

Synthesis of poly(ether ketone) by Friedel–Crafts acylation: effects of reaction conditions

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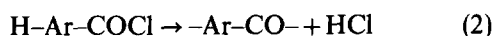
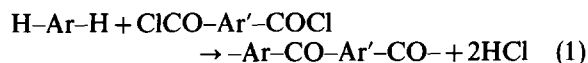
The influence of reaction conditions on the preparation of poly(ether ketone) by Friedel–Crafts acylation of diphenyl ether and isophthaloyl chloride in 1,2-dichloroethane with aluminium trichloride as a catalyst was examined. The following factors were considered: catalyst quantity, reaction temperature, monomer ratio and polymer concentration. One of the characteristics of this reaction was precipitation of polymer/catalyst complexes. Polymerization proceeded even in the precipitate by the reaction between the chain-ends. At low polymer concentrations, crystalline grains appeared, and the reaction between the chain-ends was accelerated. As the polymerization of the precipitate proceeded, the precipitate could contact more effectively with fresh solvent because the hydrogen chloride formed by the acylation was easily removed from the reaction site.

(Keywords: poly(ether ketone); polymerization; Friedel–Crafts acylation; reaction conditions; precipitate)

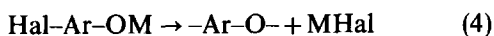
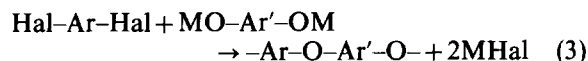
INTRODUCTION

Poly(ether ketone)s (PEK) are well known high performance semicrystalline polymers having high thermal stability and excellent mechanical properties. PEKs may be synthesized by two methods^{1,2}:

1. acylation, in which ketone linkages are formed:



2. aromatic nucleophilic displacement between activated aromatic halides and alkali metal phenoxides, in which ether linkages are formed:



In the acylation method, Friedel–Crafts acylations are carried out either in an organic solvent with aluminium trichloride as a catalyst^{3,4}, or in systems with hydrogen fluoride/boron trifluoride as catalyst/solvent complexes^{5,6}. Alternatively, the polymerization involves dehydrative acylation reactions in polyphosphoric acid^{7,8}, in trifluoromethanesulfonic acid⁹, or in methanesulfonic acid/phosphorus pentoxide medium¹⁰.

Polycondensation in an organic solvent catalysed by aluminium trichloride can be carried out under moderate conditions, and is a convenient method to obtain PEKs at the laboratory scale. AA–BB type polymerization, such as a reaction between diphenyl ether and isophthaloyl chloride, and AB type polymerization, such as a self-condensation of 4-phenoxybenzoyl chloride, are

possible. Therefore, various combinations of monomers afford a number of polymer structures^{11–17}.

However, the reaction behaviour of the Friedel–Crafts polyacylation has not been reported in detail. Of particular interest is the polymerization in 1,2-dichloroethane with aluminium trichloride catalyst, in which polymer/catalyst complexes⁶ precipitate during the reaction, thereby displaying a different approach from general solution polycondensations. In this report, the synthesis of PEK was examined using the reaction between diphenyl ether and isophthaloyl chloride.

EXPERIMENTAL

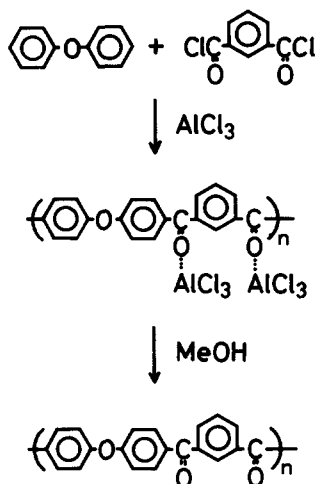
Materials

Isophthaloyl chloride (IPC, Mitsubishi Gas Chemical Co., Inc.) and aluminium trichloride (AlCl₃, Nacalai Tesque, EP) were ground to powders in nitrogen atmosphere. 1,2-Dichloroethane (DCE, Nacalai Tesque, GR) was dried over molecular sieves. Diphenyl ether (DPE, Nacalai Tesque, GR) was used without further purification.

