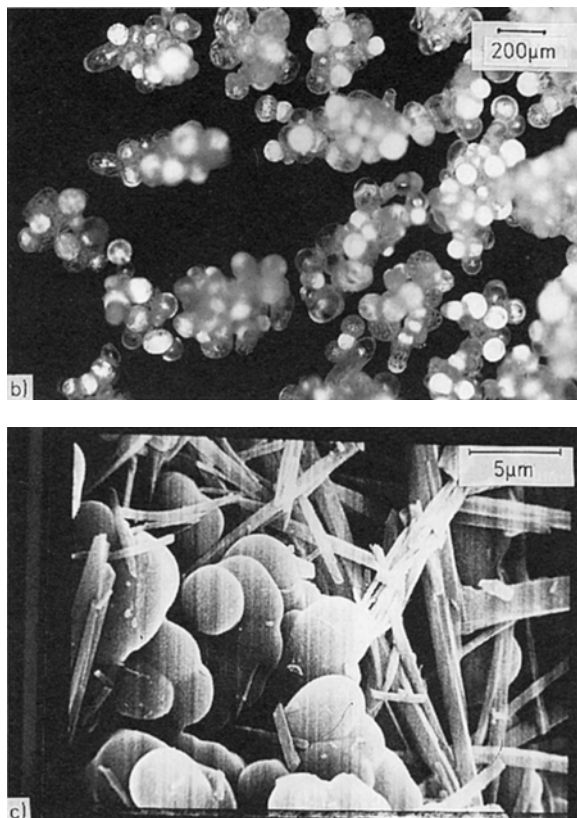


Fig. 2a.

Fig. 2. Optical photo-
graphs of aromatic
polyketones "as
obtained". (a): P1; (b)
P2; (c) SEM micro-
graph of P3

some of them become isolated after manipulation of powder sample. The needles
exhibit average length of 150–250 µm and width of 1–5 µm.

*NMR study*

The structure of the polymers was studied by NMR spectroscopy. Fig. 3 shows
the $^{13}$C NMR spectra of P1. The assignments of carbon signals (see *Scheme 1*) were
made by means of additive scheme calculations[13] using the substitution increments
((CO)Ph(CO), (CO)PhO and OPh) reported by Ewing[14] and found from the spectra
of the model compounds 1,2-dibenzoylbenzene and 4-methoxybenzophenone pre-
sented by Aldrich[15].

All the signals in the $^{13}$C NMR spectrum of P1 can be completely ascribed to the
polymer with *para*-substituted diphenyl ether fragments in the main chain. The $^{13}$C
NMR spectra of polyketones P2 and P3 were practically identical to that of P1.

The assignment of proton signals was also made (see Fig. 4 and *Scheme 1*) by
means of the additive scheme calculations (using increments reported in ref.[16]),
together with analysis of signal multiplicity. $^{1}$H NMR spectroscopy proved to be a
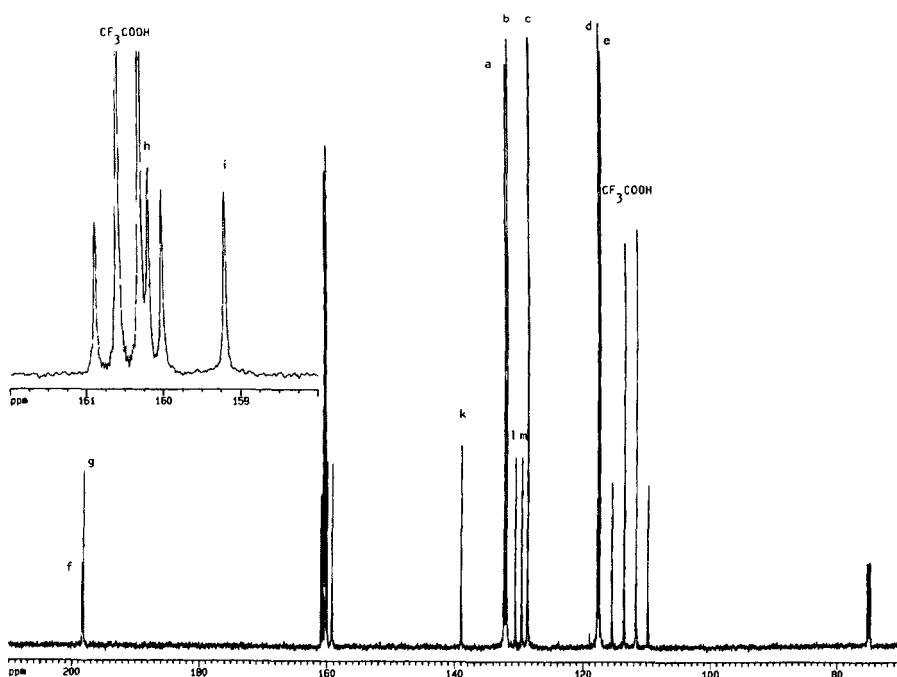
Fig. 3.    $^{13}C$ NMR spectra of sample P1. Carbon designation in accordance with *Scheme 1*

