

Aromatic polymers obtained by precipitation polycondensation: 4*. Synthesis of poly(ether ketone ketone)s

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High molecular weight aromatic poly(ether ketone ketone)s were synthesized by the Friedel–Crafts polyacylation condensation of iso- and terephthaloyl chlorides with diphenyl ether, 1,4- and 1,3-bis(4-phenoxybenzoyl)benzenes. Depending on the monomers used for polycondensation, polyketones of regular structure with different iso-/tereisomer repeating unit ratio (100/0, 50/50, 0/100) in the main chain were obtained. Polymers of each repeating isomer unit were prepared in two different ways. All the polymer syntheses were performed as precipitation polycondensations and the resulting polymers were obtained in particle form. The influence of reaction conditions and preparation route on the polymer properties were examined. The monomer concentration and monomer stoichiometric ratio were found to affect the polymer viscosity. The size and shape of the polyketone particles obtained were also found to be governed by reaction conditions and preparation route. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Aromatic poly(ether ketone)s comprise a class of polymers in which arylene groups are linked by ether or carbonyl groups^{1–3}. These materials are of great interest at the present time because of their high temperature stability and mechanical strength. Polyketones are, in addition, semicrystalline and therefore resistant to attack by solvents.

While crystallinity gives the poly(ether ketone)s a unique set of enhanced properties among thermoplastics, it is this property, coupled with melting points generally above 320°C, which makes their synthesis so difficult. The problem is to keep the polymer in solution and so obtain high molecular weight polymers. The insolubility of these polymers presents a major synthetic problem as it limits the molecular weight that can be obtained before the growing chains crystallize out from the polycondensation system. Preparation of poly(ether ketone)s by two different approaches has been described in the literature^{1–3}. The first approach is a synthesis involving electrophilic aromatic substitution, in which an aryl ketone linkage is formed. The second one is a synthesis involving nucleophilic aromatic substitution, in which an aryl ether linkage is obtained. Normally, the preparation involving nucleophilic aromatic substitution is

conducted at 300°C and even higher temperatures, using solvents like diphenylsulfone. In the preparation, involving Friedel–Crafts electrophilic aromatic polycondensation, good results can be achieved by working in strongly acidic medium (i.e., HF–BF₃), or in a mixture composed of a large excess of AlCl₃ as a catalyst, a Lewis base such as dimethylformamide or lithium chloride, and a chlorinated organic solvent such as methylene chloride or dichloroethane. Under these conditions the polymer can be maintained in solution or, to be more precise, in a reactive gel state.

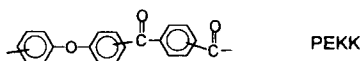
It is generally accepted that premature polymer precipitation from initially homogeneous solution in polycondensation syntheses prevents further macromolecular chain growth reactions. However, it has been found^{4,5} that polymer forming reactions can occur in the precipitate, i.e. after phase separation. Recently we have shown^{6–10} that precipitation electrophilic Friedel–Crafts polycondensation can be performed in such a way that the polymer precipitate presents quite uniform small particles. This process has unquestionable technological advantages, since pure polymer can be recovered just by filtration followed by washing with organic solvents and drying. The application of this method for the preparation of both novel and standard polymers is very promising.

The aim of the present paper is to describe the preparation of aromatic poly(ether ketone ketone)s by the precipitation electrophilic polycondensation method. These regularly structured polyketones are usually

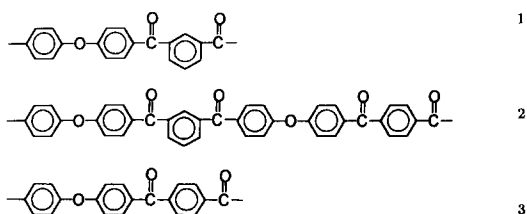
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considered as all-*para*-linked polymers but they may contain isomer (*meta*- or *ortho*-) units as well.