Polymerization

A standard procedure for the preparation of PEK is described below. In a 300 ml four-necked flask equipped with a nitrogen inlet and a stirring rod, 12.22 g of DPE (0.07182 mol) and 14.58 g of IPC (0.07182 mol) were dissolved in 200 ml of DCE. After the solution was cooled below 5°C in an ice bath, 24.96 g of AlCl₃ (0.1872 mol) was added, and the reaction mixture was stirred for 2 h. Thereafter, the reaction was continued at room temperature for 16 h. The DCE was decanted from the reaction mixture, the obtained mass mixed with methanol to decompose the complex, and the methanol supernatant was removed by filtration. The product was washed with

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Scheme 1

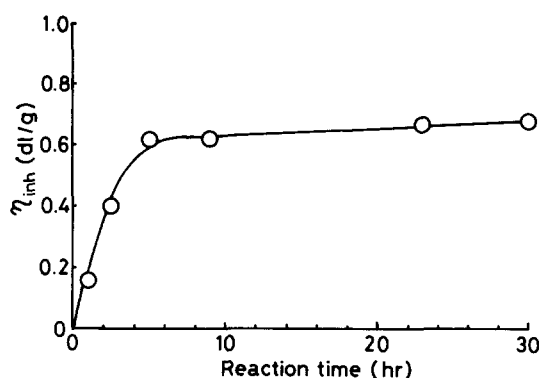


Figure 1 Change in inherent viscosity of poly(ether ketone) with reaction time at a polymer concentration of 8 wt% at room temperature. Viscometry in 95% sulfuric acid at 30°C

10% hydrochloric acid twice, then with water several times using a blender. The polymer was dried at 150°C under vacuum for 17 h.

The reaction behaviour was examined with different reaction conditions.

Characterization

Inherent viscosities were measured with an Ostwald type viscometer at 0.1 g dl⁻¹ in 95% sulfuric acid at 30°C. Infra-red spectra were recorded on a Hitachi 270-30 infra-red spectrometer with KBr discs. N.m.r. spectra were measured on a Varian Gemini-200 spectrometer in a mixture of dichloromethane-d₂ and trifluoroacetic acid-d.

RESULTS AND DISCUSSION

The preparation of PEK from DPE and IPC by Friedel-Crafts acylation with AlCl₃ is shown in Scheme 1. Figure 1 shows the change in the inherent viscosity of the polymers with reaction time at a polymer concentration of 8 wt% in DCE. The polymerization was carried out below 5°C for 2 h, then at room temperature. The molar ratio of AlCl₃ to IPC was 2.6. When the reaction proceeded for 1–2 h, precipitation occurred, and thereafter the amount of precipitate gradually increased. The inherent viscosity almost levelled off within 5 h.

In general, Friedel-Crafts acylation gives a 1:1 complex

of AlCl₃ and the carbonyl group formed^{18–21}. Therefore, an excess of AlCl₃ relative to the carbonyl groups formed should be used to catalyse the reaction. In the preparation of PEK, formations of the same type of complexes have been reported⁶, and a similar effect in the feed ratio of AlCl₃ and IPC was obtained, as shown in Table 1. The reaction with two equivalents of AlCl₃ to IPC gave a polymer with a low inherent viscosity of 0.27 dl g⁻¹; a molar excess of AcCl₃ over the monomers was necessary to obtain polymers with higher viscosity. However, a large excess of AlCl₃, for example a four-fold excess, seemed to induce unfavourable side reactions, since the polymer obtained under this condition contained a fraction that was insoluble in 95% sulfuric acid. Therefore, a suitable quantity of AlCl₃ was two to three molar equivalents relative to IPC.

The effect of reaction temperature is shown in Table 2. Although the reaction at room temperature gave polymers that were completely soluble in sulfuric acid, higher reaction temperature resulted in an insoluble part. When polymerized at 85°C, the polymer was completely insoluble in sulfuric acid, and the yield (109%) was higher than the theoretical value. Figure 2 compares the i.r. spectra of the polymers obtained at room temperature and at 85°C. The polymer obtained at 85°C showed sp³ C–H stretching at 2900–3000 cm⁻¹. This means that the Friedel-Crafts acylation with DCE occurred as a side reaction, and a cross-linked polymer was obtained.

Table 3 shows the effect of the DPE/IPC feed ratio on the inherent viscosity of the polymer obtained. A monomer ratio of 1:1 gave the maximum inherent viscosity, and deviations from the stoichiometry gave lower viscosities. Although this polymerization involved the precipitation of polymer/AlCl₃ complexes during the reaction, the molar ratio effect was similar to those in the usual solution polycondensation reactions.

The acylation-type polymerization also showed a characteristic effect of monomer concentration on the inherent viscosity of polymers. As shown in Table 4, lower

Table 1 Effect of AlCl₃ quantity on PEK polymerization^a

AlCl ₃ (molar ratio to IPC)	Yield (%)	η_{inh}^b (dl g ⁻¹)
2.0	89	0.27
2.6	95	0.68
3.0	95	0.74
4.0	90	0.68

^a Polymerized at room temperature with a polymer concentration of 8 wt% for 16 h

^b Measured with a concentration of 0.1 g dl⁻¹ in 95% sulfuric acid at 30°C

Table 2 Effect of reaction temperature on PEK polymerization^a

Temperature (°C)	Yield (%)	η_{inh}^b (dl g ⁻¹)	Solubility in H ₂ SO ₄
r.t.	95	0.68	soluble
50	94	0.66	some insoluble part
85	109	–	insoluble

