Synthesis of Poly(arylene ether ketone)s Containing Trifluoromethyl Groups via Nitro Displacement Reaction

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Received December 2, 1997
Revised Manuscript Received March 13, 1998

Poly(arylene ether ketone)s are well-recognized high-performance engineering thermoplastics. These materials have outstanding physical properties, including high modulus, toughness, and good thermal and chemical resistance, and find applications in many areas. Poly(arylene ether ketone)s can be prepared via electrophilic or nucleophilic polycondensation.[1,2] The electrophilic route using the Friedel−Craft acylation reaction has some limitations because of the mechanistic problem. The nucleophilic route has been the most commonly used method to prepare various kinds of poly(arylene ether ketone)s. The synthetic route involves generation of an ether linkage by nucleophilic aromatic substitution (S_NAr) as a polymer-forming reaction and uses activated aromatic ketone monomers in which the carbonyl group serves as the activating moiety. While high molecular weight poly(aryl ether sulfone)s[3] and poly(ether imide)s[4] have been made by the nitro displacement reaction, the report[5] that claimed synthesis of high molecular weight crystalline poly(arylene ether ketone)s has some questionable points.[1,6] Most poly(arylene ether ketone)s syntheses employed fluoride as a leaving group, and the nitro group was rarely used because of the generation of nitrite ions that become reactive and cause side reactions at elevated temperature.[7] However, the problem of the nitro leaving group in an S_NAr reaction can be avoided, if the nitro group of a ketone monomer is displaced at mild conditions. In this study, we select as a second activating group a trifluoromethyl group that is known as an effective activating group for the nitro displacement reaction without side reactions.[8] Trifluoromethyl groups in monomer exert not only an activating effect on a leaving group but also a bulky substituent effect on a polymer main chain, which may prevent crystallization of a polymer chain, resulting in amorphous polymers. In this case, a high temperature to overcome premature crystallization during synthesis of poly(arylene ether ketone) is not necessary and nucleophilic nitro displacement can be carried out at mild conditions.

Here we report the synthesis and characterization of novel poly(arylene ether ketone)s through nucleophilic nitro displacement reaction with an AA type monomer that is doubly activated by carbonyl and trifluoromethyl groups. To our knowledge, this report is the first example of synthesis of high molecular weight amorphous poly(arylene ether ketone) through the nucleophilic nitro displacement reaction.

A novel AA type monomer (**3**) was synthesized with quantitative yield through a masked acyl anion equivalent, bis(α-aminonitrile) derivative,[9] from terephthalaldehyde (Scheme 1).

The chemical structure of the monomer was confirmed by spectral analyses.[10] To demonstrate whether doubly activated monomer (**3**) would undergo facile nucleophilic aromatic substitution and whether polymerization is feasible, the model reaction was studied with *m*-cresol in anhydrous DMSO solvent. The model reaction revealed that nucleophilic aromatic substitution of the nitro groups began to occur at room temperature and was completed at 80 °C. The model compound (**4**) was obtained in very high isolated yield (95%) within 2 h (Scheme 2).

The ^{1}H NMR, ^{13}C NMR, and FT-IR spectrum were in good agreement with the structure **4**.[11] The monomer (**3**) was very reactive in the S_NAr reaction because the nitro leaving group was doubly activated by the carbonyl moiety at para position and the trifluoromethyl group at the ortho position. In addition, the bulky trifluoromethyl group imparts steric congestion so that formation of a stable Meisenheimer complex was facilitated with release of steric strain. Polymerization of the monomer with bisphenoxide, which was generated from each of biphenol, Bisphenol A, and 4,4-(9-fluorenylidene)-diphenol in anhydrous DMSO at 140 °C with removal of water by azeotropic distillation of benzene, was carried out at 80−120 °C for 6 h (Scheme 3).

The polymerization temperature was limited up to 120 °C to minimize side reactions caused by the nitrite ion byproduct. The polycondensation through the nucleophilic nitro displacement reaction rapidly proceeded at relatively mild temperature.[12] The polymers were obtained by precipitation of the reaction mixture into water. The polymer was further purified by reprecipitation in methanol/acetone and was subjected to spectral analysis, which showed the expected spectral data. However, only low molecular weight polymers were obtained when the polymerization was carried out above 170 °C in NMP. The polymer obtained at 180 °C had an inherent viscosity of 0.13 in NMP at 25 °C and showed a complicated NMR spectrum. It seems that the carbonyl groups of the polymers, especially the carbonyl at the end of growing polymer chains activated with a nitro group, become susceptible to nitrite ions at high temperatures.

