Novel Poly(paraphenylene)s via Nucleophilic Aromatic Substitution of Poly(4′-fluoro-2,5-diphenyl sulfone)

Paul D. Bloom and Valerie V. Sheares*

Department of Chemistry, Iowa State University, Ames, Iowa 50011-3011

Received July 7, 2000; Revised Manuscript Received January 16, 2001

ABSTRACT: Poly(4′-fluoro-2,5-diphenyl sulfone) was synthesized via Ni(0)-catalyzed coupling and was reacted with various nucleophiles via aromatic substitution (S_NAr) to produce derivatized poly(paraphenylene) (PPP) thermoplastics and thermosets. Substitution by the nucleophiles was determined to be nearly quantitative by GPC and ^{1}H NMR. The largest increase in the glass transition temperature relative to poly(4′-fluoro-2,5-diphenyl sulfone) was from 144 °C to 189 °C after displacement of fluoride with morpholine to give poly(4′-morpholino-2,5-diphenyl sulfone). Two graft copolymers were synthesized with low molecular weight poly(ethylene oxide) (PEO) and a poly(arylene ether ketone) (PAEK). The resulting PEO graft copolymer was soluble in water and in polar, aprotic solvents. The PAEK graft copolymer produced transparent, creasable PPP-based films that had 5% weight loss temperatures in nitrogen and air of 510 and 513 °C, respectively. Furthermore, a PPP epoxy cure agent was synthesized by the reaction of 4-aminophenol with poly(4′-fluoro-2,5-diphenyl sulfone). Finally, diethylenetriamine was reacted with poly(4′-fluoro-2,5-diphenyl sulfone) to produce a solvent resistant, cross-linked PPP film with a T_g of 240 °C.

Introduction

Poly(paraphenylene)s, PPPs, are an interesting class of rigid rod polymers that have excellent thermal and mechanical properties. Synthesis of poly(paraphenylene)s via Ni(0)-catalyzed coupling of bis(aryl halide)s is a flexible route to a variety of high performance materials. The polymer chemistry stems from the synthesis of biphenyl from chlorobenzene at mild temperatures with quantitative conversion, first reported by Colon and Kelsey.[1] Since 1986, the Ni(0)-catalyzed coupling reaction has been utilized in the synthesis of soluble, amorphous, high T_g polythiophenes[2,3]and poly(paraphenylene)s,[4−10] containing aromatic pendant groups. More recently, Maxdem Inc. reported an extensive number of poly(paraphenylene)s with functionalized pendant groups.[11] These studies led to the production of partially reactive rigid rod polymers via copolymerizations or post-polymerization reactions. Specific bis(aryl halide) monomers, containing the desired functionality, were required for the copolymer synthesis. One monomer contained the solubilizing pendant group and the other, the desired functionality. In each case, it was essential that the compatibility of functional groups with the catalyst system be considered. Furthermore, it was necessary that the pendant group effect on the ability of the monomer to polymerize, from a steric and electronic persective, be assessed. To reach the same end, rigid rod homopolymers were reacted with a second reagent to synthesize partially modified PPPs. In essence, this partial modification produced a random copolymer containing the added reactive site and the unmodified solubilizing group.

In this paper, an alternative approach to functionally diversify poly(paraphenylene)s is described. This new method requires the synthesis of only one monomer that includes both solubilizing group and reactive site. The resulting polymer can be readily modified to produce a fully substituted PPP using any nucleophile capable of nucleophilic aromatic substitution (S_NAr). This methodology allows for selective control of polymer solubility and hydrophilicity, increase in the glass transition temperature, improvement in thermooxidative stability, creation of flexible, film-forming PPPs through grafting and production of themoset PPPs through cross-linking.