sensitive method for polyketones structure identification. Thus, in the expanded $^1H$ NMR spectrum for the ring proton resonances of P1, acquired with a high digital resolution (Fig. 5), one can observe a number of signals whose intensities are considerably smaller than those of proton signals corresponding to the main structural units (*para*-isomer). The spectrum proved to be very complex due to the carbon-13

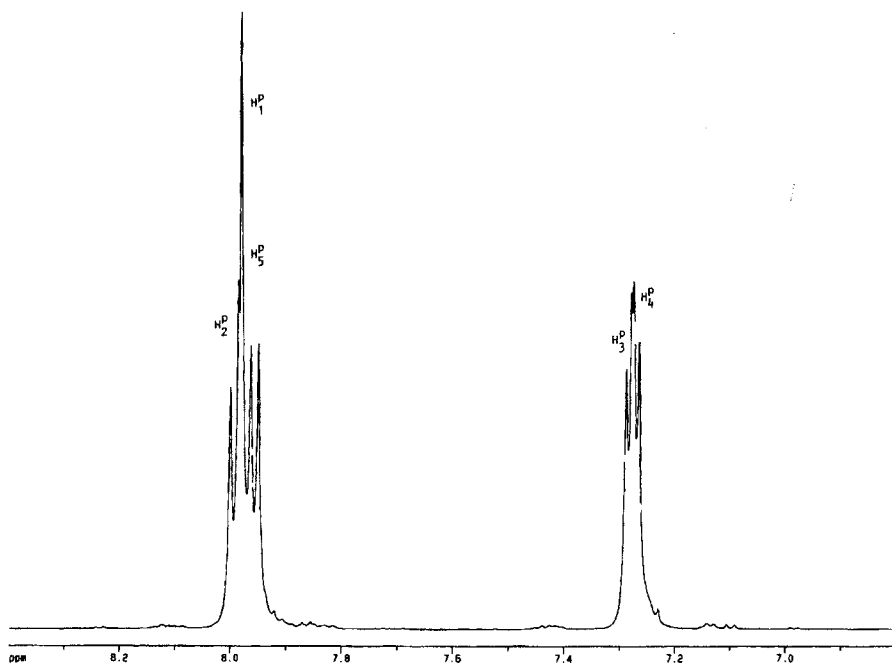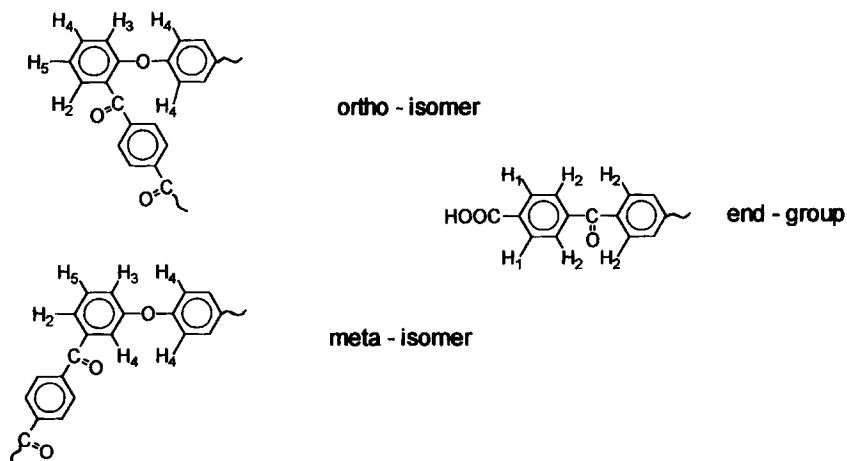*Scheme 1:*
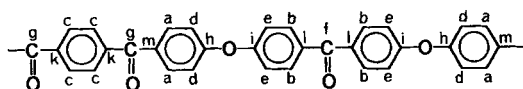