^a Polymerized at a polymer concentration of 8 wt% with 2.6 molar ratio of AlCl₃ for 16 h

^b Measured with a concentration of 0.1 g dl⁻¹ in 95% sulfuric acid at 30°C

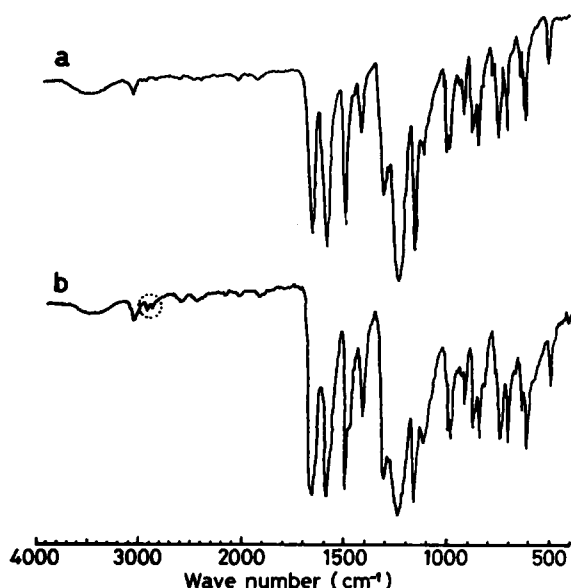


Figure 2 I.r. spectra of poly(ether ketone) obtained at (a) room temperature and (b) 85°C

Table 3 Effect of monomer ratio on PEK polymerization^a

Monomer ratio		Yield (%)	η_{inh}^b (dl g ⁻¹)
DPE	IPC		
1.00	0.99	90	0.57
1.00	1.00	95	0.68
1.00	1.01	92	0.47

^a Polymerized at room temperature at a polymer concentration of 8 wt% with 2.6 molar ratio of AlCl₃ for 16 h

^b Measured with a concentration of 0.1 g dl⁻¹ in 95% sulfuric acid at 30°C

Table 4 Effect of polymer concentration on PEK polymerization^a

Polymer concentration (wt%)	Yield (%)	η_{inh}^b (dl g ⁻¹)
19	95	0.57
8	95	0.68
4	94	0.75
2.5	97	0.87

^a Polymerized at room temperature with 2.6 molar ratio of AlCl₃ for 16 h

^b Measured with a concentration of 0.1 g dl⁻¹ in 95% sulfuric acid at 30°C

monomer concentrations resulted in higher viscosities. At 8 wt% of monomers, the reaction formed a gelatinous mass with an inherent viscosity of 0.68 dl g⁻¹. On the other hand, at 2.5 wt% the polymerization gave a number of hexagonal grains, several millimetres in length, that were apparently single crystals, and the inherent viscosity was 0.87 dl g⁻¹. Therefore, differences in the features of the precipitations seemed to affect polymerization.

The relation between the formation of precipitate and the polymerization rate was examined. Polymerization was terminated at several reaction times, as shown in Table 5. After separating the precipitate and the solution, both parts were treated with methanol to obtain the products. As shown in Table 5, the substance remaining

in the solution was a PEK oligomer having an inherent viscosity of around 0.1 dl g⁻¹; when the viscosity exceeded 0.2 dl g⁻¹, precipitation occurred. Thereafter, the quantity of precipitate and the inherent viscosity increased with reaction time. The increase in viscosity was remarkable compared to the increase in quantity of precipitate, suggesting that the reaction could proceed in the solid state.

To clarify the possibility of a reaction between the IPC chain-end and DPE chain-end in the precipitate, in addition to the reaction between a chain-end in the precipitate and a monomer or oligomer in the solution, the reaction shown in Scheme 2 was carried out. The precipitate which appeared at an early stage was separated, and fresh DCE was added to it. Without further addition of monomers or oligomers, the polymerization proceeded in the precipitate, where the inherent viscosity increased from 0.28 to 0.88 dl g⁻¹ in 7 h. From this result, the reaction between the two chain-ends in the precipitate was confirmed.