Polymer functionalization via nucleophilic aromatic substitution requires the presence of reactive sites along an existing PPP polymer chain. Several poly(paraphenylene) derivatives previously reported contain pendant groups with active sites available for nucleophilic aromatic substitution. Two of the most reactive polymers include poly(4′-fluoro-2,5-benzophenone)[7,8] and poly(4′-fluoro-2,5-diphenyl sulfone).[9] Of these two polymers, poly(4′-fluoro-2,5-diphenyl sulfone) is the more reactive substrate for nucleophilic aromatic substitution due to the stronger electron-withdrawing nature of the sulfone. An example of a model reaction is the displacement of fluoride by primary and secondary amines in methyl *p*-fluorophenyl sulfone which gives high yields in polar, aprotic solvents under moderate conditions.[12] The present study focuses on the pendant group extension of poly(4′-fluoro-2,5-diphenyl sulfone) via nucleophilic aromatic substitution. Although the molecular weight of poly(4′-fluoro-2,5-diphenyl sulfone) is low ($\langle M_n \rangle = 1.2 \times 10^3$, PD = 1.6), the product exhibits excellent high-temperature stability.[9] Much higher molecular weights were achieved with poly(4′-fluoro-2,5-benzophenone).[7] However, it was anticipated that the partial reduction of the carbonyl in poly(4′-fluoro-2,5-benzophenone), which was observed for other poly(2,5-benzophenone)s, would significantly reduce the active sites for substitution.[10]

In addition to avoiding the complications of multiple monomer syntheses, nucleophilic aromatic pendant group substitution allows for the synthesis of functionalized PPPs, which are difficult to make directly from the Ni(0) coupling of bis(aryl halide)s, due to incompatible functional groups. For example, primary aromatic amines are one of several desired functional groups needed to expand the use of PPPs in polyimides and epoxies. However, the presence of primary aromatic

10.1021/ma0011791 CCC: $20.00

amines or nitro groups, that could be reduced to amines, cause the Ni(0) coupling reaction to fail.[1] In contrast, given the proper nucleophile, such as 4-aminophenol, using nucleophilic aromatic substitution, it is possible to synthesize PPPs with primary aromatic amine functionality. This reaction, in addition to the substitution using a variety of readily available nucleophiles, is described herein to determine the influence of the pendant group on the physical properties of the polymer.

Although the substitution of small molecules along the PPP backbone serves as a model study to answer some fundamental structure/property questions, substitution of larger macromonomers can be used to significantly increase the molecular weight, solubility, and film forming ability of PPP derivatives. These unique high molecular weight PPP-based materials may find applications as rheology modifiers, compatibilizing agents and gas separation membranes. The details of these grafting reactions and the final polymer properties are described herein.

Finally, in addition to the model studies and grafting reactions, two types of cross-linking via nucleophilic aromatic substitution are examined. In the first case, a PPP derivative containing primary aromatic amine functionality is used to cure Dow epoxy resin D.E.N. 431. Second, poly(4′-fluoro-2,5-diphenyl sulfone) is cross-linked with diethylenetriamine. In both cases, these reactions address one of the major problems in synthesizing soluble, amorphous, high-temperature polymers: that is, the need for solvent resistance of the final material. The cross-linking reactions are described and the solvent resistance is determined.

Experimental Section

Materials. All reagents were purchased from Aldrich and used as received unless otherwise noted. Toluene and *N*,*N*-dimethylacetamide were dried over calcium hydride and distilled before use. Dimethyl sulfoxide was distilled from 4 Å molecular sieves. 2,2′-Dipyridyl and triphenylphosphine were purified by recrystallization from ethanol and *n*-heptane, respectively. Morpholine, 4-hydroxybiphenyl, 4-aminophenol, and 3-hydroxybenzotrifluoride were purchased from AlfaAESAR and used as received. 4′-Fluoro-2,5-dichlorodiphenyl sulfone was recrystallized twice and vacuum distilled (+99% by GC/MS) before polymerization. Poly(ethylene oxide) (Aldrich), containing one hydroxy end group, had an $\langle M_n \rangle$ of 2.4×10^3 g/mol and a polydispersity index (PDI) of 1.29 by gel permeation chromatography GPC relative to narrow polystyrene standards. The Dow Chemical Company provided the novolac epoxy resin, D.E.N. 431. Zinc powder (−100 mesh, 99.998%) was purchased from Aldrich and stored under nitrogen.

Characterization. All ^{1}H NMR (300 MHz) and ^{13}C NMR (75.5 MHz) monomer spectra were acquired in $CDCl_3$ with a Varian VXR-300. All polymer ^{13}C NMR spectra were acquired using a Bruker AC-200 (50.3 MHz). Molecular weights were determined relative to polystyrene standards with a Waters gel permeation chromatography (GPC) system consisting of a Waters 510 pump, Waters 717 autosampler and a Waters 410 refractive index detector. The system was equipped with four styragel columns (Waters HR 1, 2, 4, and 5) at 40 °C with THF as the mobile phase at a flow rate of 1.0 mL/min. Glass transition temperatures were determined using a Perkin-Elmer Pyris 1 differential scanning calorimeter (DSC) with a heating rate of 20 °C/min. Thermogravimetric analysis was carried out using a Perkin-Elmer TGA 7 with a heating rate of 10 °C/ min.

