

Synthesis and Characterization of Poly(arylene ether)s Containing Benzoxazole Pendants from Novel Aromatic Difluoride Monomer

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A study was done on the synthesis of new poly(arylene ether)s and poly(arylene sulfide) with rigid benzoxazole pendants using nucleophilic aromatic substitution reaction. As a new aromatic monomer, 1,4-bis(2-benzoxazolyl)-2,5-difluorobenzene [I] was synthesized in three steps starting from 1,4-dibromo-2,5-difluorobenzene. A model reaction of difluoro monomer [I] with two equivalents of *m*-cresol or thiophenol in a typical ether condensation reaction conditions gave very high yields (> 93%) of the desired disubstituted product, suggesting the feasibility of polymer formation in these reaction system. Monomer [I] was polymerized with bisphenols and bisbenzenethiol in NMP using K₂CO₃ as base. The molecular weight of the resulting polymers, however, seemed relatively low according to their solution viscosity values ($\eta_{inh} = 0.15\text{--}0.29$ dL/g). The poly(arylene ether)s were soluble in several common organic solvents including chloroform, pyridine and *N,N'*-dimethylformamide. The poly(arylene sulfide) was, however, only soluble in strong acids like sulfuric acid and trifluoroacetic acid. The glass transition temperatures were found to be 175–215 °C. These polymers were stable up to 380–420 °C in both nitrogen and air, as determined by the temperature that a significant weight loss began to appear on TGA.

Introduction

A large number of poly(arylene ether)s and poly(arylene sulfide)s has been reported and studied during the past few decades as heat resistant, high performance polymers.^{1–4} Also it is well known that poly(benzoxazole)s and poly(benzothiazole)s are among the most thermally stable polymers containing highly rigid heterocycles in the backbone. The most efficient means of introducing an aryl ether linkage in aromatic polymer system is through nucleophilic aromatic substitution mechanism, which involves the nucleophilic displacement of an activated aromatic dihalides by alkali metal bisphenoxides in a polar aprotic medium. Other methods of poly(aryl ether) synthesis include oxidative coupling, Ullmann condensation, and so on.^{5,6} As the activating group of the dihalide monomer, a variety of functionality has been employed so far, including sulfone, ketone, many different heterocycles, fluoroalkyl, etc.^{1,3,7–9} The activating group not only serves as an electron withdrawing group but also stabilizes the negative charge developed through a formation of Meisenheimer complex, the reaction intermediate. Many different heterocycles such as oxadiazole, triazoles, and benzoxazoles have been employed as the activating groups so far to produce a variety of polyaromatic heterocyclics.^{2,10} Among them benzoxazole-activation of aryl fluorides has been shown to be a general route to aryl ether substituted poly(benzoxazoles) and poly(benzthiazoles). Also aryl fluoride ortho to the benzoxazole ring has been shown to be activated towards nucleophilic aromatic substitution analogous to conventional halophenyl ketones and sulfones for which both the ortho and para positions are activated.^{11,12}

In our previous report,⁶ a new aryl dibromide monomer with two benzoxazole pendants, *ie.* 1,4-bis(2-benzoxazolyl)-

2,5-dibromobenzene [BOBr], was synthesized and the polymerization reaction has been studied. The BOBr monomer did not exhibit high enough reactivity toward phenolate (ArO⁻), presumably resulting from the lower reactivity of bromide compared to chloride or fluoride in a typical nucleophilic aromatic substitution (SnAr) reaction. The same monomer did show, however, high reactivity in an Ullmann condensation reaction catalyzed by CuCl-pyridine, where the ease of halogen displacement was known to be the reverse of that observed in the usual activated halide systems, *ie.* I ~ Br > Cl >> F.¹ The synthesis of aromatic poly(aryl ether)s from BOBr monomer under the Ullmann reaction condition was reported previously.