The general chemical structure of the poly(ether ketone ketone)s can, therefore, be represented by the formula



We have chosen for this study three polyketones (1–3) of regular structure with different types of substitution in the phthaloyl fragments



Investigation of the polyketones with different iso-/tere-ratios [100/0 (1), 50/50 (2) and 0/100 (3)] should prove useful for more rigorous synthesis–structure–properties correlation in this very interesting class of polymers.

EXPERIMENTAL

Materials

1,2-Dichloroethane, isophthaloyl chloride, terephthaloyl chloride and diphenyl ether, all from Aldrich, were distilled prior to use. Aluminium chloride was sublimed prior to use. 1,4-Bis(4-phenoxybenzoyl)benzene and 1,3-bis(4-phenoxybenzoyl)benzene were obtained according to published methods⁹.

Polycondensation

A standard procedure for the preparation of PEKK is described below. A 300-ml, three-neck flask equipped with a magnetic stirrer, nitrogen inlet, thermometer, solids addition funnel and gas outlet, was purged with dry nitrogen and charged with 1.70 g of diphenyl ether (0.01 mol), 2.03 g of terephthaloyl chloride (0.01 mol) and 125 ml of 1,2-dichloroethane. The addition funnel was charged with 3.72 g of high purity AlCl_3 (0.028 mol). The transparent, colourless solution was cooled to -15°C , aluminium chloride was added to the solution and the 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 allowed to dry in air. The air-dried product was heated at 100°C overnight under vacuum to give 2.78 g of the polymer (92% yield). The intrinsic viscosity of the polymer, measured in concentrated sulfuric acid at 25°C was 1.42 dl g^{-1} .

Measurements

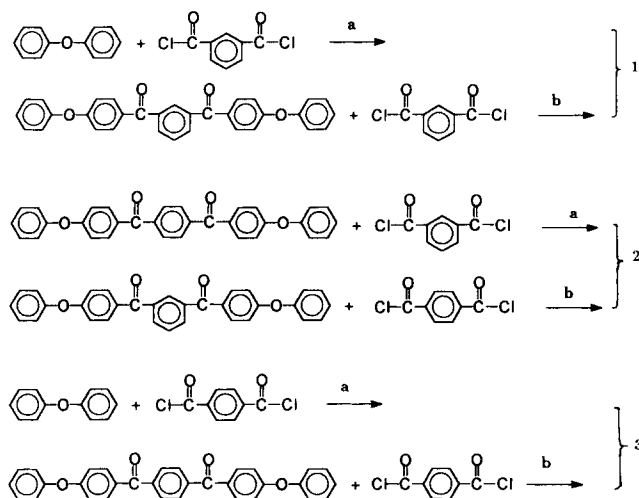
Viscosities of polymer solutions in 94.5% sulfuric acid were measured at 25°C in a viscometer of the Ubbelohde

type. The intrinsic viscosity was calculated by extrapolating the reduced viscosity to zero concentration.

RESULTS AND DISCUSSION

In principle, condensation polymers of the same chemical composition can be prepared by several routes. As a rule, however, specific features of synthesis and polymer properties depend strongly on the preparation route.

It is easily shown that each polymer 1–3 can be obtained in at least two different ways



Obviously, the reactivity of diphenyl ether in comparison with (phenoxybenzoyl)benzenes will be different. As a result, the structure and properties of polymers obtained by routes **a** and **b** may also be different.

From this point of view, comparison of the results of the syntheses by the different routes can be very useful for a better understanding of the precipitation polycondensation method.