Monomer Synthesis. 4′-Fluoro-2,5-dichlorodiphenyl Sulfone. 2,5-Dichlorobenzenesulfonyl chloride (25.0 g, 0.102 mol) and iron(III) chloride (8.76 g, 0.0540 mol) were dissolved in excess fluorobenzene (25.0 g, 0.271 mol) in a three-neck, round-bottom flask, equipped with a condenser, mechanical stirrer, and a nitrogen purge. The solution was heated to 80 °C and allowed to stir for 3 h. Hydrogen chloride was evolved and collected in a water gas trap. Thereafter, the reaction mixture was poured into 500 mL of 10% HCl in ice water. The precipitate was collected by suction filtration, decolorized with activated charcoal, and recrystallized from ethanol to give white crystals in 52.2% yield (16.25 g, 0.05325 mol). Mp: 145 °C (DSC). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.33 (d, $J_{\text{meta}} = 2.7$ Hz, 1H), 7.99 (ddd, $J_{\text{ortho}} = 8.7$ Hz, $J_{\text{metaF}} = 4.8$ Hz, $J_{\text{meta}} = 2.1$ Hz, 2H), 7.49 (dd, $J_{\text{ortho}} = 8.7$ Hz, $J_{\text{meta}} = 2.7$ Hz, 1H), 7.37 (d, J_{ortho} 8.7 Hz, 1H), 7.21 (ddd, $J_{\text{ortho}} = 8.7$ Hz, $J_{\text{orthoF}} = 6.9$ Hz, $J_{\text{meta}} = 2.1$ Hz, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 165.8 (d, $^1J_{\text{C-F}} = 257.5$ Hz), 139.6, 135.30 (d, $^4J_{\text{C-F}} = 3.1$ Hz), 134.6, 133.7, 133.2, 131.7(d, $^3J_{\text{C-F}} = 9.8$ Hz), 131.0, 130.7, 116.4 (d, $2J = 22.8$ Hz). Anal. Calcd: C, 47.23; H, 2.31. Found: C, 47.20; H, 2.23. No ortho isomer was recovered from recrystallization.

Polymer Synthesis. Poly(4′-fluoro-2,5-diphenyl sulfone) (1). To a previously flame-dried 100 mL two-neck, pear-shaped flask, equipped with an overhead stirrer, were added zinc (3.56 g, 52.9 mmol), nickel chloride (0.221 g, 1.71 mmol), 2,2′-dipyridyl (0.266 g, 1.71 mmol), and triphenylphosphine (1.79 g, 6.83 mmol). Additions of the catalyst mixture to the reaction flask were made in a drybox under a nitrogen atmosphere. The flask was then sealed with a septum and 3 mL of anhydrous *N*,*N*-dimethylacetamide (DMAc) was added via syringe. The stirred mixture was heated in an oil bath to 80 °C under nitrogen. The catalyst mixture color changed from yellow-brown to deep green and finally to blood red, before addition via syringe of 4′-fluoro-2,5-diphenyl sulfone (5.20 g, 17.04 mmol), dissolved in 2 mL of anhydrous DMAc. The reaction was allowed to proceed for 24 h before precipitation into 40% HCl/methanol to remove zinc. The mixture was neutralized with saturated aqueous sodium bicarbonate and filtered. The recovered solid was reprecipitated from chloroform into methanol, stirred for an additional 24 h, filtered, and dried in a vacuum oven to give 3.02 g (76% yield) of poly(4′-fluoro-2,5-diphenyl sulfone). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.75, 8.23, 8.05, 7.92, 7.70, 7.46, 7.08, 6.84. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 165.5 (d, $^1J_{\text{C-F}} = 254.8$ Hz), 141.1−125.8 (m), 116.5 (m). Anal. Calcd: C, 61.52; H, 3.01. Found: C, 61.42; H, 3.44.

