Novel Macrocyclic Precursors of Phenolphthalein Poly(arylene ether ketone) and Poly(arylene ether sulfone): Synthesis and Polymerization

Hongyan Jiang,* Tianlu Chen, Shuqin Bo, and Jiping Xu

Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, P. R. China

Received June 12, 1997
Revised Manuscript Received September 3, 1997

Introduction. In recent years, the advantages of using cyclic (arylene ether ketone)s[1−16] and cyclic (arylene ether sulfone)s[12,16−22] as precursors of high-performance thermoplastics have been well recognized. The cyclic oligomers offer a unique combination of low melt viscosity and the possibility of undergoing controlled polymerization in the melt without the liberation of volatile byproducts. These features are particularly valuable for the manufacture of advanced composite materials. However, only a few cyclic precursors of commercially available poly(arylene ether)s have been prepared.[14,17−21] In addition, the cyclic (arylene ether ketone)s prepared are generally crystalline or semicrystalline.

Phenolphthalein-based poly(arylene ether ketone) (PEK-C)[23] and poly(arylene ether sulfone) (PES-C)[24] are a kind of commercialized high-performance, amorphous polymers that exhibit excellent mechanical properties, thermal and environmental stability, high glass transition temperature (T_g), and good solubility in a few polar aprotic solvents such as DMF, DMSO, and some chlorohydrocarbons. The commercial process of preparing PEK-C or PES-C is through the aromatic nucleophilic substitution reaction of phenolphthalein with 4,4′-dichlorobenzophenone or 4,4′-dichlorodiphenyl sulfone in sulfolane in the presence of potassium carbonate. However, these polymers, as well as other poly(arylene ether)s, suffer greatly from the high softening temperatures and especially the high melt viscosities, which combine to limit the application of these excellent materials in areas such as fiber impregnation and microscale fabrication. An alternative route to produce PEK-C and PES-C is through ring-opening polymerization of macrocyclic precursors. Herein, we disclose our preliminary results in this endeavor.

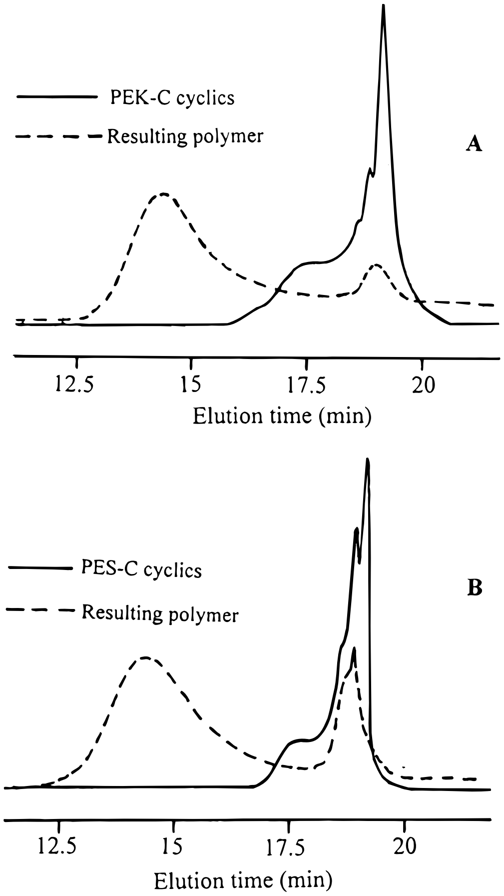
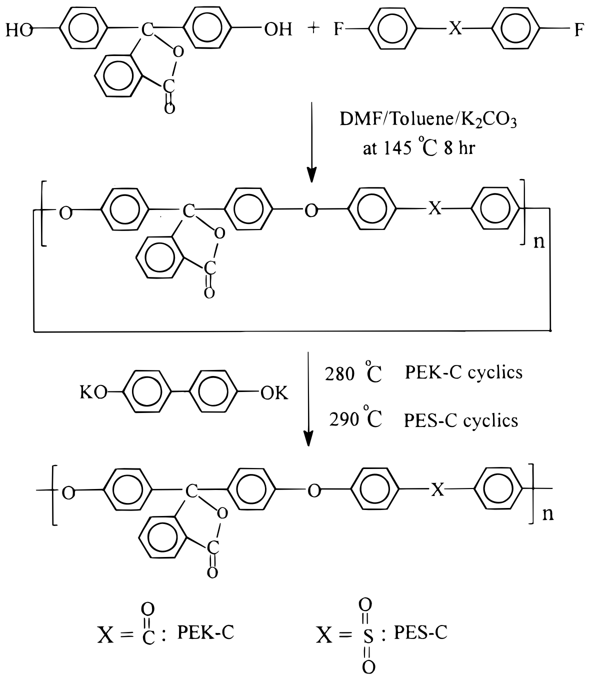


Figure 1. GPC traces of (A) PEK-C cyclic oligomers and resulting polymer and (B) PES-C cyclic oligomers and resulting polymer.