All the syntheses were carried out in the same manner: reactions of isophthaloyl and terephthaloyl chlorides with diphenyl ether or bis(4-phenoxybenzoyl)benzenes, conducted in 1,2-dichloroethane, in presence of a Lewis acid catalyst, such as anhydrous aluminium chloride. The reactions proceeded as typical Friedel–Crafts polyacylations involving dicarboxylic acid chloride and aromatic hydrocarbons, with elimination of hydrogen chloride as a by-product. Concentration of the catalyst is an important factor for preparation of high molecular weight polyketones. Because the carbonyl groups of the reactants and the reaction products are complexed with AlCl_3 , and thereby deactivate it, AlCl_3 is generally employed at more than one equivalent of carbonyl groups in the reaction medium. The optimum ratio of AlCl_3 to $-\text{COCl}$ group was reported^{7,11,12} to be 1.35–1.45. Furthermore, if a co-monomer containing other carbonyl groups is used (i.e., bis(4-phenoxybenzoyl)benzenes), an additional amount of Lewis acid is required.

The preparation of the polyketones generally starts at low temperature. A coloured, homogeneous solution is formed when catalyst is added at low temperature to the monomer mixture dispersed in the solvent. The initial

low temperature is needed to maintain control over the reaction rate. A reaction temperature of about -15°C to -5°C has been found to be particularly effective. Thereafter, the reaction temperature is slowly increased and continued at room temperature.

In the course of polymer synthesis, the polymer/catalyst complex begins to precipitate from the reaction medium. Because of the relatively low monomer concentration, the precipitate appears in the form of swollen, isolated particles. After completion of the reaction, the particles formed are isolated from the reaction medium by filtration. Pure polyketone particles are recovered by washing with methanol and acetone followed by drying. The washed and dried polymer particles of dimensions 0.1–0.5 mm, are smooth and glass-like, and many of them are spherical. The particles are completely soluble in sulfuric acid and a $\text{CF}_3\text{COOH}/\text{CDCl}_3$ mixture. The satisfactory solubility of the synthesized polyketones has allowed us to characterize them by viscosity and n.m.r. measurements.

A basic tenet of precipitation polycondensation is the assumption of polymer forming reaction in both precipitate and solution. Therefore, it is crucially important to know the molecular weight (viscosity) changes of precipitated polymer and polymer remaining in solution during synthesis. Unambiguous evidence for these processes can be obtained from analysis of samples of precipitate and solution taken from the reaction medium during the course of the synthesis.

Taking into account (1) that the determination of polymer viscosity as well as the amount of polymer in both precipitate and solution requires a significant volume of reaction medium, (2) that isolation of a statistically representative sample from the heterogeneous system is quite difficult, and (3) that frequent sampling can affect the electrophilic reaction, which is very sensitive to impurities and moisture, we have chosen another method by which to analyse reaction-medium state changes during polycondensation: a set of polymer syntheses was started under similar reaction conditions and stopped at different reaction times. The results thus obtained correspond to changes of reaction medium in the course of the polycondensation.

The characteristic features of the precipitation polycondensation are well illustrated by the polycondensation of isophthaloyl chloride with diphenyl ether (route 1a). Some data on polycondensation of the monomers were previously reported^{7,11,12}.

Polymer precipitation usually begins at early stages of the synthesis. Thus, in polycondensation of isophthaloyl chloride with diphenyl ether the precipitation occurs in the first 40–60 min. From Figure 1 one sees that during the first hour, the viscosities of the polymer in the precipitate and the polymer which still remains in solution are rather close. However, as reaction times increase, the viscosity of the polymer in the precipitate increases, while the viscosity of the polymer in solution remains practically constant.

It should be noted that the viscosity (molecular weight) of the polymers is quite high, and this is probably due to high local concentration of active end groups in the particles. Consequently, each particle can be considered as a molecular-scale reactor.

The conclusion about the reaction in the precipitate during polycondensation of diphenyl ether with isophthaloyl chloride was also drawn recently¹².