Pendant Group Substitution. 4-Hydroxybiphenyl (2). Poly(4′-fluoro-2,5-diphenyl sulfone) (0.50 g, 4.31×10^{-4} mol),[13] 4-hydroxybiphenyl (0.40 g, 2.35×10^{-3} mol), and anhydrous potassium carbonate (0.32 g, 2.35×10^{-3} mol) were added to a 50 mL, three-neck, round-bottom flask, equipped with an overhead stirrer, Barret-style distilling receiver, and a condenser. The glassware was flame-dried after assembly. The flask was kept under a constant flow of N_2 at all times. *N*,*N*-Dimethylacetamide (5 mL) and toluene (10 mL) were added to the flask by syringe, and the flask was immersed in an oil bath preheated to 130 °C. Dehydration was carried out at 130 °C for 4 h. The reaction temperature was then increased to 145 °C for 12 h. The solution changed from peach-bronze color to dark brown during the course of the reaction. The solution was poured into 100 mL of methanol and was stirred for 2 h. The white precipitate was then collected by suction filtration and vacuum-dried to give an overall yield of 95%. ^{1}H NMR (300 MHz, $CDCl_3$): 8.8, 7.9−6.7. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 162.2, 154.3, 140.1−138.1, 134.7, 133.4, 131.6, 130.1, 128.8, 127.4, 127.0, 120.7, 118.0, 117.5. Similar procedures were used for the nucleophilic aromatic substitution of poly(4′-fluoro-2,5-diphenyl sulfone) with nonylamine, *m*-cresol, morpholine, piperidine, 3-hydroxybenzotrifluoride, 4-*tert*-butylphenol, and 4-aminophenol. Reaction times for the nonylamine, piperidine, and morpholine derivatives were decreased to 6 h.

Sodium Thiomethoxide (3). Sodium thiomethoxide was reacted with poly(4′-fluoro-2,5-diphenyl sulfone) in anhydrous dimethyl sulfoxide for 6 h at 80 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 8.8, 8.3−6.8, 2.6. ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 147.8, 141.3−124.7, 116.5, 14.6. Yield (recovered): 89%.

Nonylamine (4). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.8 (m), 8.2−6.2 (m), 4.3, 3.1, 1.6, 1.3, 0.9. ^{13}C NMR ($CDCl_3$, 50.3

MHz): δ 152.5, 142.4, 139.0, 133.9−126.3, 111.4. Yield (recovered): 90%.

Morpholine (5). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.8−6.5, 3.8, 3.3. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 154.0, 144.0−125.4, 116.0, 113.7, 112.9, 66.3, 47.0. Yield (recovered): 92%.

Piperidine (6). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.7−6.5, 3.3, 1.6. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 154.2, 143.0, 141.0, 139.3, 134.1, 133.1, 132.0−125.8, 113.7, 113.1, 48.3, 25.1, 24.2. Yield (recovered): 88%.

4-Aminophenol (7). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.7−6.6, 5.1. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 163.2, 146.4, 143.7, 140.9, 140.4, 138.6, 137.9, 134.4, 133.9, 133.3, 132.2, 130.1, 129.7, 128.0, 126.7, 121.4, 120.5, 116.7, 115.8, 114.9. Yield (recovered): 81%.

***m*-Cresol (8).** ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.7, 8.2−6.6, 2.3. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 162.4, 154.8, 140.5−138.1134.5−125.8, 121.2, 117.5, 21.3. Yield (recovered): 90%.

3-Hydroxybenzotrifluoride (9). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.8, 8.2−6.7. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 161.5, 165.3, 141.5−138.0, 135.6−126.9, 125.2, 123.9−123.2, 121.5, 118.4−116.9. Yield (recovered): 99%.

4-*tert*-Butylphenol (10). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.7, 8.2−6.7, 1.3. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 162.5, 152.2, 148.0, 142.0−137.4, 135.4−126.9, 119.8, 117.5, 116.8, 34.4, 31.4. Yield (recovered): 94%.