Polymers **5** and **6** were quite soluble in chloroform, tetrahydrofuran, and 1,1,2,2-tetrachloroethane and slightly soluble in NMP and DMPU at room temperature. However, polymer **7** showed limited solubility in DMSO and NMP at elevated temperature. The gel permeation chromatograms of **5** and **6** showed unimodal distribution of high molecular weight polymers, 6.4×10^4 and 6.85×10^4 weight average molecular weight, respectively. Inherent viscosities were 0.44 for **5,** 0.49 for **6**, and 0.61 for **7** (Table 1).

In thermal analysis, polymers **5**−**7** did not show melting endotherms but showed relatively high T_g values, 171 °C for **5**, 229 °C for **6**, and 187 °C for **7**, and 5% weight loss at 500 °C for **5**, 502 °C for **6**, and 521 °C for **7** (Figure 1), revealing their high thermal stability.

It is somewhat unexpected that polymer **7** from biphenol exhibited amorphous character, but it seems that trifluoromethyl substituents are bulky enough to prevent crystallization of the polymer chains in this

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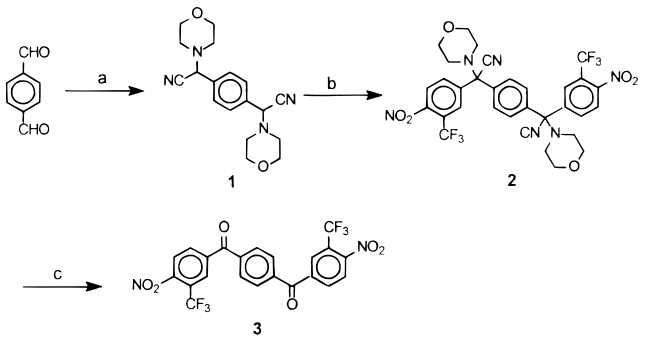
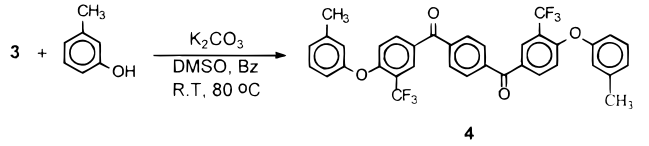
S0024-9297(97)01759-2 CCC: $15.00
Published on Web 04/22/1998

Scheme 1[a]



[a] (a) (1) $NaHSO_3/H_2O$, RT; (2) morpholine; (3) NaCN, 73%. (b) 5-Chloro-2-nitrobenzotrifluoride, NaH/DMF, 66%. (c) AcOH/H_2O (70%), 96%.

Scheme 2



Scheme 3

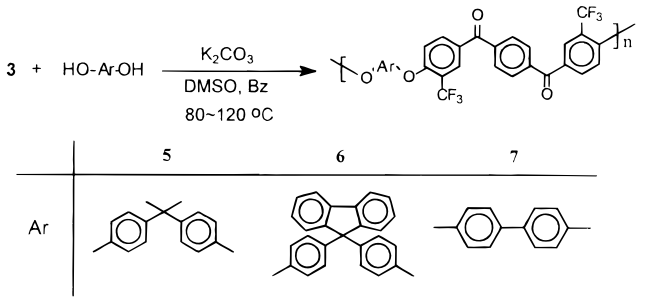


Table 1. Properties of the Polymers

polymer	η_{inh} (dL/g)[a]	M_w[b]/10^4	M_n[b]/10^4	M_w/M_n	T_g (°C)[c]	T_{d5} (°C)[d]
5	0.44	6.40	1.61	3.98	171	500
6	0.49	6.85	1.70	4.02	229	502
7	0.61[e]				187	521

[a] The inherent viscosities were measured at a concentration of 0.5 g/dL in NMP at 25 °C. [b] Determined by GPC using THF as eluent and polystyrenes as standards. [c] Measured by DSC at the second run with a heating rate of 10 °C/min under a N_2 atmosphere. [d] Onset of 5% weight loss on TGA with a heating rate of 10 °C/min under a N_2 atmosphere. [e] In NMP containing 3% LiCl at 25 °C.

case. Transparent and flexible films were easily prepared by solution casting from chloroform solution of each of the polymers **5** and **6**.

In conclusion, new amorphous poly(arylene ether ketone)s with relatively high molecular weights were prepared through nucleophilic nitro displacement reaction. The polymers showed outstanding thermal stability and good film-forming properties. Preparation of a series of poly(arylene ether ketone) with various substituents is in progress.