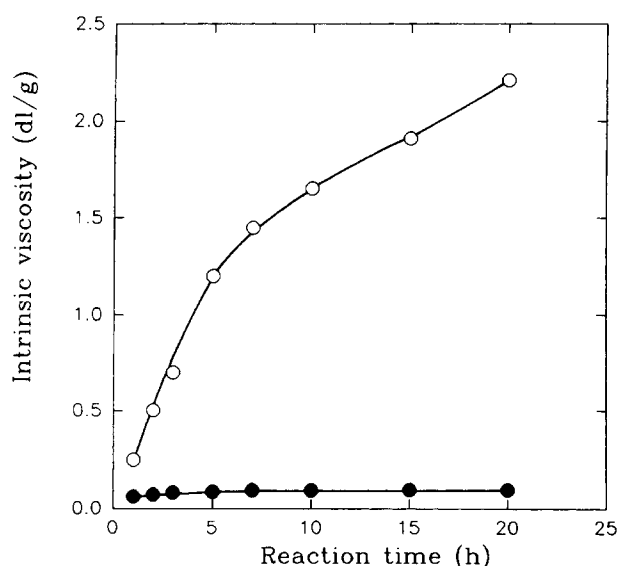


Figure 1 Dependence of the polymer viscosity on reaction time in polycondensation of isophthaloyl chloride with diphenyl ether: (○) precipitated polymer; (●) polymer in the solution

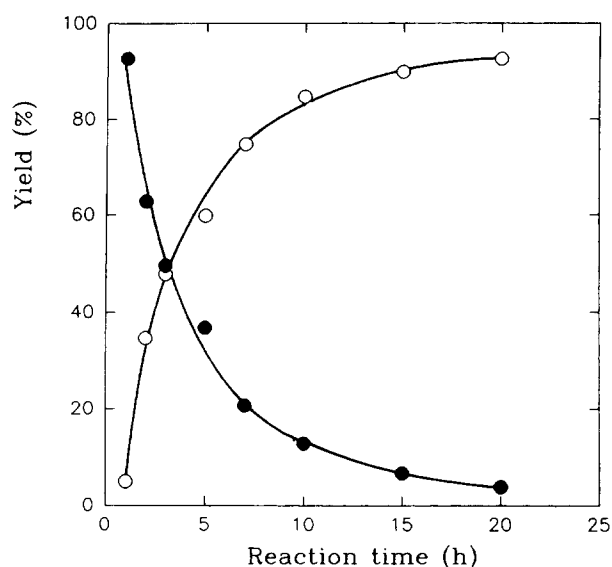


Figure 2 Dependence of polymer yield on the reaction time: (○) precipitated polymer; (●) polymer in the solution

In that study, precipitate which appeared at an early stage was separated and fresh dichloroethane was added to it. Without further addition of monomers or oligomers, polycondensation yielded a polymer with increased viscosity. However, the reason given by the authors for acceleration of the reaction in the precipitate with solvent exchange—extraction of hydrogen chloride from the reaction site—seems to be questionable. The acceleration is more likely to be due to morphological changes in the precipitate, for example, due to different swelling of the particles in 'old' and 'fresh' solvents.

Figure 2 shows the change in yield of polymer (1a) with reaction time in the precipitate and in solution. One may see that the amount of precipitate increases during synthesis, with a concurrent decrease in the amount of polymer in solution (Figure 2). Analysis of data of Figures 1 and 2 unambiguously confirms that oligomers dissolved in solution, after reaching a certain molecular weight, precipitate from solution, and that reaction does continue in the precipitate.

It was mentioned above that polymer **1** can be prepared in two ways. The second route involves 1,3-bis(4-phenoxybenzoyl)benzene instead of diphenyl ether. Obviously, that reactivity of 1,3-bis(4-phenoxybenzoyl)benzene is different from that of diphenyl ether. The electron density on the carbons of the terminal phenoxy-groups in bis(4-phenoxybenzoyl)benzenes is reduced in comparison with that on the carbons of phenyl groups of diphenyl ether due to the presence of the carbonyl groups. Therefore, diphenyl ether is more reactive with electrophiles like isophthaloyl chloride, than are bis(4-phenoxybenzoyl)benzenes. On the other hand, in electrophilic aromatic substitution of this type, a high reactivity usually implies a low selectivity. From this point of view, one may expect that polyketone **1b** would contain less defect structures than **1a**.