In this study, a new analogous difluoride monomer bilaterally substituted with rigid benzoxazole groups was synthesized efficiently. The benzoxazole activated difluoride monomer was expected to exhibit much higher reactivity toward usual nucleophilic displacement reaction. The reactivity and model reactions as well as the subsequent polymerization with bisphenols and thiobisbenzenethiol to afford novel poly(arylene ether)s are discussed in the present article.

Experimental Section

All materials and solvents were purchased in highest purity available and used as-received unless otherwise indicated. 1-Methyl-2-pyrrolidinone(NMP), *N,N*-dimethyl acetamide, and toluene were dried over CaH₂ and distilled before use. Bisphenol A, 4,4'-dihydroxydiphenyl ether, and 4,4'-thiobisbenzenethiol were purified by recrystallization and sublimation.

IR spectra were obtained on a Unicam 1000 FT-IR spectrometer. NMR spectra were taken on a Varian Unity Inova

500 MHz Spectrometer at room temperature. Thermal analysis (DSC/TGA) was carried out on a Perkin Elmer 7 Series thermal analysis system. Mass spectra (MS) were obtained on a Kratos Concept-S (double-focusing type) spectrometer. Solution viscosity was measured by Ubbelohde capillary viscometer using chloroform or trifluoroacetic acid as the solvent.

1,4-Bis(2-benzoxazolyl)-2,5-difluorobenzene [BOF] (I) was synthesized with high yield by well-known polyphosphoric acid (PPA) catalyzed condensation reaction between 2-aminophenol and 2,5-difluoroterephthalic acid which was prepared by acid hydrolysis of 2,5-difluoroterephthalonitrile. 2,5-Difluoroterephthalonitrile was prepared by bromine substitution of 1,4-dibromo-2,5-difluorobenzene using CuCN in DMF. M.p. (DSC): 316 °C; IR (KBr pellet): 3088, 1610 (oxazole), 1449, 1374, 1276, 1243, 1171 (Ar-F), 807, 751 cm^{-1} ; ^1H NMR (trifluoroacetic acid-*d*): 8.39 (2H, *s*), 7.90 (4H, *dd*), 7.55 (4H, *tt*) ppm; ^{13}C NMR (trifluoroacetic acid-*d*): 158.9, 156.7, 149.9, 131.8, 130.4, 130.3, 119.8, 117.4, 117.0, 113.1 ppm; ^{19}F NMR(trifluoroacetic acid-*d*): -111.3 ppm.

1,4-Bis(2-benzoxazolyl)-2,5-bis(3-methylphenoxy)benzene (Model Compound, IIA) was prepared from BOF monomer (I) and *m*-cresol in a typical aryl ether synthesis using DMAc and K_2CO_3 as the solvent and base, respectively. In a 3-neck reaction flask equipped with a nitrogen inlet and Dean-stark trap fitted with a condenser and a nitrogen outlet, 0.576 g (4.17 mmol) of K_2CO_3 and 0.410 g (3.79 mmol) of *m*-cresol in a mixture of DMAc (8 mL) and toluene (12 mL) were kept with stirring and the temperature was increased to 150 °C to remove water *via* an azeotrope with toluene. After 4-6 h, the system was dehydrated and the reaction was cooled to about 60 °C. BOF monomer (I) (0.6 g, 1.72 mmol) in DMAc (8 mL) was added and stirred for 20 h at 155 °C. The reaction mixture was precipitated into 250 mL of water containing 1 vol% of acetic acid. The yellow precipitate was filtered, washed and dried in vacuum at 80 °C for 24 h. Above crude product was flash column chromatographed (CH_2Cl_2 , silica gel) to remove impurities to obtain a light-yellow crystalline product (yield: 95%); M.p. (DSC): 274 °C; IR (KBr pellet): 3051, 1598, 1544, 1463, 1413, 1250 (Ar-O-Ar), 1196, 752 cm^{-1} ; ^1H NMR (trifluoroacetic acid-*d*): 8.03 (2H, *s*), 7.86-7.75 (8H, *m*), 7.51 (2H, *t*), 7.35 (2H, *d*), 7.09 (4H, *t*), 2.44 (6H, *s*) ppm; ^{13}C NMR (trifluoroacetic acid-*d*): 160.9, 156.7, 154.7, 151.1, 145.5, 133.5, 133.3, 132.1, 131.6, 130.4, 123.5, 119.8, 119.7, 118.2, 118.1, 114.9, 22.0 ppm; MS (EI): 524 (M^+).