Poly(ethylene oxide) Substitution. Poly(4′-fluoro-2,5-diphenylsulfone)-*graft*-poly(ethylene oxide) (11). Poly(ethylene oxide) (1.28 g, 4.74 × 10^{-4} mol) and sodium hydride (0.015 g, 6.4 × 10^{-4} mol) were added to 1.5 mL of anhydrous dimethyl sulfoxide in a 10 mL round-bottom flask with stirring under a nitrogen purge and heated to 80 °C. A solution of poly(4′-fluoro-2,5-diphenyl sulfone) (0.15 g, 1.3 × 10^{-4} mol) in 0.5 mL of anhydrous dimethyl sulfoxide was added dropwise to the solution of the sodium salt of poly(ethylene glycol) methyl ether. The reaction was allowed to continue for 6 h at 80 °C. The reaction mixture was quenched with water, poured into a Petri dish, and evaporated under vacuum at 70 °C. The GPC chromatograph of the recovered material had a single retention time corresponding to the PEO−PPP graft copolymer. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.8, 8.3−6.6, 3.6, 2.2. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 162.9, 141.5−136.7, 134.5−124.8, 114.9, 114.2, 72, 59.

Poly(arylene ether ketone) Substitution. Poly(4′-fluoro-2,5-diphenylsulfone)-*graft*-poly(arylene ether ketone) (12). The desired polyarylene ether ketone (PAEK) was synthesized from 4,4′-difluorobenzophenone and bisphenol A (4,4′-isopropylidenediphenol). Low molecular weight PAEK was targeted using an excess of bisphenol A to give hydroxy-terminated polymer. Poly(4′-fluoro-2,5-diphenyl sulfone) (0.0819 g, 7.060 × 10^{-5} mol), anhydrous potassium carbonate (0.217 g, 1.575 × 10^{-3} mol), and hydroxy-terminated PAEK (3.413 g, 8.533 × 10^{-4} mol) with a number-average molecular weight of 4.1 × 10^{3} g/mol and a PDI of 1.97 were added to a 100 mL, three-neck, round-bottom flask, equipped with an overhead stirrer, Barret-style distilling receiver and a condenser. The flask was kept under a constant flow of N_2 at all times. *N*,*N*-Dimethylacetamide (35 mL) and toluene (10 mL) were added to the flask by syringe. This was followed by immersion of the flask in an oil bath preheated to 130 °C. Dehydration was carried out at 130 °C for 4 h. The reaction temperature was then increased to 145 °C for an additional 4 h. The reaction mixture was precipitated into ethanol and recovered by suction filtration. The recovered solid (96% yield) was further purified by reprecipitation from chloroform into ethanol. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.8, 7.3, 7.0, 1.7. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 194.2, 161.4, 153.4, 146.7, 132.2, 128.3, 119.5, 117.1, 42.3, 31.0.

Thermoset Synthesis. Reaction of D.E.N. 431 Novolac Epoxy with 7 (13). Derivative **7** was calculated to have an amine equivalent weight (molecular wt. of amine/ number of active hydrogens) of 161. DOW resin D.E.N. 431, with an epoxy equivalent weight of 179, was then mixed and reacted with an equivalent amount of **7** at 150 °C for 1 h and 200 °C for 6 h. The resulting thermoset was dark brown and had a glassy appearance.

Reaction of 1 with Diethylenetriamine (14). Poly(4′-fluoro-2,5-diphenylsulfone) (0.300 g, 1.28 mmol) and diethylenetriamine (0.044 g, 0.426 mmol) were added to 1.0 mL of anhydrous DMAc in a 10 mL round-bottom flask with stirring under a nitrogen purge and heated to 130 °C for 1 h. After 1 h, the viscous solution was cast on a glass plate and placed in a heated vacuum oven. Heating was continued at 140 °C in the oven without vacuum for 4 h. The temperature was then increased to 170 °C with vacuum to remove residual DMAc from the film. After cooling, the yellow, semitransparent film was easily removed from the glass plate with a cold water wash.

Results and Discussion

Monomer Synthesis. The polymer chosen for the nucleophilic aromatic substitution approach required the synthesis of 2,5-dichloro-4′-fluorodiphenyl sulfone. It is important to point out that fluorinated aromatics do not undergo Ni(0) catalytic aryl−aryl coupling, allowing their use as reactive sites in the resulting polymers.[1] Furthermore, 2,5-dichloro-4′-fluorodiphenyl sulfone cannot be functionalized by nucleophilic aromatic substitution before polymerization due to the high reactivity of the chlorine atom in the 2 position. Friedel−Crafts sulfonylation of fluorobenzene with 2,5-dichlorosulfonyl chloride gave 2,5-dichloro-4′-fluorodiphenyl sulfone in 52% yield.