In general, the difference in reactivity should appear at the very beginning of synthesis, during dimer and trimer formation. Later, the oligomers (and polymers) structures prepared by two paths (**a** and **b**) should be similar.

Apart from reactivity, these monomers also have a different solubility. Thus, the solubility of diphenyl ether is greater than that of 1,3-bis(4-phenoxybenzoyl)benzene. Nevertheless, polycondensation **b** proceeds very similarly to **a**. The only difference is that precipitation of the polymer/catalyst complex during preparation of **1b** begins at a later stage (after 2 h).

It is also to be noted that, despite the poor solubility of 1,4-bis(4-phenoxybenzoyl)benzene in dichloroethane, the reaction media of **2b** and **3b**, containing the monomer, become completely homogeneous after adding the catalyst. Thereafter the reaction proceeds as a precipitation synthesis.

Thus, the syntheses of polyketones **1–3** all proceed by precipitation polycondensation. It should be noted that, in the syntheses involving the 'large' monomers (**1b**, **2a**, **2b**, **3b**) precipitation of polymer/catalyst complex from homogeneous solution only starts after longer times. A possible explanation of this as being due to low reactivity of the 'large' molecules does not agree with the observations that the viscosity of polymers based on these 'large' molecules (for example, **1b** and **3b**) is usually higher than the viscosity of polymers produced from 'small' molecules (**1a** and **3a**). It is very likely that chain conformation of the polyketones in the initially homogeneous solution also plays a significant role.

In a polycondensation reaction the polymer properties are significantly influenced by the monomer concentration. *Figure 3* shows the influence of the monomer concentration on the polymer viscosity in the course of preparation of polymers **1a** and **1b**.

For both polycondensation routes used, maximum viscosity values were obtained for the same monomer concentration range (0.05–0.1 mol l⁻¹). The viscosities of the polyketone based on isophthaloyl chloride and 1,3-bis(4-phenoxybenzoyl)benzene (**2b**) are significantly higher. It should be mentioned that the sharp viscosity peaks in that range show very good reproducibility. However, this viscosity maximum was not observed in the reported work¹² and, in addition, the polymer viscosities reported in the publication were significantly lower.

Apart from viscosity, the monomer concentration strongly affects the polymer particle morphology. Thus, for monomer concentrations 0.4–0.6 mol l⁻¹ large macroscopic aggregates are formed instead of small

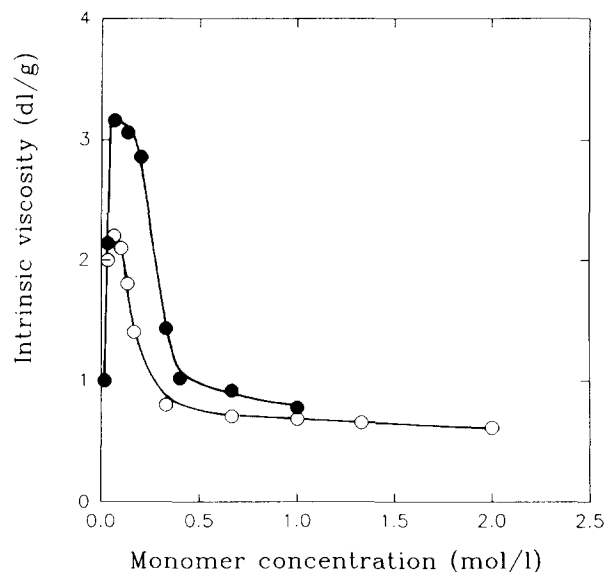


Figure 3 Dependence of polymer viscosity on monomer concentrations: (O) polycondensation of isophthaloyl chloride with diphenyl ether; (●) polycondensation of isophthaloyl chloride with 1,3-bis(4-phenoxybenzoyl)benzene