1,4-Bis(2-benzoxazolyl)-2,5-bis(thiophenoxy)benzene (Model Compound, IIB) was prepared by similar procedure from BOF(I) and thiophenol. (yield: 93%). M.p. (DSC): 285 °C; IR (KBr): 3050, 1620, 1244, 810 cm^{-1} ; ^1H NMR (trifluoroacetic acid-*d*): 8.24 (2H, *s*), 8.0 and 7.94 (each 2H, *d*), 7.9 (4H, *m*), 7.4-7.6 (10H, *m*) ppm; ^{13}C NMR (trifluoroacetic acid-*d*): 162.2, 150.5, 142.4, 136.0, 134.5, 132.1, 131.8, 131.1, 129.9, 129.4, 125.5, 117.2, 113.9 ppm; MS (EI): 529 (M^+).

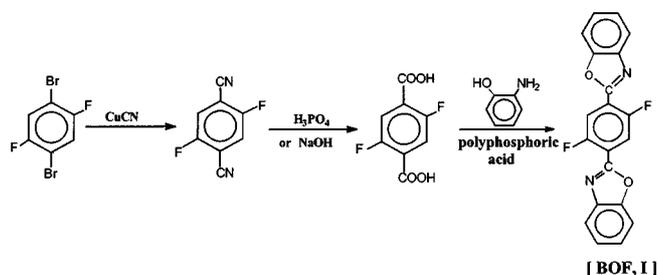
Synthesis of Poly(aryl ether)s (III-b) A typical example

of polymerization follows; In a 3-neck reaction flask equipped with a nitrogen inlet and Dean-stark trap fitted with a condenser and nitrogen outlet, 4,4'-dihydroxydiphenyl ether (0.430 g, 2.127 mmol) was dissolved in 30 mL NMP, and then K_2CO_3 (0.588 g, 4.254 mmol) was added under N_2 purge. To the solution were added 20 mL toluene portionwise at the bath temperature of 150 °C to remove water of bisphenolate formation *via* an azeotrope with toluene. After 4-6 h, the system was dehydrated completely and the reaction was cooled to 80 °C. BOF monomer (I) (0.74 g, 2.127 mmol), in 8 mL of NMP were added subsequently and stirred for 20 h at 180 °C. Then the reaction mixture was precipitated into 350 mL of water with 1 vol% of acetic acid. The precipitate was filtered, washed and dried in vacuum at 90 °C for 24 h. The product was dissolved in 25 mL CHCl_3 and reprecipitated into methanol, which was filtered, washed, and dried in vacuum. (yield 85%) IR (KBr): 3055, 2965, 1560, 1489, 1250 (Ar-O-Ar), 749 cm^{-1} ; ^1H NMR (CDCl_3): 7.5-8.3 (aromatic protons, 18H) ppm