para - isomer

*Scheme 1* (continued):



ortho - isomer

end - group

meta - isomer
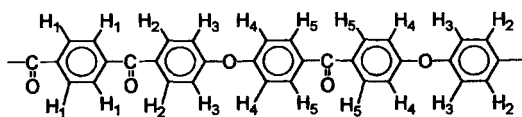


Fig. 4. ^{1}H NMR spectrum of sample P1. Proton designation in accordance with *Scheme 1*
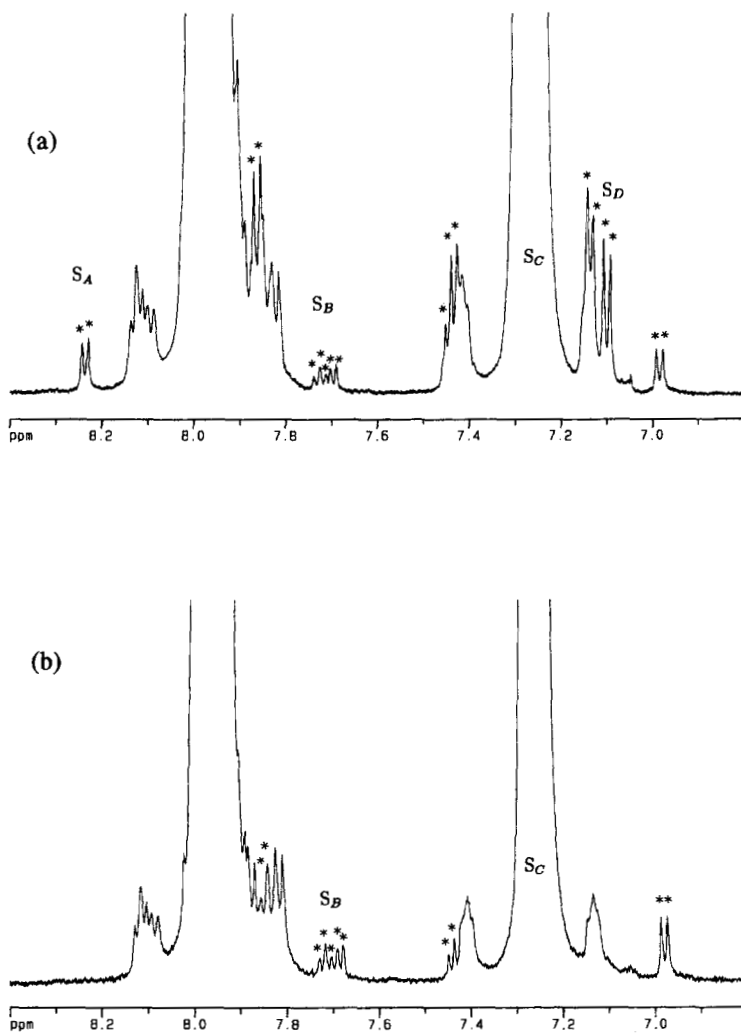
Fig. 5. Expanded regions for the ring proton resonances of sample P1 (a) and P3 (b). Signals of defect structures are marked by *

satellites which arise from proton coupling to carbon-13[17] and overlap some signals ascribed to isomer structures. The assignment of these new signals was made (Tab. 2) on the basis of the following criteria:

