

Synthesis of Aromatic Poly(ether ketone)s Containing C36 Aliphatic Unsaturated Groups in the Main Chain

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ABSTRACT: Aromatic poly(ether ketone)s (PEKs) were modified with various amount of C36 dimer acid Pripol 1017 obtained from polymerization of unsaturated C18 fatty acids. To obtain modified PEKs, polycondensation was carried out using various dicarboxylic acids with diphenylether at 75°C in phosphorus pentoxide/methanesulfonic acid as condensing agent and solvent. The reduced viscosities of polymers are relatively low, up to 0.13 dL/g. PEK with a structure (molar ratio of aliphatic to aromatic segment : 0.33) is soluble in organic polar solvents and can be cast from a tetrahydrofuran solution with cobalt naphthenate air dryer in order to obtain crosslinked film at room temperature. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1275–1278, 1997

Key words: aromatic poly(ether ketone); C36 aliphatic unsaturated group

INTRODUCTION

Since poly(aryl ether ketone) (PAEK) has shown promise as an excellent engineering plastic due to its good mechanical and thermooxidative stability, the synthesis of aromatic poly(ether ketone)s (PEKs) has been of interest in recent years.¹

A number of synthetic routes for producing PEKs have already been described in the literature.¹ PEKs can be prepared by means of two procedures: (i) by nucleophilic substitution and (ii) by electrophilic substitution reactions. In the latter method, polycondensation has been carried out by Friedel–Crafts acylation. In this manner a number of Friedel–Crafts catalysts have been used. HF/BF₃, strong acids such as trifluoromethanesulfonic acid,³ and combination of methanesulfonic acid/P₂O₅⁴ are useful catalysts as well as solvents for electrophilic substitution.

Although PAEKs are opaque, tough engineering thermoplastics showing excellent high temperature and hydrolytic, chemical, solvent,

and stress-crack resistance, they have some drawbacks: relatively lower glass transition temperature (T_g) compared with aromatic poly(ether sulfone), the necessity of high temperature to fabricate parts, insolubility in typical organic solvents, and others. From this point of view, the most structural modifications have been achieved to improve the properties of PAEK for various applications and different purposes. The first method in the modification of PAEK has involved structural changes in the main chain, such as the introduction of various groups along the chain, e.g., alkyl,⁵ —SO₂—,⁶ —CF₃, Si—O—Si,⁸ amide,⁹ imide,¹⁰ heterocycles,^{11,12} phosphorus,^{13,14} and biphenyl groups,¹⁵ variation of meta-to-para ratio,⁴ and variation of ether-to-ketone ratio.¹⁶ The second method for the modification of PAEK is to introduce pendent groups into the polymer chain. PAEK-type polymers with sulfonylchloride,¹⁷ sulfonamide,¹⁷ methyl,¹⁸ bromomethyl,¹⁹ phenyl,²⁰ ethynyl,²¹ and long alkyl chain substituents²² were prepared. An alternative approach to the modification of PAEK was achieved to introduce amino²³ and ethynyl²⁴ groups into the polymer terminal for further purposes.

From this point of view, we are interested in

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Table I Reaction Conditions and Properties of Aromatic PEK Containing Pripol 1017

Polymer No.	Pripol 1017 (mmol)	Diphenylether (mmol)	4,4'-dicarboxydiphenylether (mmol)	Aliphatic Seg./Aromatic Seg (mol/mol)	Conversion		η_{red}^a (dL/g)
					g	%	
1	0	2.07	2.0	0.000	0.76	97	0.11
2	0.2	2.07	1.8	0.052	0.79	94	0.13
3	0.4	2.07	1.6	0.109	0.95	100	— ^b
4	0.6	2.07	1.4	0.173	1.01	100	0.13
5	0.8	2.07	1.2	0.245	1.01	98	0.12
6	1.0	2.07	1.0	0.326	1.00	92	0.09
7	1.2	2.07	0.8	0.418	1.20	100	— ^b

Reaction 3 h; Eaton's reagent = 6 mL; at 75°C.

^a Measured in H₂SO₄ at 30°C.

^b Undissolved in H₂SO₄.

modifying PEK by introducing various amounts of a dimer fatty acid (Pripol 1017) as a soft segment to the main chain. Pripol 1017 is a C36 aliphatic dibasic acid and produced by the polymerization of unsaturated C18 fatty acid. Its structure is essentially that of a long-chain dicarboxylic acid with two alkyl side chains. It appears to contain at least one ethylenic bond.

The polymerization was carried out by direct polycondensation of 4,4'-dicarboxy diphenylether and Pripol 1017 with diphenylether using phosphorus pentoxide/methanesulfonic acid (Eaton's reagent)²⁵ as condensing agent and solvent in a weight ratio of 1 : 10.

EXPERIMENTAL

Materials

The Eaton's reagent was prepared according to the reported procedure. Diphenylether (Aldrich WI, USA) was recrystallized from ethanol; 4,4'-dicarboxy diphenylether was prepared by reaction of 4,4'-diacetyl diphenylether with NaOCl solution. Recrystallization from acetic acid yielded white powder (m.p. 331–333°C). Pripol 1017 (acid value: 195 mg KOH/g; iodine value: 33 g I₂/100 g), a kind gift from Unichema Chemicals Ltd. (UK), is viscous liquid and was used as received. Solvents were purified.