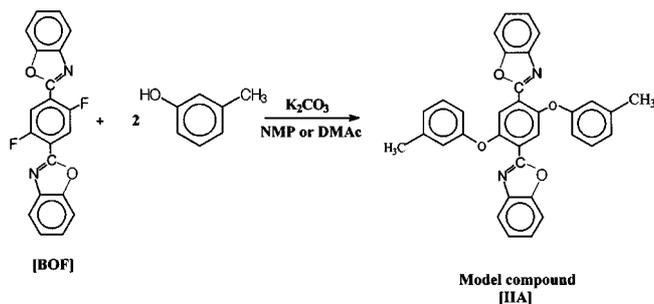
Synthesis of Poly(arylene sulfide) (IV) Similar reaction conditions were employed to prepare analogous poly(arylene sulfide) using 4,4'-thiobisbenzenethiol as the counter nucleophilic monomer. The light-brown precipitate was filtered, washed with water and toluene repeatedly, then dried in vacuum at 90 °C for 24 h (yield 98%). IR (KBr): 3060, 1612, 1564, 1473, 1450, 1231, 1040, 801, 746 cm^{-1} ; ^1H NMR (trifluoroacetic acid-*d*): 8.48 (2H, *s*), 8.2 (8H, benzo protons, *m*), 7.7 (8H, *dd*) ppm.

Results and Discussion

1,4-Bis(2-benzoxazolyl)-2,5-difluorobenzene (BOF, I) was prepared in three steps starting from 1,4-dibromo-2,5-difluorobenzene, as the reaction scheme shown below (Scheme 1). First 1,4-dibromo-2,5-difluorobenzene was treated with CuCN in DMF to prepare 2,5-difluoroterephthalonitrile (yield 70%), which was subsequently hydrolyzed to produce 2,5-difluoroterephthalic acid using phosphoric acid (yield 85%). In the next step, the prepared 2,5-difluoroterephthalic acid was reacted with two equivalent 2-aminophenol to obtain 1,4-bis(2-benzoxazolyl)-2,5-difluorobenzene monomer *via* well-known polyphosphoric acid catalyzed condensation and heterocyclization (yield 83%). Figure 1 and 2 show the FT-IR and ^1H NMR spectrum of monomer I, respectively. Two benzoxazolyl groups on the ortho position to each fluorine substituent on the same benzene ring should exhibit



Scheme 1



strong electron-withdrawing effect and are expected to function as an activating group for the nucleophilic substitution of fluorine atom *via* stabilization of Meisenheimer complex as the reaction intermediate. To demonstrate the reactivity of BOF monomer for a typical NAS reaction, model reaction with *m*-cresol was performed (Scheme 2).

The reaction seems to proceed quite clean at mild reaction condition in DMAc. The desired disubstituted product (model compound IIA) was obtained with high reaction yield (95%). FT-IR showed a strong absorption band at 1250 cm^{-1} , characteristic of the aromatic ether linkage. $^1\text{H NMR}$ spectrum also showed each aromatic protons and methyl protons with correct integration ratios. MS(EI) also exhibited molecular ion mass (M^+) of 524 Da, coincident with the calculated value.

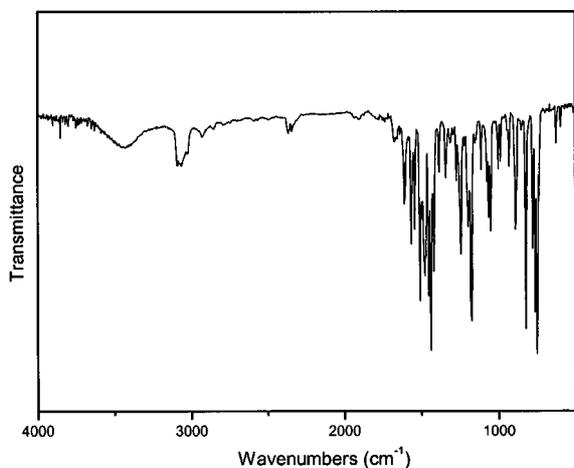


Figure 1. FT-IR spectrum of BOF monomer [I].