Scheme 1



Results and Discussion. Phenolphthalein Poly(arylene ether ketone) (PEK-C). PEK-C cyclics were prepared by reaction of phenolphthalein with 4,4′-difluorobenzophenone under pseudo-high-dilution conditions, as shown as in Scheme 1. A 0.2 M DMF solution (40 mL) of phenolphthalein and 4,4′-difluorobenzophenone was added dropwise into a mechanically stirred vessel containing solvent (DMF) and base (K_2CO_3) over a period of 8 h. The refluxing temperature was controlled at 145 °C by varying the amount of the azeotropic solvent toluene. Following the addition of the reactants, the violet-red solution was refluxed for another 10 h when it turned pale yellow. The isolated yield of PEK-C cyclic oligomers was 54%. Gel permeation chromatographic (GPC) analysis of the product reveals a series of resolved peaks in the low molecular weight region (Figure 1A). Confirmation of the cyclic nature of the oligomers was based on the absence of end groups in the ^{1}H NMR and matrix-assisted laser desorption/ionization-time of flight mass spectrometry (MALDI-TOF MS). MALDI-TOF MS of PEK-C cyclics (Figure 2A) reveals cyclic oligomers from dimer ($n = 2$, $m/z = 994.1$) up to octamer ($n = 8$, $m/z = 3973.2$) with reasonable signal to noise ratio. The MS spectrum of PEK-C cyclic oligomers shows two signals for each oligomer. For example, the signals for cyclic trimer are located at 1490.6 and 1512.6 Da. The signal at 1490.6 Da corresponds to the protonated molecular ion peak;

S0024-9297(97)00857-7 CCC: $14.00 © 1997 American Chemical Society

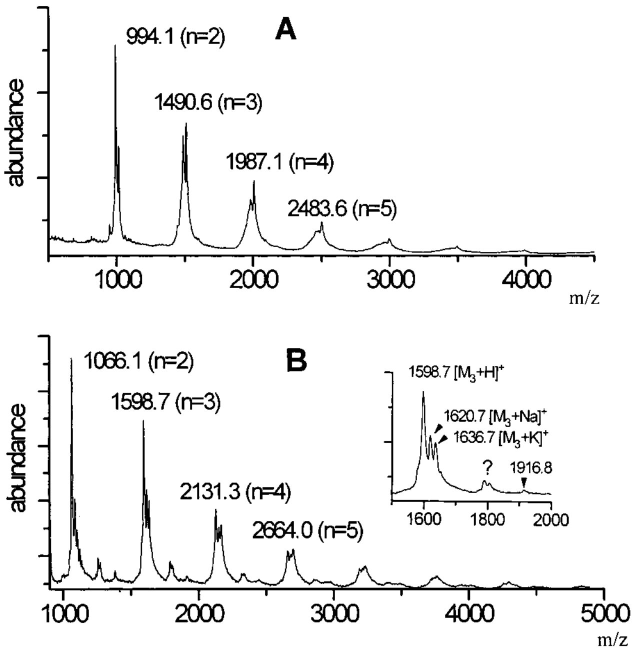


Figure 2. MALDI-TOF-MS spectra of (A) PEK-C and (B) PES-C cyclic oligomers.

that at 1512.6 Da is due to the adduct of the trimer with a sodium cation. On the basis of GPC and MS analysis, PEK-C cyclic oligomers contain 41.9% cyclic dimer, 13.8% cyclic trimer, 6.6% cyclic tetramer, and 37.7% higher homologues.