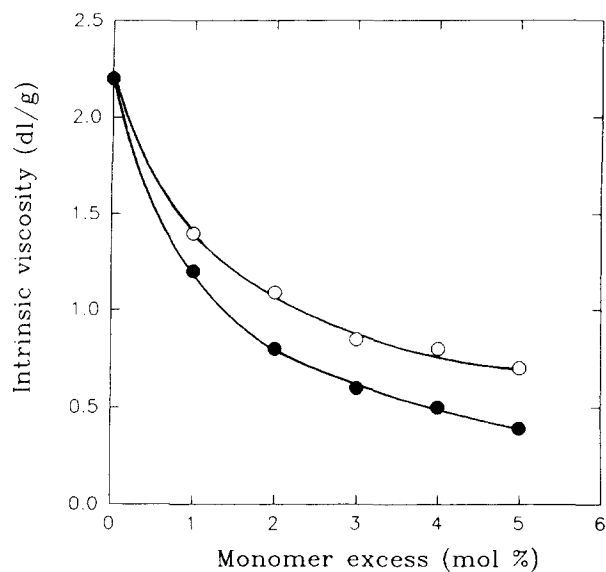


Figure 4 Dependence of the polymer viscosity on monomer stoichiometric ratio in polycondensation of isophthaloyl chloride with diphenyl ether: (●) excess of isophthaloyl chloride; (O) excess of diphenyl ether

uniform particles. Still higher monomer concentrations result in a polymer mass aggregate with low viscosity.

In classical polycondensation of two monomers, the molecular weight of the polymer formed is strongly dependent on monomer stoichiometric ratio. An excess of one of the two monomers usually results in a dramatic decrease in molecular weight of the product. On the other hand, a viscosity maximum at a non-stoichiometric monomer ratio usually points to side reactions or impurities in the monomers.

Obviously, the monomer ratio dependence is very important for precipitation polycondensation where phase separation can result in stoichiometric imbalance.

However, the dependence of viscosity on monomer ratio in the case of polycondensation of isophthaloyl chloride with diphenyl ether (*Figure 4*) shows a surprisingly 'classical' pattern, with maximum viscosity