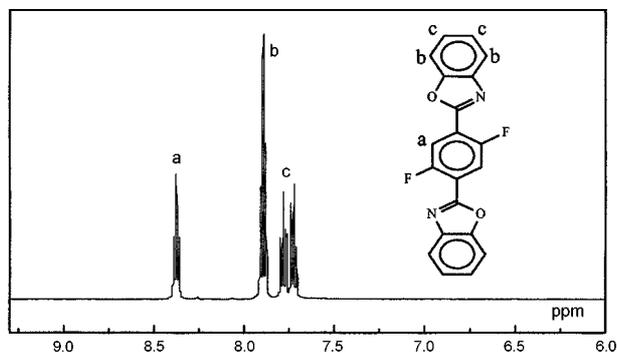
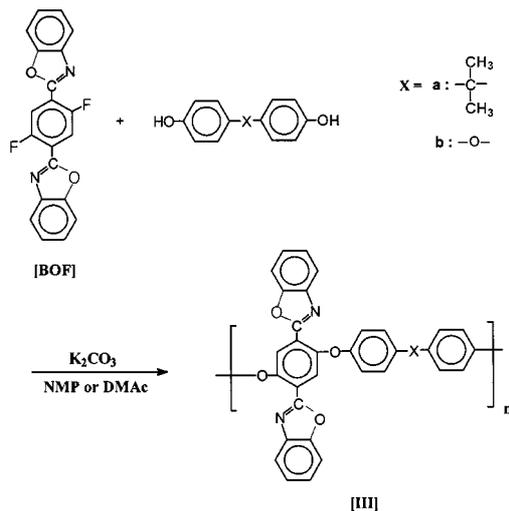


Figure 2. $^1\text{H NMR}$ spectrum of BOF monomer [I].



The model reaction demonstrated that both fluoro groups at ortho positions is easily replaced by phenoxide as a result of activation by the benzoxazole, suggesting the feasibility of polymer formation in this reaction system.

BOF monomer was polymerized with 2,2-bis(4'-hydroxyphenyl)propane (Bisphenol A) and 4,4'-dihydroxydiphenyl ether (Bisphenol-O) to give the corresponding polymers, the benzoxazole-substituted poly(arylene ether)s, as the reaction scheme is shown below (Scheme 3). Figure 3 shows the IR spectra of these polymers with model compound IIA.

Table 1 shows the results of the inherent viscosity and glass transition measurements. The polymers possessed inherent viscosity of 0.15 (III-a) and 0.29 dL/g (III-b) measured at $25\text{ }^\circ\text{C}$ in chloroform and trifluoroacetic acid, respectively. The glass transition temperatures were observed at $175\text{ }^\circ\text{C}$ (III-a) and $203\text{ }^\circ\text{C}$ (III-b), respectively, as judged by the midpoint of the heat capacity change in DSC. The polymers were soluble in many common organic solvents including chloroform, pyridine, DMF and DMSO.

Thiophenoxide (ArS^-) is another strong nucleophile compared to phenoxide (ArO^-) for the usual nucleophilic aromatic substitution reaction of activated aryl halide.¹¹ So, it

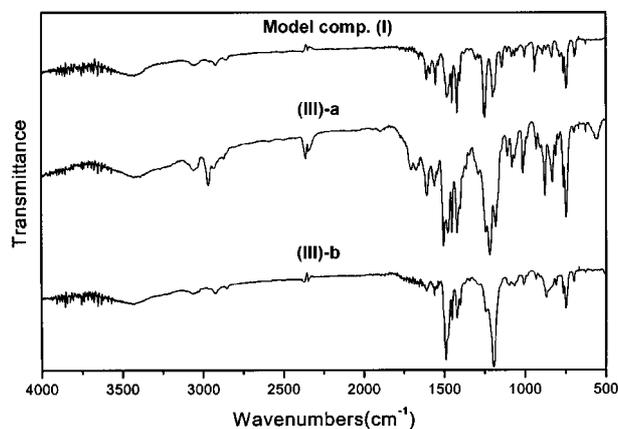
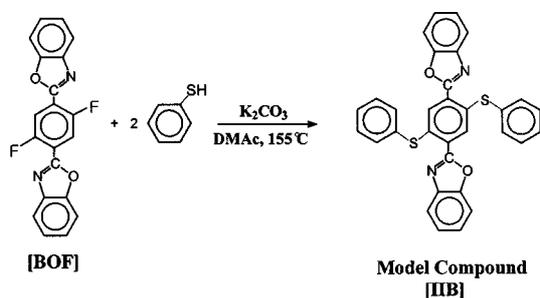


Figure 3. IR spectra of model compound [IIA] and poly(arylene ether)s [III-a] & [III-b].