Polymer Synthesis. Polymerization of 2,5-dichlorodiphenyl sulfone, 4′-methyl-2,5-dichlorodiphenyl sulfone and 2,5-dichloro-4′-fluorodiphenyl sulfone via Ni(0) coupling was previously examined.[9] In each case, high molecular weight polymer was not achieved. Attempts to increase the molecular weight of poly(4′-fluoro-2,5-diphenyl sulfone), including the variation of catalyst ratios, concentration, solvent, and reaction times, were unsuccessful.[14] The main obstacle to polymerization is thought to be the large steric hindrance of the sulfonyl moiety ortho to the site of polymerization. Percec et al.[15] reported similar difficulties, due to steric hindrance, in the homocoupling of ortho-substituted aryl sulfonates. Because of the steric hindrance of the sulfonyl substituent, longer reaction times were needed for the coupling reaction to take place. These longer times increased the probability of terminal side reactions, including reduction from a proton source in the reaction and/or transfer of aryl groups from the triphenylphosphine ligand.[1]

Nonetheless, for the present model studies, low molecular weight material was sufficient. Poly(4′-fluoro-2,5-diphenyl sulfone) **1** was prepared via Ni(0) catalysis from 4′-fluoro-2,5-dichlorodiphenyl sulfone in 76% yield. The number-average molecular weight was determined to be 1.16 × 10^{3} with a polydispersity of 1.41 by gel permeation chromatography (GPC) relative to polystyrene standards. Oligomeric poly(2,5-diphenyl sulfone)s exhibited good thermooxidative stability and excellent solubility in dipolar aprotic solvents including *N*,*N*-dimethylacetamide, *N*,*N*-dimethylformamide, and tetrahydrofuran. The glass transition temperature, T_g, of poly(4′-fluoro-2,5-diphenyl sulfone) was 144 °C with 10% weight loss in N_2 at 484 °C, 49 °C higher than previously reported.[9] The increase in thermal stability was attributed to the use of additional purification steps to remove trace amounts of catalyst reagents.

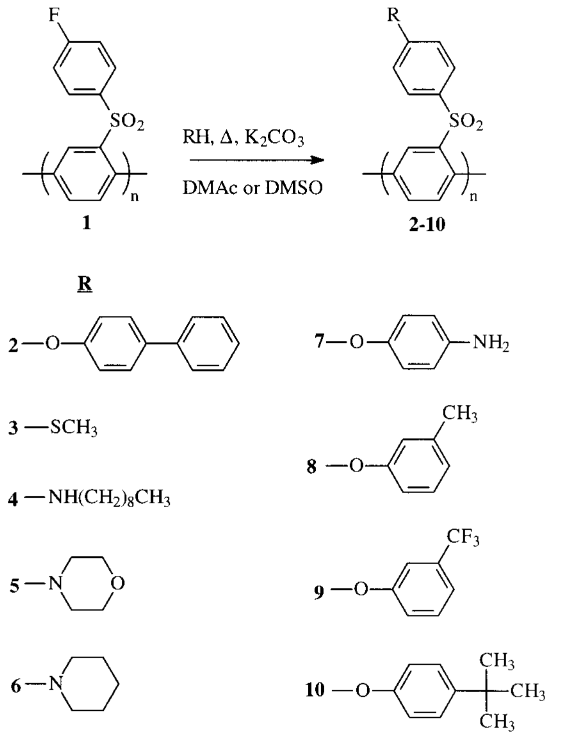
Model Studies. Oligomeric poly(4′-fluoro-2,5-diphenyl sulfone) is a prime substrate for functionalization via nucleophilic aromatic substitution by the addition−elimination mechanism. The strong electron-withdrawing nature of the sulfonyl group activates nucleophilic

Table 1. Characterization of Poly(4′-fluoro-2,5-diphenyl sulfone) and Derivatives

						TGA results			
sample	$\langle M_n \rangle$ theor[a]	$\langle M_n \rangle$[b]	PDI[b]	substitution (%)[c]	T_g (°C)[d]	5% N_2 (°C)[e]	5% air (°C)[e]	10% N_2 (°C)[e]	10% air (°C)[e]
1 (unsubst)		1160	1.43		144	443	437	484	476
2	1910	1940	1.39		142	465	498	490	518
3	1300	1200	1.43	92	134	393	396	409	409
4	1780	2260	1.39	94	85	420	385	436	416
5	1500	1590	1.50	99	189	413	412	426	427
6	1490	1560	1.48	91	186	431	430	440	442
7	1610	1610	1.34	100	167	434	437	485	486
8	1600	1640	1.40	100	109	426	432	448	454
9	1870	1980	1.42		109	425	454	447	492
10	1810	2450	1.36	100	147	454	445	469	464