Thermal analysis of PEK-C cyclics shows a small T_g peak at 127 °C (midpoint, $\Delta C_p = 0.211$ J/(g °C)) and another T_g peak near 222.1 °C (midpoint, $\Delta C_p = 0.343$ J/(g °C)). No melt endotherm was observed up to 450 °C, indicating an amorphous material. PEK-C cyclics begin to soften near 260 °C and form a clear, homogeneous melt state near 280 °C.

The polymerization of PEK-C cyclic oligomers was carried out in a nitrogen atmosphere at 280 °C in the presence of 2.0% (w/w) potassium 4,4′-biphenoxide for 40 min. Polymerization of PEK-C cyclics resulted in a flexible and tough material that, unlike the commercial PEK-C sample, was only partially soluble in chloroform and tetrahydrofuran. About 80% (weight) of the resulting polymer is soluble in THF. A GPC trace of the soluble fraction is presented in Figure 1A, which clearly shows the formation of high molecular weight linear polymer. The high molecular weight fraction has an M_w of 52.3 and M_n of 17.2k with a molecular weight distribution of 3.0. GPC analysis also shows that about 10.5% cyclic oligomers remained in the final polymer. Prolonging the polymerization time to 1 h gave fewer cyclic oligomers (6.5%), but the soluble fraction of the high molecular weight materials was considerably reduced to 65%. The insolubility of PEK-C prepared from cyclics probably resulted from branching side reactions occurring at the high reaction temperatures employed. About 85% (weight) of the PEK-C prepared from ring-opening polymerization is soluble in chloroform, and the soluble fraction has a reduced viscosity of 0.26 dL/g (0.5% in chloroform at 25 °C), which is approximately one-third the value of the reduced viscosity of the commercial PEK-C sample (0.79 dL/g). The lower viscosity of the PEK-C prepared from cyclics may originate from the presence of linear oligomers in the cyclic oligomers, which acted as chain-transfer agents in the ring-opening polymerization reaction. Furthermore, the lower viscosity can also be attributed to the residual cyclic oligomers in the final polymer. Thermal analysis of the resulting PEK-C polymer shows a glass transition temperature of 216.1 °C (midpoint), which is a little lower than that for the commercial PEK-C sample ($T_g = 228$ °C) and shows a 5% weight loss at 407.5 °C in a nitrogen atmosphere.

Phenolphthalein Poly(arylene ether sulfone) (PES-C). PES-C cyclic oligomers were prepared by reaction of phenolphthalein with 4,4′-difluorophenyl sulfone in an analogous manner to PEK-C cyclics (Scheme 1). The yield of the PES-C cyclics was 49%. GPC analysis was consistent with low molecular weight oligomers (Figure 1B). The MALDI-TOF mass spectrum in Figure 2B shows that PES-C cyclics consist of macrocyclces from cyclic dimer to octamer ($n = 2-8$). The expanded scale of the MS spectrum of PES-C cyclic oligomers shows three signals for each oligomer. For example, the signals for cyclic trimer are located at 1598.7, 1620.7, and 1636.7 Da. The signal at 1598.7 Da corresponds to the protonated molecular ion peak, that at 1620.7 Da is due to the adduct of the trimer with a sodium cation, and that at 1636.7 Da is due to the adduct of the trimer with a potassium cation. Traces of linear oligomers were also observed, as an example, at $m/z = 1916.9$ (trimer plus phenolphthalein) and $m/z = 1790$ and 1806 Da, which have not been correctly ascribed. The level of detection was about 8% according to the relative abundance. Based on the integration of the peak area, GPC analysis indicates that PES-C cyclics contain 41.7% cyclic dimer, 20.6% cyclic trimer, 6.5% cyclic tetramer, and 31.2% higher homologues.

Thermal analysis of PES-C cyclics shows a small T_g peak at 133.4 °C (midpoint, $\Delta C_p = 0.242$ J/(g °C)) and another T_g peak at 246.8 °C (midpoint, $\Delta C_p = 0.553$ J/(g °C)). No melt endotherm peak was observed up to 450 °C. PES-C cyclics begin to soften at 268 °C and form a homogeneous melt near 290 °C. PES-C cyclic oligomers were polymerized at 290 °C for 40 min using potassium 4,4′-biphenoxide as an initiator. The resulting polymer is also partially soluble in chloroform and THF. About 90% of the PES-C prepared from ring-opening polymerization is soluble in chloroform, and the soluble fraction has a reduced viscosity of 0.23 dL/g (0.5% in chloroform at 25 °C) compared with 0.67 dL/g for the commercial PES-C sample. The soluble fraction in THF makes up 85% (weight) of the resulting polymer. GPC analysis shows that the high molecular weight fraction has an M_w of 59.1 and an M_n of 20.1k with a molecular weight distribution of 2.9, and about 18.6% cyclic oligomers remained in the final polymer (Figure 1B). Thermal analysis of the resulting PES-C polymer shows a glass transition temperature of 251.3 °C (midpoint) compared with a T_g of 260 °C (midpoint) for the commercial PES-C sample and shows a 5% weight loss at 434.0 °C in a nitrogen atmosphere.