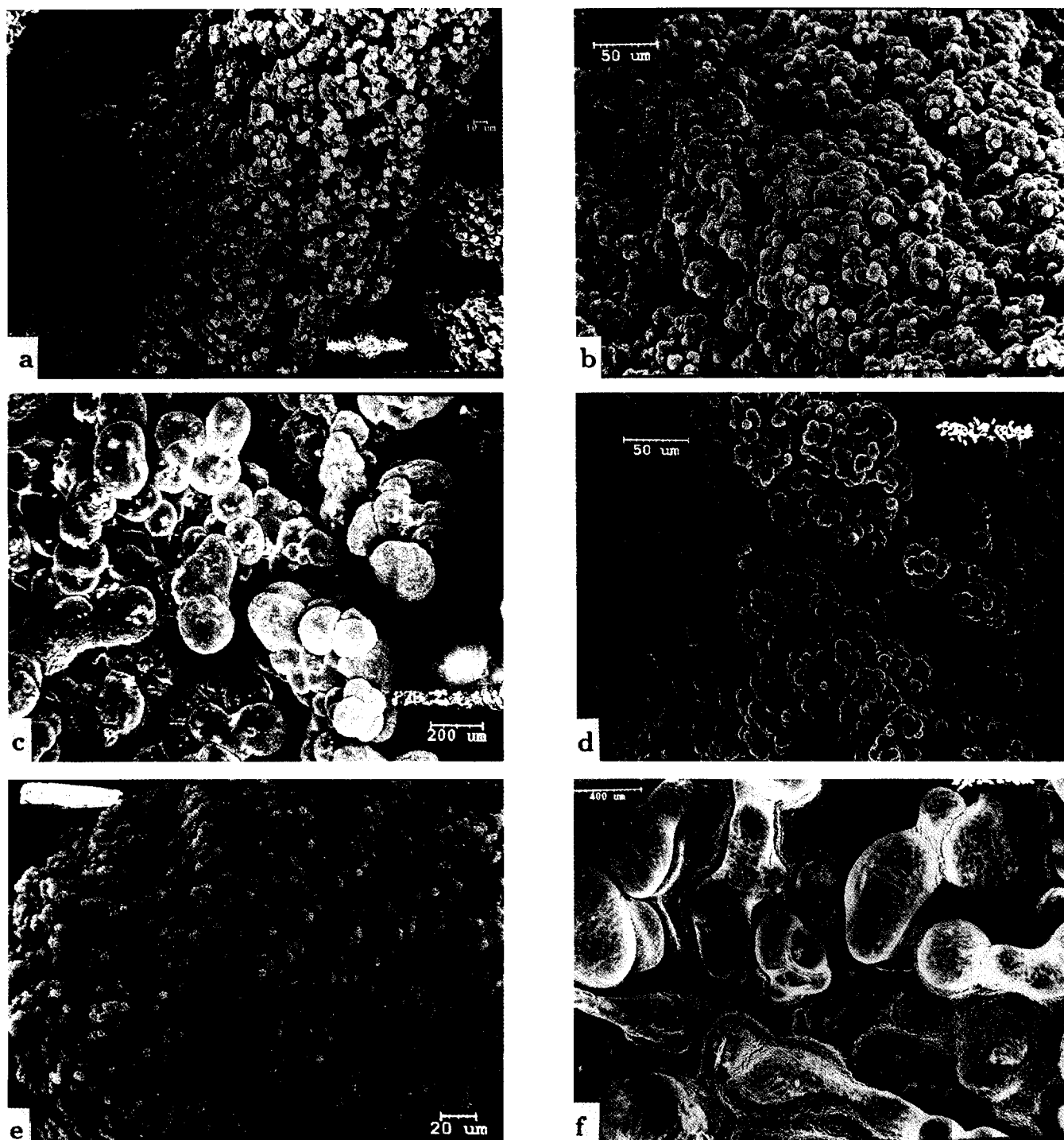


Figure 5 Scanning electron micrographs of polyketone particles: (a) 1a; (b) 1b; (c) 2a; (d) 2b; (e) 3a; (f) 3b

values corresponding to a 1/1 monomer ratio. It is noteworthy that an increase of the monomer imbalance causes only a slow reduction of the polymer viscosity. For example it is still possible to obtain high viscosity polymers at 5 mol% excess of diphenyl ether. Thus the preparation of oligomers with either type of end groups desired, reactive acyl chloride or non-reactive, thermally stable phenoxy ones, is made possible.

Similar dependences (and maximum viscosities at the 1/1 monomer stoichiometric ratio) were also observed during preparation of the rest of the polymers 1b, 2a, 2b, 3a, 3b.

It should be noted that the results obtained were analysed assuming the linear structure of the polyketones.

However, 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. Another possible type of side reaction in electrophilic acylation is an intramolecular cyclization of *ortho*-substituted phenoxy-units resulting in xanthidrol groups. The xanthidrol groups have been detected by absorbance in the u.v. at 455 nm and were reported¹³ to be responsible for melt instability.

A detailed spectral study¹⁴ of the polyketones obtained has revealed that the polymers contain defect structures. Nevertheless, the presence of these side structures does

not essentially affect the polymer viscosity values, and, therefore, does not influence conclusions, obtained from viscosity data.

After extraction with methanol and acetone the polyketone particles contain about 50 ppm of aluminium. Additional treatment of these particles with solvents by means of continuous extraction reduces the amount of residual catalyst to just a few ppm. It should be noted that washing and extraction of the particles did not change their shape.

As already mentioned, the particle morphology depends on the monomer concentration. Apart from this, for the same reaction conditions, the preparation route also affects the particle shape. Thus, the particles of polymers based on 'small' molecules (**1a**, **3a**) are smaller than particles of polymers **1b** and **3b**, based on large monomers (Figure 5). All these particles are made up of many smaller ones. (The size of the smallest particles is in the range of 5–10 μm). Very likely that the smallest particles are formed during phase separation producing larger ones by agglomeration.