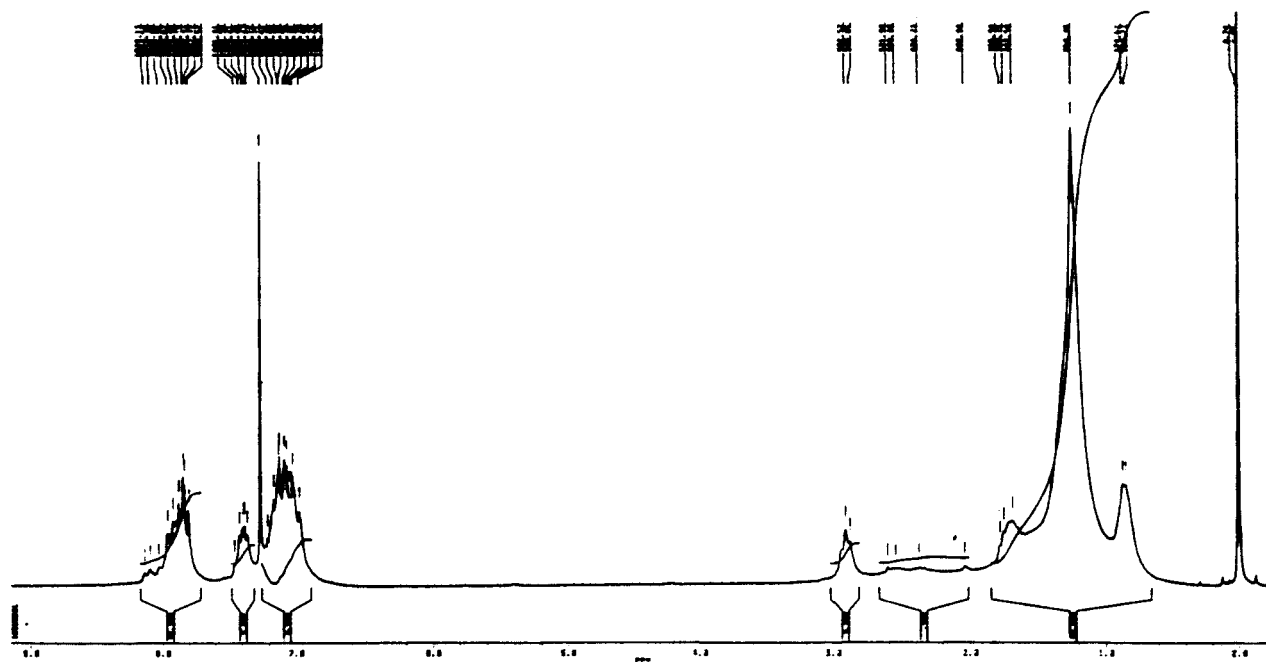


Figure 1 ¹H-NMR of polymer no. 6 in CDCl₃; TMS as an internal standard.

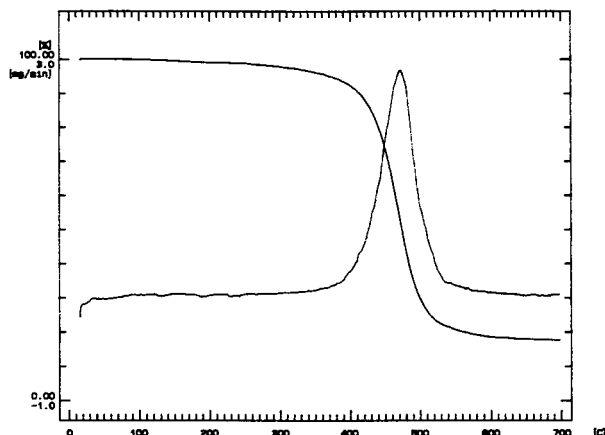


Figure 2 TGA curve of polymer no. 6 in air at a heating rate of $10^{\circ}\text{C}/\text{min}^{-1}$.

Measurements

Infrared (IR) spectra were recorded on a Jasco FTIR spectrophotometer. $^1\text{H-NMR}$ spectra were obtained on a Bruker AC200 spectrometer at 200 MHz in CDCl_3 with tetramethylsilane as an internal standard. Differential scanning calorimetry (DSC) was performed with a Mettler TA4000 at a heating rate of $10^{\circ}\text{C}/\text{min}$. Thermogravimetric analysis (TGA) was obtained by a Shimadzu TG50 thermal analyzer in air at a heating rate of $10^{\circ}\text{C}/\text{min}$.