Acknowledgment. We thank the Korea Science and Engineering Foundation (KOSEF) for financial support of this work through contract number 95-0501-08-01-3.

Supporting Information Available: IR, NMR, and DSC data of polymers **5**−**7** and GPC data of polymer **5** and **6** (6 pages). See any current masthead page for ordering and Internet access instruction.

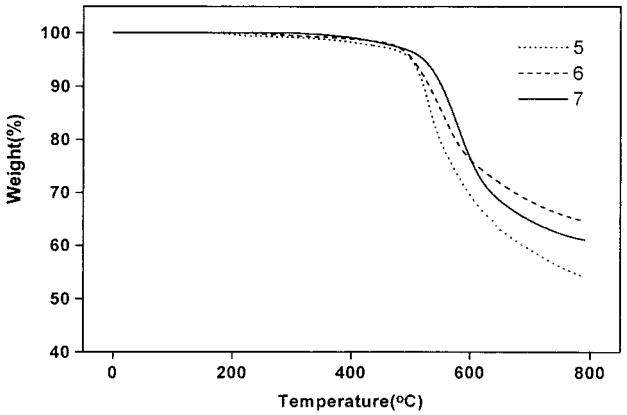


Figure 1. TGA thermograms of polymers **5**−**7** at a heating rate of 10 °C/min in N_2.

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(10) Spectral data of **3**: ^{1}H NMR (acetone-d_6) δ 8.35−8.38 (m, 4H), 8.27−8.30 (d, 2H, J = 8.6 Hz), 8.08 (s, 4H); ^{13}C NMR (acetone-d_6) δ 193.40, 150.7, 141.60, 140.54, 136.13, 131.07, 129.90 (quadruplet, J_{C-F} = 5.2 Hz), 126.53, 123.59 (quadruplet, J_{C-F} = 34.0 Hz), 122.88 (quadruplet, J_{C-F} = 271.0 Hz); FT-IR (KBr, cm^{-1}) 3108, 3054, 1667 (C═O), 1550 (NO_2, asy st), 1373 (NO_2, syst), 1290, 1259, 1154, 1047, 936, 852, 732.
(11) Spectral data of **4**: ^{1}H NMR ($CDCl_3$) δ 8.18 (d, 2H, J = 2.0 Hz), 7.88−7.94 (dd, 2H, J = 2.0 Hz, 8.6 Hz), 7.86 (s, 4H), 7.30 (t, 2H, J = 7.7 Hz), 7.04−7.08 (d, 2H, J = 7.4 Hz), 6.89−6.93 (m, 6H), 2.37 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 193.36, 160.02, 154.49, 140.68, 140.36, 135.32, 130.36, 129.94, 129.73 (quadruplet, J_{C-F} = 4.8 Hz), 129.60, 126.34, 122.86 (quadruplet, J_{C-F} = 271.0 Hz), 121.12, 119.93 (quadruplet, J_{C-F} = 32.0 Hz), 117.46, 116.99, 21.27. FT-IR (KBr, cm^{-1}): 3068, 1660 (C═O), 1609, 1580, 1486, 1329, 1292, 1258 (C−O−C, asy st), 1139, 1120 (C−O−C, sy st), 1052, 962, 734, 662.
(12) Polymer **5** synthesis with Bisphenol A: The mixture of Bisphenol A (0.6682 g, 2.9294 mol), potassium carbonate (0.8080 g, 5.8588 mmol) in 6 mL of anhydrous DMSO and 6 mL of benzene for azeotropic distillation of water was mechanically stirred at 140−150 °C for 2 h under an argon

atmosphere. After the reaction mixture was cooled to room temperature, the monomer (**3**, 1.500 g, 2.9294 mmol) was added to the solution with 2 mL of DMSO and then stirred at the ambient temperature for 2 h. The temperature was raised to 80 °C, and the stirring was continued for several hours until the solution became viscous. The temperature was then raised to 120 °C, and the stirring was continued for an additional 4 h. A small amount of 2-nitrobenzotrifluoride was added to the solution for end-capping of polymer, and the stirring was maintained for additional 1 h at this temperature. The reaction mixture was cooled to room temperature, acidified with 1 mL of acetic acid, and precipitated into water. The polymer was collected by filtration and washed many times with water, methanol, and acetone. Further purification was carried out by dissolving the polymer in THF, filtering the polymer solution, and then precipitating it into methanol/acetone mixture. The obtained polymer was dried in a vacuum oven at 120 °C to give 1.68 g in 89% yield.

MA9717597