CONCLUSIONS

High molecular weight, soluble aromatic poly(ether ketone ketone)s of regular structure with different tere-/iso- isomer ratios were prepared by the Friedel–Crafts electrophilic aromatic polyacylation condensation of isophthaloyl and terephthaloyl chlorides with diphenyl ether and 1,3- and 1,4-bis(4-phenoxybenzoyl)benzenes. The polymer syntheses were performed as precipitation polycondensations, and polyketones were obtained in the form of particles. The size and shape of the polyketone particles obtained are governed by the preparation route and reaction conditions. Basically, the particles are 0.1–0.5 mm in diameter. Despite the large structural difference between diphenyl ether and bis(4-phenoxybenzoyl)benzenes, polycondensations involving these monomers proceeded in a quite similar manner. The viscosity of the polyketones obtained depends on the reaction conditions and on the preparation route. Maximum polymer viscosity values were obtained at monomer concentration range 0.05–0.1 mol l⁻¹. Polycondensations

involving 'large' monomers (1,3- and 1,4-bis(4-phenoxybenzoyl)benzenes) afford polyketones with higher viscosity. On the whole, precipitation polyacylation condensation turned out to be a versatile method for preparation of high molecular weight aromatic polyketones in particle form.

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REFERENCES

- 1 Staniland, P. A. in 'Comprehensive Polymer Science' (Ed. G. Allen), Vol. 5, Pergamon Press, Oxford, 1989, pp. 483–497
- 2 Rose, J. B. in 'High Performance Polymers: Their Origin and Development' (Eds R. B. Seymour and G. S. Kirshenbaum), Elsevier, New York, 1986, pp. 187–193
- 3 Mullins, M. J. and Woo, E. P. *J. Macromol. Sci., Rev. Macromol. Chem. Phys. C* 1987, **27**, 313
- 4 Vasnev, V. A. and Vinogradova, S. V. *Usp. Khim.* 1979, **48**, 30
- 5 Rusonov, A. L. *Vysokomol. Soed., Ser. A* 1986, **28**, 1571
- 6 Zolotukhin, M. G., Gileva, N. G., Sedova, E. A., Egorov, A. E., Sangalov, Yu. A., Salazkin S. N. and Lebedev, Yu. A. *Dokl. AN SSSR* 1989, **304**, 378
- 7 Gileva, N. G., Zolotukhin, M. G., Salazhin, S. N., Sultanova, V. S., Horhold, H. H. and Raabe, D. *Acta Polym.* 1988, **39**, 452
- 8 Zolotukhin, M. G., Kozlov, V. G., Sorokina, Yu. L., Sedova, E. A., Nefediev, K. V. and Gileva, N. G. *Angew. Makromol. Chem.* 1993, **212**, 1
- 9 Zolotukhin, M. G., Dosiere, M., Fournies, C., Villers, D., Gileva, N. G. and Fatykhov, A. A. *Polymer* 1995, **36**, 3575
- 10 Zolotukhin, M. G., Rueda, D. R., Balta Calleja, F. J., Bruix, M. and Gileva, N. G. *Macromolecular Reports* 1995, **A32**, 897
- 11 Gileva, N. G., Zolotukhin, M. G., Salazkin, S. N., Rafikov, S. R., Horhold, H. H. and Raabe, D. *Acta Polym.* 1984, **35**, 282
- 12 Sakaguchi, Y., Tokai, M. and Kato, Y. *Polymer* 1993, **34**, 1512
- 13 Angelo, R. J., Darms, R. and Wysong, R. D. US Patent 3767620, 1973. *Chem. Abstr.*, 1973, **79**, 67280
- 14 Bulai, A., Zolotukhin, M. G., Rueda, D. R., Bruix, M., Cagiao, M. E., Balta Calleja, F. J. and Gileva, N. G. *Polymer* in press