– comparison of the spectra of polyketone samples with different molecular weights (analysis of signal intensity and multiplicity), keeping in mind that multiplicity of satellites and the central signal (Fig. 4) are identical;

Tab. 2. The assignment of proton signals in the spectra of PEKEKK[a] (Figs. 4, 5)

| Proton[a] | Chemical shifts[b] $\delta$ in ppm | Signal multiplicity[c] J/Hz |
|---|---|---|
| $H_2^{p}$ [d] | 7.98 | doublet |
| $H_3^{p}$ | 7.27 | doublet |
| $H_4^{p}$ | 7.26 | doublet |
| $H_5^{p}$ | 7.95 | doublet |
| $H_2^{o}$ | 7.87 | doublet |
| $H_3^{o}$ | 7.27[e] | doublet |
| $H_4^{o}$ | 7.44 | triplet |
| $H_5^{o}$ | 7.10 | doublet/doublets |
| $H_2^{m}$ | 7.69 | doublet |
| $H_3^{m}$ | 6.98 | doublet |
| $H_4^{m}$ | 7.86[e] | singlet |
| $H_5^{m}$ | 7.72 | triplet |
| $H_1^{centre}$ | 7.97 | singlet |
| $H_1^{end}$ | 8.25 | doublet |

[a]   Proton designation in accordance with *Scheme 1*.
[b]   Chemical shifts of the multiplet centre.
[c]   $J_{ortho\text{-}ortho} = 12$ Hz.
[d]   *p*, *m* and *o* refer to *para-*, *meta-* and *ortho-*isomer, respectively.
[e]   Calculated chemical shifts, experimental chemical shifts cannot be determined due to signal overlapping.

– additive scheme calculations[16] based on the chemical shifts of protons in the main *para*-structure (Fig. 4) using substitution increments (CO)Ph(CO) and OPh, also estimated from the proton spectrum shown in Fig. 4.

As a result, signals corresponding to the end-terephthalic acid groups (A) and to *ortho-* (D) and meta-isomer (B) defect structures, along with the main signal (C) (*para*-isomer), were identified (Fig. 5 and *Scheme 1*).

Assuming the assignment presented in *Scheme 1*, relative signal intensities (which are proportional to the isomer concentration and to the number of protons corresponding to the signal) are given by:

$$2S_D = Y \tag{2}$$

$$S_B = 2Z \tag{3}$$

$$S_C = 4X + 3Y + 2Z \tag{4}$$

where $X$, $Y$ and $Z$ are the mole fractions of main *para-* and defect *ortho-* and *meta-* structures, respectively (see *Scheme 1*). It is clear that

$$X + Y + Z = 1 \tag{5}$$

Taking into account that

$$S = S_C + 2S_D + S_B = 4(X + Y + Z) = 4 \tag{6}$$

Tab. 3. Content of isomer structures in the polyketones

| Sample | Inherent viscosity $\eta_{inh}$/(dL/g) | Isomer molar ratio in % | | |
|--------|--------|--------|--------|--------|
| | | *para* | *ortho* | *meta* |
| P1 | 1.46 | 93.3 | 6.0 | 0.7 |
| P2 | 1.85 | 95.0 | 4.0 | 1.0 |
| P3 | 2.42 | 97.6 | 0 | 2.4 |

the relationships for calculation of the $X$, $Y$ and $Z$ values may be expressed as:

$$\frac{2 \times S_D}{S} = \frac{Y}{4} \qquad Y = \frac{8 \times S_D}{S} \tag{7}$$

$$\frac{S_B}{S} = \frac{2 \times Z}{4} \qquad Z = \frac{2 \times S_B}{S} \tag{8}$$

$$X = 1 - (Y + Z) \tag{9}$$

The isomer contents thus calculated are presented in Tab. 3. It is noteworthy that lower initial monomer concentrations result in less defect structures. Additionally, the ratio of isomers is also influenced by the initial monomer concentration.