Conclusion. We have demonstrated the feasibility of using the ring-opening polymerization of cyclic oligomers to produce a kind of commercialized PEK-C and PES-C polymers. These preliminary experiments produced good yields of the cyclic oligomers without a serious effort to optimize the preparative conditions. Ring-opening polymerization produced the corresponding polymers. While the PEK-C and PES-C prepared from ring-opening polymerization are only partially soluble in chloroform and tetrahydrofuran, and the reduced viscosity of the soluble fraction in chloroform of either polymer was lower than that for the corresponding commercial sample, we believe that changes in catalyst structures and removal of linear oligomers from the cyclics will produce soluble PEK-C and PES-C polymers with higher reduced viscosities. Further work will be directed toward optimization of the cyclization reaction and detailed polymerization study.

Experimental Section. General Procedure. GPC analysis was performed on a Shimadzu LC-4A apparatus equipped with two columns of DuPont ZORBAX-PSM-60S and 100S, and a UV detector (254 nm) using tetrahydrofuran (THF) as the eluent at a flow rate of 0.5 mL/min. The columns were calibrated with a mixture of six polystyrene standards. MALDI-TOF MS spectra were recorded on a LDI-1700 instrument at a wavelength of 337 nm (N_2 laser light) using 2,5-dihydroxybenzoic acid as the matrix. The MALDI instrument was operated in a linear mode. Thermal analysis was carried out on a Perkin-Elmer 7 Series Thermal Analysis System. The heating rate was 10 °C/min in a nitrogen atmosphere. The commercial samples of PEK-C and PES-C were obtained from Xu Zhou Engineering Plastics Co.

Phenolphthalein Based on Poly(arylene ether ketone) (PEK-C) Cyclic Oligomers. The cyclization reaction was conducted in a 500 mL four-neck round-bottom flask equipped with a nitrogen inlet, thermometer, and condenser. The flask was charged with 300 mL of DMF, 30 mL of toluene, and 2.0 g of anhydrous potassium carbonate. The solution was mechanically stirred and heated to 145 °C. A solution of phenolphthalein (2.55 g, 8.00 mmol) and 4,4′-difluorobenzophenone (1.75 g, 8.00 mmol) in 40 mL of DMF was added over a period of 8 h. After the addition was complete, the resulting solution was refluxed until the violet-red solution was turned pale yellow. The reaction was cooled and filtered to remove all the salt. The solvent was then removed from the filtrate at reduced pressure. The residue was refluxed in distilled water for a period of 1 h. The desired cyclic oligomers were obtained as a pale yellow powder and dried in a vacuum oven (100 °C) for 12 h. The yield of PEK-C cyclics was 2.14 g (54%). GPC analysis of the product shows an M_w of 5.1 and an M_n of 0.80k. IR (KBr): 1770.7 (ester C=O), 1654.6 (C=O) cm^{-1}; ^1H-NMR ($CDCl_3$): δ 7.98 (m, 1H), 7.79 (m, 5H), 7.60 (m, 2H), 7.37 (m, 4H), 7.05 (m, 8H).

PEK-C Polymer. In a 50 mL flask, PEK-C cyclics (0.50 g) were intimately mixed with potassium 4,4′-biphenoxide (0.01 g). The flask was heated in a nitrogen atmosphere at 280 °C for 40 min to give PEK-C polymer. The resulting polymer was only partially soluble in chloroform and THF. GPC analysis shows that the soluble fraction of the resulting PEK-C has an M_w of 52.3 and an M_n of 17.2k. The reduced viscosity of the soluble fraction in chloroform was 0.26 dL/g compared with 0.79 dL/g for the commercial PEK-C sample.