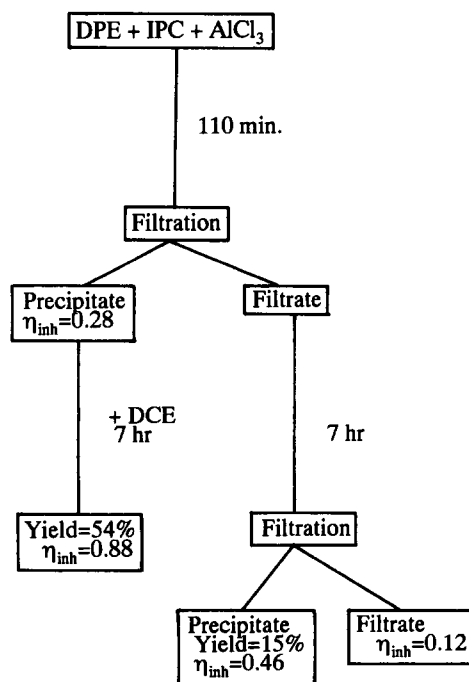
The crystalline precipitate formed during the polymerization at lower concentration seems to have an advantage in the reaction between the chain-ends due to the regular

Table 5 Polymerization behaviour of PEK^a

Reaction time (h)	From gelatinous mass		From solution		Total yield (%)
	Yield (%)	η_{inh}^b (dl g ⁻¹)	Yield (%)	η_{inh}^b (dl g ⁻¹)	
1	0	—	—	0.13	—
1.5	65	0.24	20	0.12	85
2.5	81	0.44	5	0.14	86
5.0	91	0.71	1	0.10	93

^a Polymerized at room temperature at a polymer concentration of 8 wt% with 2.6 molar ratio of AlCl₃

^b Measured with a concentration of 0.1 g dl⁻¹ in 95% sulfuric acid at 30°C



Scheme 2

Table 6 PEK polymerization with solvent exchange at 8 wt%

Reaction time (h)	η_{inh}^a (dl g ⁻¹)	Solvent exchange ^b
2.5	—	done
5.0	0.78	done
23.0	0.92	—

^a Measured with a concentration of 0.1 g dl⁻¹ in 95% sulfuric acid at 30°C

^b Solvent exchange: extraction of 100 ml of DCE from the reaction mixture and addition of 100 ml of fresh DCE

Table 7 PEK polymerization with solvent exchange at 19 wt%

Reaction time (h)	η_{inh}^a (dl g ⁻¹)	Solvent exchange ^b
2.0	0.34	done
2.5	0.46	done
3.5	0.48	done
5.5	0.58	done
21.0	0.68	—

^a Measured with a concentration of 0.1 g dl⁻¹ in 95% sulfuric acid at 30°C

^b Solvent exchange: extraction of 100 ml of DCE from the reaction mixture and addition of 100 ml of fresh DCE

alignment of the polymer chains. This is considered to be one of the reasons why polymerization at lower concentration gave a higher inherent viscosity.

The addition of fresh DCE to the precipitate may cause extraction of the hydrogen chloride formed by the acylation reaction from the reaction site. On the basis of this theory, solvent exchange was carried out, i.e. polymerization in which DCE was removed from the precipitate and fresh DCE was added several times. *Tables 6 and 7* show the results of the solvent exchange experiments at polymer concentrations of 8 wt% and 19 wt%, respectively. The polymerization without solvent exchange resulted in polymers with inherent viscosities of 0.68 and 0.57 dl g⁻¹, respectively (*Table 4*, first two lines). In contrast, the solvent exchange method gave higher molecular weight polymers (η_{inh} = 0.92 and 0.68 dl g⁻¹, respectively, at 8 and 19 wt%). *Figure 3* shows the advantage of solvent exchange for a wide range of polymer concentration. At lower concentration in particular, the effect of solvent exchange was remarkable. This effect is attributed to the formation of the crystalline precipitate at lower concentration, which accelerates the reaction among the polymer chain-ends.

CONCLUSIONS

The influence of reaction conditions on the Friedel–Crafts polycondensation of diphenyl ether and isophthaloyl chloride in 1,2-dichloroethane with aluminium trichloride catalyst was examined. A 1:1 DPE/IPC monomer ratio, two–three-fold molar excess of AlCl₃ over IPC, and lower reaction temperature gave PEK with sufficiently

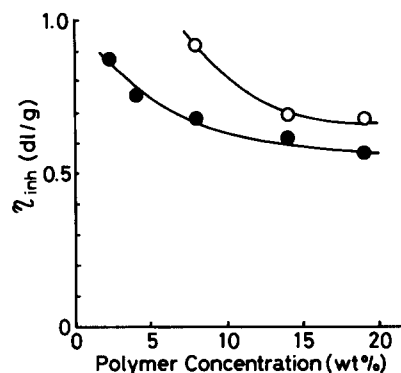


Figure 3 Effect of solvent exchange: O, with the solvent exchange; ●, without solvent exchange

high molecular weight and good solubility in 95% sulfuric acid. The polymerization formed a precipitate of polymer/catalyst complexes; it proceeded even in the precipitate, through the reaction between the polymer chain-ends. When the polymerization was performed at low polymer concentration, crystalline grains appeared and the reaction between the chain-ends was accelerated. Contacting the precipitate with fresh solvent, i.e. the solvent exchange procedure, induced further polymerization, because the hydrogen chloride formed by the acylation was easily removed from the reaction site.

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