**Discussion**

*Synthetic aspects*

In principle, poly(oxy-1,4-phenylenecarbonyl-1,4-phenyleneoxy-1,4-phenylene-carbonyl-1,4-phenylenecarbonyl-1,4-phenylene) (PEKEKK) can be prepared in several possible ways. Among these are electrophilic polycondensations of 1,4-diphen-oxybenzophenone with terephthaloyl chloride (Eq. (1)) (mentioned above) and 1,4-bis(4-phenoxybenzoyl)benzene with phosgene (Eq. (10)), and also nucleophilic polycondensation of 1,4-dihydroxybenzophenone with 1,4-bis(4-fluorobenzoyl)ben-zene (Eq. (11)):



$$ (10) $$



$$ (11) $$
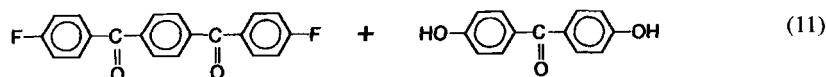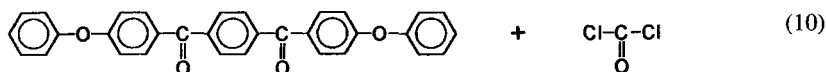
It should be mentioned that electrophilic polycondensation involving phosgene (route 10) usually results in low molecular weight, branched or even cross-linked polymers. The other two synthetic routes allow linear, high molecular weight poly-

mers to be obtained using low-temperature electrophilic (route 1) or high-tempera-
ture nucleophilic (route 11) methods. The former has been applied for commercial
production of PEKEKK. The characteristic features of the process are described in
the patents[18-21]. Accordingly, the polycondensation of aromatic dicarboxylic acid
chlorides with multinuclear aromatic hydrocarbons is conducted in chlorinated ali-
phatic hydrocarbons (such as methylene chloride or dichloroethane) in the presence
of aluminium chloride combined with Lewis base. A wide variety of Lewis bases
may be employed, but DMF, dimethyl sulfone, ammonium chloride and lithium
chloride seemed to be favored. The function of Lewis base is not completely under-
stood, but it appears to form a complex with the aluminium chloride which acts as a
solvent for the polymer/catalyst complex during the polycondensation, thereby
maintaining the polymer in solution or in a reactive gel state. The pure polymer is
recovered by water treatment of the reaction medium. Inherent viscosity of the poly-
ketones ranged from 0.8 to 1.8 dL/g.

On the contrary, during polycondensation, performed at low monomer concentra-
tion without a Lewis base, precipitation of the polymer/catalyst complexes occurs.
As seen from Fig. 1, the precipitation begins at an early stage of the synthesis. It is
very important that, as reaction time increases, the viscosity of the polymer in the
precipitate increases, while the viscosity of the polymer in solution remains practi-
cally constant. Therefore, oligomers of low degree of polymerization are formed in
the homogeneous state, and, as soon as degree polymerization exceeds a critical
value, precipitate from solution and reaction proceeds further in the precipitate. It is
logical to conclude that low-soluble (or even insoluble) polyketones can be also
obtained by this method.

The viscosity (molecular weight) of the polymers synthesized is quite high, and
this is probably due to the high local concentration of active end groups in the parti-
cles.

It is to be noted that isolated particles are obtained at low monomer concentration.
High monomer concentrations result in a polymer mass aggregate with low viscos-
ity. It is noteworthy that at low monomer concentration quite uniform polymer parti-
cles are obtained (P2). Still lower monomer concentrations result in needle-like par-
ticles together with uniform spheres (P3). The IR spectrum of the needles (to be dis-
cussed in a following paper[10]), performed on a spectrometer with microbeam and
polarizing device, shows a high absorption anisotropy for parallel and perpendicular
directions to the longest size of the needles. It is possible that the needles are
extended chain crystals. Detailed analyses of the structure of these needles are cur-
rently under study and will be reported separately.