Phenolphthalein Poly(arylene ether sulfone) (PES-C) Cyclic Oligomers. PES-C cyclic oligomers were prepared according to the method used for PEK-C cyclics. The yield of PES-C cyclics was 2.09 g (49%). GPC analysis of the product shows an M_w of 5.2 and an M_n of 0.90k. IR (KBr): 1770.3 (C=O), 1322.9 (SO_2) cm^{-1}. ^1H-NMR ($CDCl_3$): δ 7.98 (m, 1H), 7.86 (m, 4H), 7.75 (m, 1H), 7.59 (m, 2H), 7.37 (m, 4H), 7.01 (m, 8H).

PES-C Polymer. PES-C cyclic oligomers were polymerized according to the method used for PEK-C cyclics but at 290 °C. The reduced viscosity of the soluble fraction in chloroform was 0.23 dL/g compared with 0.67 dL/g for the commercial PES-C sample. GPC analysis shows that the soluble fraction has an M_w of 59.1 and an M_n of 20.1k.

Acknowledgment. We thank the Polymer Chemistry Laboratory, Changchun Institute of Applied Chemistry and Chinese Academy of Sciences (CAS) and Chinese Petrol-Chemical Corp. for financial support.

References and Notes

(1) Cella, J. A.; Talley, J. J.; Fukuyama, J. M. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1989**, *30* (2), 581.
(2) Colquhoun, H. M.; Dudman, C. C.; Thomas, M.; O'Mahoney, C. A.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1990**, 336.
(3) Fukuyama, J. M. U.S. Patent 4 959 454, 1990.
(4) Fukuyama, J. M. U.S. Patent 5 110 893, 1992.
(5) Mullins, M. J.; Woo, E. P.; Balon, K. E.; Murray, D. J.; Chen, C. C. U.S. Patent 5 264 538, 1993.
(6) Chan, K. P.; Wang, Y.; Hay, A. S. *Macromolecules* **1995**, *28*, 653.
(7) Chan, K. P.; Wang, Y.; Hay, A. S. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1995**, *36*, 653.
(8) Wang, Y.; Chan, K. P.; Hay, A. S. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1995**, *36*, 130.
(9) Gao, C. P.; Hay, A. S. *Polymer* **1995**, *36* (21), 4141.
(10) Chan, K. P.; Wang, Y.; Hay, A. S.; Hronowski, X. L.; Cotter, R. J. *Macromolecules* **1996**, *28*, 6705.
(11) Ding, Y.; Hay, A. S. *Macromolecules* **1996**, *29*, 3090.
(12) Wang, Y-F.; Paventi, M.; Chan, K.; Hay, A. S. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 2135.
(13) Wang, Y.; Chan, K. P.; Hay, A. S. *J. Appl. Polym. Sci.* **1996**, *59*, 831.
(14) Chen, M. F.; Gibson, H. W. *Macromolecules* **1996**, *29*, 5502.
(15) Jiang, H. Y.; Qi, Y. H.; Chen, T. L.; Xing, Y.; Xu, J. P. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 1753.
(16) Wang, Y.; Paventi, M.; Hay, A. S. *Polymer* **1997**, *38* (2), 469.
(17) Mullins, M. J.; Galvan, R.; Bishop, M. T.; Woo, E. P.; Gorman, D. B.; Chamberlin, T. A. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1991,** *32* (2), 174. According to this paper and refs 18 and 19, the mixture of cyclic (aryl ether sulfone)s prepared is amorphous and begins to soften at 250 °C.
(18) Mullins, M. J.; Galvan, R.; Bishop, M. T.; Woo, E. P.; Gorman, D. B.; Chamberlin, T. A. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1992**, *33* (1), 414.
(19) Mullins, M. J.; Woo, E. P.; Murry, D. J.; Bishop, T. M. *CHEMTECH* **1993** (August), 25.
(20) Ganguly, S.; Gibson, H. W. *Macromolecules* **1993**, *26*, 2408.
(21) Xie, D.; Gibson, H. W. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1994**, *35* (1), 401.
(22) Colquhoun, H. M.; Williams, D. J. *Macromolecules* **1996**, *29*, 3311.
(23) Zhang, H. C.; Chen, T. L.; Yuan, Y. G. CN Patent 85 108 751.5, 1985.
(24) Liu, K. J.; Zhang, H. C.; Chen, T. L. CN Patent 85 101 721, 1985.

MA970857P