Table 1. Characteristics of Poly(aryl ether)s Containing Benzoxazole Pendants

Polymer	η_{inh} (dL/g) ^a	T _g (°C)
III-a	0.15 ^a	175
III-b	0.29 ^b	203
IV	0.17 ^b	215

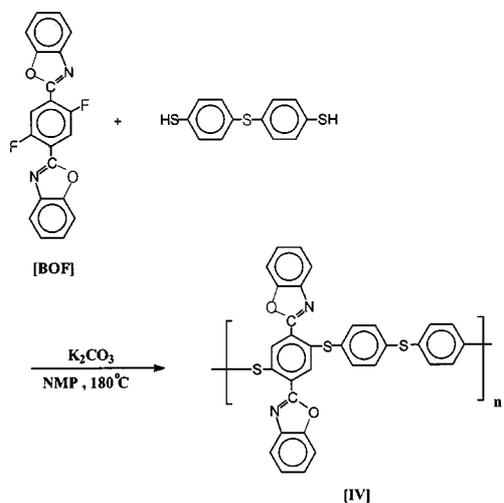
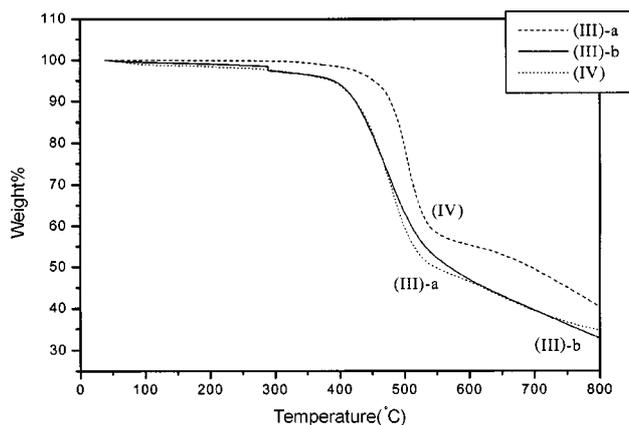
*measured at a concentration of 0.5 g/dL. ^ain chloroform. ^bin trifluoroacetic acid

**Scheme 4**

was worthwhile to try thiophenoxide to prepare analogous model compound and polymer using the same monomer.

The model reaction of monomer (I) with thiophenol under usual 'NAS' reaction conditions using a base, K₂CO₃, in DMAc was carried out under argon atmosphere (Scheme 4). The substitution reaction proceeded quite clean to give the desired disubstituted product (model compound IIB) with high reaction yield (> 93%).

Characteristic oxazole absorption bands at 1620 and 1244 cm⁻¹, and aryl sulfide C-S-C absorption band at 810 cm⁻¹, respectively, were observed from FT-IR. ¹H NMR spectrum shows protons of the central ring at chemical shift of 8.24 (2H, s), protons of the benzo ring at 7.8-8.0 (8H, m), and aromatic protons of thiophenol at 7.4-7.5 (10H, m), respectively, with correct integration ratios. MS(EI) also exhibited molecular ion mass (M⁺) of 529 Da, coincident with the calculated value. The polymerization with 4,4'-thiobisbenzene-

**Scheme 5****Figure 4.** TGA thermograms of Poly(arylene ether)s [III-a & III-b] and Poly(arylene sulfide) [IV].

thiol was carried out in an analogous fashion to the polymerization described above (Scheme 5).