On the other hand, it should not be forgotten that precipitation polycondensation
proceeds in a two-phase system, one phase being the precipitated polymer particles.
From this point of view, formation of ordered precipitated structures should favour
the polymer-forming reaction because of the regular alignment of the polymer
chains. This is very likely the case for polymer P3, where uniform, small, needle-
like patrticles were obtained. Therefore, monomer concentration affects both the
reaction and the state of the precipitate, the former is also influenced by precipitate
state.

*Defect structures*

For a better understanding of the electrophilic precipitation method used in this study, let us briefly consider possible side reactions (and defect structures) during nucleophilic and electrophilic solution polycondensations.

It is believed that the nucleophilic path (Eq. (11)), in which chain growth occurs by reaction between functional phenolic and halide-activated groups, leads to a linear polymer with well-defined structure. The presence of functional groups (and, as a result, conclusion about reaction between these groups only) may be the reason that, in most cases, the structure of the polymer obtained was not fully determined.

However, the following side reactions have been suggested for nucleophilic poly-(ether ketone) and poly(ether sulfone) syntheses[22]:
1) ether interchange or transetherification,
2) chain cleavage by the fluoride anion,
3) nucleophilic reactions involving hydroxyl anion.

In addition, side reactions resulting from subtraction of a proton from halide-activated aromatic rings have been reported[23] to give a carbanion which then reacts further either to give a trifunctional branching co-monomer, or adds across a carbonyl group to give a triphenyl carbonyl derivative:
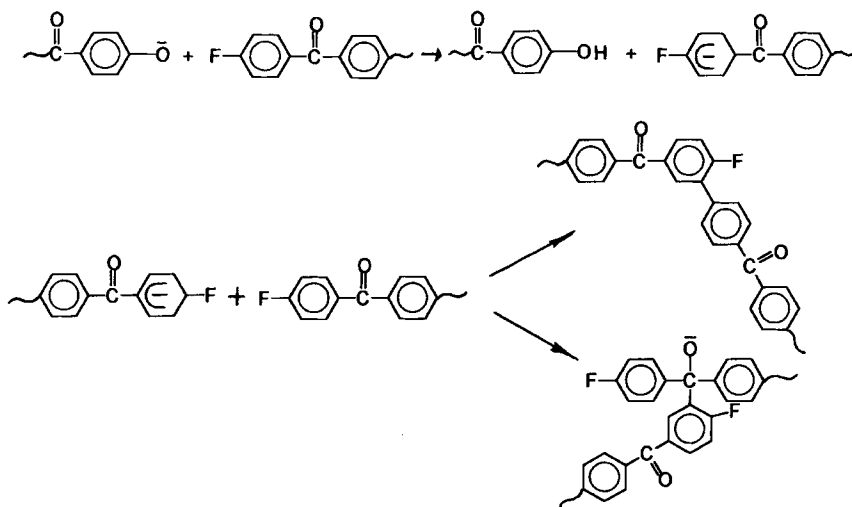


The latter, incorporated in the polymer, would lead to the red colour observed in sulfuric acid solution. In this respect, red sulfuric acid solutions of polyketones, as well as the presence of an insoluble fraction reported in many polyketone preparations, can be considered as evidence for such kinds of reactions. Clearly, the contribution of these side reactions would increase with increasing temperature (nucleophilic syntheses are usually carried out at 300–330 °C in diphenyl sulfone). It should be mentioned that elemental analysis of polyketones obtained by high temperature

nucleophilic synthesis very often shows the presence of sulfur as a result of the side reaction with diphenyl sulfone.

Thus, despite apparent high selectivity, the nucleophilic path (Eq. (11)) may produce polyketones with a significant amount of defect structures.