Polymer Synthesis

Synthesis of polymer no. 6 shows a typical polymerization procedure: A solution of 4,4'-dicarboxy diphenylether (0.258 g, 1 mmol), Pripol 1017 (0.560 g, 1 mmol), and diphenylether (0.360 g, 2.07 mmol) in Eaton's reagent was stirred at 75°C

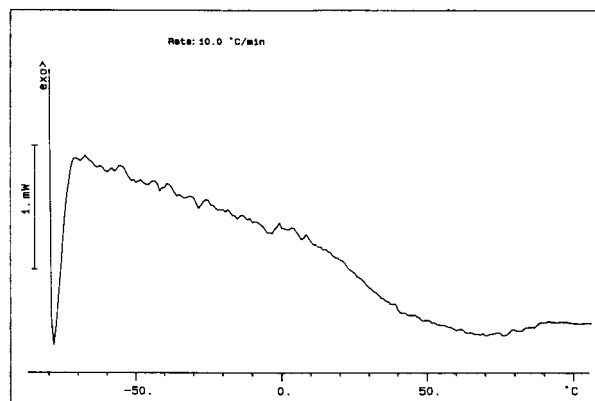
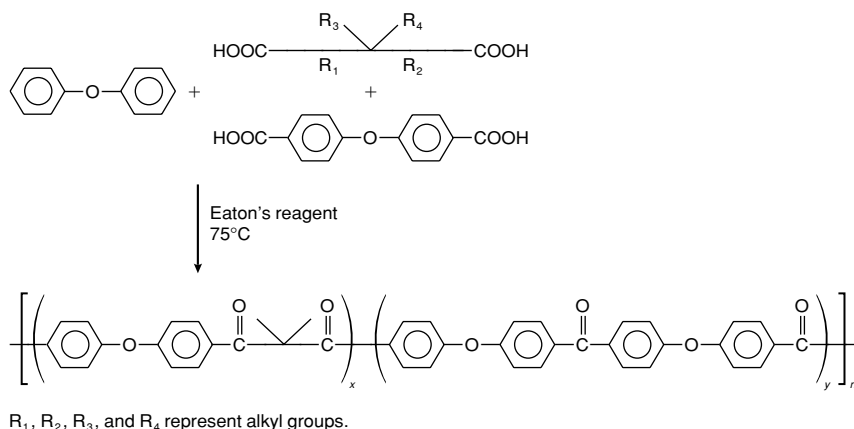


Figure 3 DSC thermogram of polymer no. 6 at a heating rate of $10^{\circ}\text{C}/\text{min}^{-1}$.

for 3 h. This solution was poured into water and filtered. The collected polymer was washed with water and ethanol. The yield was 1.0 g (92%). IR (KBr) spectrum showed absorptions at 1650 ($\text{C}=\text{O}$), 1230 ($\text{Ar}-\text{O}-\text{Ar}$), and $2800\text{--}3000$ cm^{-1} (CH_2).

RESULTS AND DISCUSSION

The modified PEKs with Pripol 1017 dimer acids were prepared via a process depicted in Scheme 1. As can be seen from Scheme 1, diphenylether was reacted with various amounts of 4,4'-dicarboxy diphenylether and Pripol 1017 in phosphorus pentoxide/methanesulfonic acid in a weight ratio of 1 : 10. The reaction conditions and properties of PEK containing Pripol 1017 are summarized in Table I. The polycondensation proceeds in homogeneous solution and gives quantitative yields of



Scheme 1

PEKs with relatively low reduced viscosities up to 0.13 dL/g, due to mild reaction conditions.

The structure of the resulting PEKs containing Pripol 1017 groups was confirmed by IR and $^1\text{H-NMR}$ spectroscopy. IR spectra of a series of polymers exhibit strong absorption peaks at around 1650, 1230, and 2800–3000 cm^{-1} due to C=O, Ar—O—Ar, and aliphatic CH_2 stretchings, respectively. $^1\text{H-NMR}$ spectrum of polymer no. 6 is shown in Figure 1 and exhibits a more detailed structure. The multiplet peaks, which are assigned to the aromatic protons, were observed at 6.8–8.0 ppm. The multiplet signals appearing around 0.8–1.7 ppm were assigned to aliphatic CH_2 protons and a triplet signal at 2.9 ppm was assigned to the aliphatic CH_2 protons adjacent to C=O group. On the other hand, the ratio of the aliphatic proton signals over the aromatic signals was found to be 0.41, agreeing well with the calculated ratio (0.33).

Thermal stability of polymer no. 6 was examined by TGA. A typical trace is shown in Figure 2. The polymer showed a 10% weight loss at 415°C in air. DSC on polymer no. 6 showed a T_g only at 15°C because of the aliphatic CH_2 groups of Pripol 1017 dimer acid (Fig. 3). However polymer no. 1 showed two endotherms at 162°C and 335°C which reflected T_g and melt temperature, respectively.

Only polymer no. 6 is soluble in common organic polar solvents. Therefore a tetrahydrofuran solution of it with cobalt naphthenate air dryer can be cast onto a glass plate and a hard, tough, crosslinked coating film can be obtained at room temperature.

CONCLUSION

We demonstrated an example of PEK containing soft segment from unsaturated dimer acid Pripol 1017. Hence olefinic groups were first introduced into the main chain of PEK. This modified PEK can be applied particularly to surface coating uses.

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