The resulting polymer possessed the inherent viscosity of 0.17 dL/g at 25 °C in trifluoroacetic acid. The polymer was insoluble in most organic solvents. It showed solubility only in strong acids such as concentrated sulfuric acid and trifluoroacetic acid, and partial solubility in DMF, NMP and 1,2-dichlorobenzene. A weak glass transition at around 215 °C was observed in DSC.

The thermal stability of polymer III and IV was examined by thermogravimetry (TG). Typical traces (Figure 4) showed decomposition onset temperature at about 440-470 °C in nitrogen, as the data were summarized in Table 2.

In conclusion, 1,4-bis(2-benzoxazolyl)-2,5-difluorobenzene (I) was synthesized in three steps starting from 2,5-dibromo-1,4-difluorobenzene with high reaction yield. A model reaction of monomer (I) with two equivalents of *m*-cresol or thiophenol provided very high yield of substitution product in a typical aromatic substitution reaction condition, suggesting not only high reactivity of this monomer for the nucleophilic displacement reactions, but the feasibility of polymer formation in this system. Monomer (I) was polymerized with two different bisphenols and 4,4'-thiobisbenzenethiol in NMP in the presence of potassium carbonate to give the corresponding poly(arylene ether)s and poly(arylene sulfide) bilaterally substituted with rigid benzoxazole group. The molecular weight of the prepared polymers, however, seemed relatively low according to their inherent viscosities of 0.15-0.29 dL/g. The prepared polymers showed excellent thermal stability and T_g's comparable to known poly(aryl

Table 2. Thermal Properties of Poly(aryl ether)s Containing Benzoxazole Pendants

Sample no.	T _d (onset, °C)		T _d (5% wt. loss, °C)	
	N ₂	Air	N ₂	Air
III-a	438	441	390	402
III-b	445	457	394	398
IV	470	486	455	408

ether) analogues.

References

1. Cotter, R. J. *Engineering Plastics: A Handbook of Polyarylethers*; Gordon and Breach Publishers: Switzerland, 1995.
 2. Hergenrother, P. M.; Connell, J. W. *Advances in Polymer Science*, vol 117; Springer-Verlag: Berlin Heidelberg, 1994; pp 67-110.
 3. Labadie, J. W.; Hedrick, J. L.; Ueda, M. In *Step-Growth Polymers for High-Performance Materials*, ACS Symp. Series 624; ACS: Washington, DC, 1996; chapter 12.
 4. Spassky, N.; Sepulchre, M.; Sigwalt, P. In *Handbook of Polymer Synthesis, part II*; Kricheldorf, H. R., Ed.; Marcel Dekker: New York, 1992; chapter 16.
 5. Jurek, M. J.; McGrath, J. E. *Polym. Prepr.* **1987**, 28(1), 180.
 6. Lee, J. I.; Kwon, L. Y.; Kim, J.-H.; Choi, K.-Y.; Suh, D. H. *Die Angew. Makrom. Chem.* **1998**, 254, 27.
 7. Labadie, J. W.; Kim, S. Y.; Carter, K. R.; *Polym. Prepr.* **1993**, 34(1), 415.
 8. MacKinnon, S. M.; Bender, T. P.; Wang, Z. Y. *J. Polym. Sci., Polym. Chem.* **2000**, 38, 9.
 9. Suh, D. H.; Chung, E. Y.; Hong, Y.-T.; Choi, K.-Y. *Die Angew. Makrom. Chem.* **1998**, 254, 27.
 10. Fink, R.; Frenz, C.; Thelakkat, M.; Schmidt, H.-W. *Macromolecules* **1997**, 30, 8177.
 11. Person, D.; Cassidy, P. E.; Fitch, J. W.; Kono, K.; Ueda, M. *Reactive & Functional Polymers* **1996**, 30, 229.
 12. Carter, K. R.; Jonsson, H.; Twieg, R.; Miller, R. D.; Hedrick, J. L. *Polym. Prepr.* **1992**, 33(1), 388.
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