As far as path (1) is concerned, it is well known that Friedel-Crafts acylation of monosubstituted aromatic rings usually results in isomer mixtures, consisting of para-, meta- and ortho-structures. Additionally, in polyacylation, formation of trisubstituted (branched) or even crosslinked fragments can be expected. Moreover, reactions of reactive acyl-oxonium intermediates leading to crosslinks have recently been reported[24].

Another possible type of side reaction in electrophilic acylation is intramolecular cyclization of ortho-substituted phenoxy units, resulting in xanthydrol groups[2]:

The xanthydrol groups were detected by absorbance in the UV at 455 nm and were reported to be responsible for melt instability. This conclusion is confirmed by the fact that chemical reduction of xanthydrol groups to the corresponding 9-phenylenexanthenes improves melt stability[2]:

Therefore, despite low reaction temperatures, the electrophilic path of polyketone preparation may also produce polymers with various defect structures.

In general, regioselectivity (or isomer ratio) of multistep reactions such as polyacylation is determined by a complex combination of various factors, the most important of which are: origin of monomer and catalyst, reaction conditions, and possibilities for transformations of reactive intermediates. It is reasonable to expect that changes in the initial monomer concentration (other things being equal) would affect both the reaction and the regioselectivity (isomer ratio). Indeed, lowering the initial monomer concentration leads to polymers with higher viscosity. Simultaneously, the total amount of defect (ortho and meta) structures decreases (Tab. 3). It is worthy to note that the high solubility of the polyketones obtained points to an absence of cross-linked structures. Furher, trisubstituted aromatic rings were not detected in the NMR spectra. The spectra also did not show signals corresponding to xanthydrol groups. Thus, the only detected defect structures for P1 are terminal terephthalic acid groups, meta- and ortho-isomers; for P2, ortho- and meta- isomers; for P3 meta-isomers only. It should be mentioned that, because of the large difference between the intensity of NMR signals resulting from main and defect structures, an

accurate determination of the amount of defect structures cannot be made. However, there is no doubt as to the tendencies observed (Tab. 3), indicating smaller amount of defect structures for the samples with the highest viscosity. Further, end-ter-ephthalic acid groups are only observed in the spectrum of P1. The absence of these signals in P2 and P3 spectra can be explained by their low concentration. As far as isomer types are concerned, it was found that the amount of *meta*-isomer increases with the viscosity of the samples, while that of the *ortho*-isomer decreases with increasing viscosity, and they were not observed at all for the P3 sample. Interest-ingly, sample P3 contains only *meta*-defect structures. This situation is not typical for electrophilic acylation in which *ortho*-structures usually dominate in side pro-ducts.

Since the polycondensation is performed in a chlorinated solvent (1,2-dichlor-ethane), there is, in principle, a possiblity of alkylation of diphenyl ether fragments by the solvent. However, neither $^{13}$C nor $^1$H NMR spectroscopy show signals corre-sponding to alkylated products.

On the whole, precipitation polycondensation of PEKEKK allows one to synthe-size polymers with quite a high regioselectivity. Although it is difficult to make detailed comparisons of the selectivity of the electrophilic path with that of the pos-sible nucleophilic one, one can expect that the method and products described will find an important place in the polymer synthetic field.

## Conclusions

A linear, high molecular weight polyarylketone, PEKEKK, was prepared by elec-trophilic precipitation polycondensation of terephthaloyl chloride with 1,4-diphen-oxybenzophenone. Three polymer syntheses were performed at different initial monomer concentrations, and polyketones in particular forms of different optical morphology were obtained. Some of these particles present highly ordered elongated needle-like structures. The monomer concentration was found to affect strongly not only the size and shape of the polymer particles, but also the viscosity and the amount of defect (*ortho*- and *meta*-)structures. Low initial monomer concentrations afford polyketones with larger molecular weight and less defect structures. Simulta-neously, the relative amount of *ortho*-defect structures decreases with the decrease in initial monomer concentration.

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