[a] Theoretical $\langle M_n \rangle$ calculated for 100% substitution of **1** with each nucleophile. [b] Data obtained by GPC. [c] Percent substitution calculated from ^{1}H NMR integration of the aliphatic proton signals from the nucleophile to the total aromatic proton signal. With no aliphatic protons present, the percent substitution of **2** and **9** could not be determined by ^{1}H NMR. [d] Data obtained by DSC. [e] Weight loss temperatures obtained by TGA.

Scheme 1. Nucleophilic Aromatic Substitution of Poly(4′-fluoro-2,5-diphenyl sulfone) with Various Nucleophiles



aromatic substitution. In contrast to S_N2 chemistry, reactivity of halogens in nucleophilic aromatic substitution is F > Cl > Br > I.[16] As mentioned previously, aryl fluorides do not participate in the Ni(0) coupling reaction.

With the substrate in hand, the model study was conducted to determine the feasibility of substitution reactions and the resulting polymer properties. Nucleophilic substitution of poly(4′-fluoro-2,5-diphenyl sulfone) was carried out as shown in Scheme 1. Displacement of fluorine in poly(4′-fluoro-2,5-diphenyl sulfone) by the various nucleophiles occurred with nearly quantitative substitution by GPC. Theoretical molecular weights based on 100% substitution have been compared to the GPC results for all derivatives in Table 1. Molecular weights increased while the polydispersity showed little change.

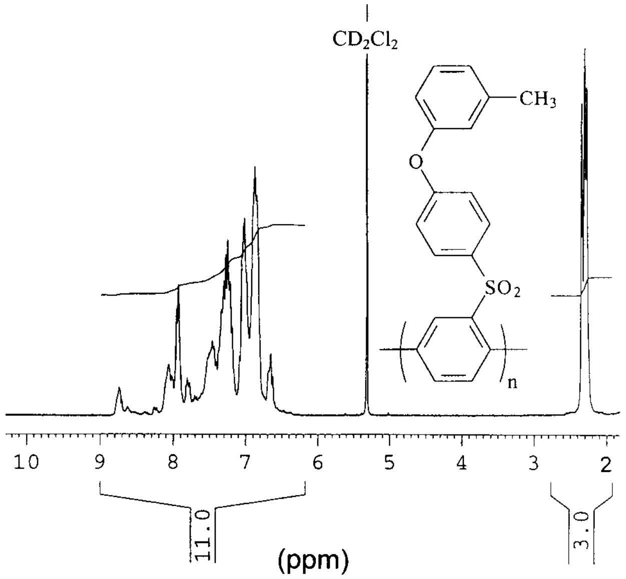


Figure 1. ^{1}H NMR spectrum of **8**. The ratio of aromatic: aliphatic protons is 11:3.

To complement GPC results, substitution was quantified by ^{1}H NMR. The extent of substitution was readily calculated from the integration of aromatic to aliphatic protons after substitution. For example, examination of the methyl group of **8** by ^{1}H NMR integration (Figure 1) showed the proper ratio of aromatic to aliphatic protons (11:3) corresponding to completely substituted product. Calculation of percent substitution by ^{1}H NMR was accomplished for derivatives **3**, **4**, **5**, **6**, **7**, **8**, and **10** (see Table 1). Substitution of phenolic nucleophiles **7**, **8**, and **10** was quantitative while that for thiol **3** and amines **4**–**6** ranged from 91 to 99%. Percent substitution could not be calculated for derivatives **2** and **9** due to overlapping aromatic signals in the ^{1}H NMR spectrum. The ^{13}C NMR spectrum of poly(4′-fluoro-2,5-diphenyl sulfone) in Figure 2 shows the ipso carbon attached to fluorine at 165.45 ppm split into a doublet (J = 253 Hz). These signals were also used to monitor the displacement of fluoride by various nucleophiles. For example, after nucleophilic aromatic substitution of poly(4′-fluoro-2,5-diphenyl sulfone) with morpholine to give **5**, the doublet at 165.45 ppm disappeared and was replaced by a singlet at 154 ppm, due to the newly formed carbon–nitrogen bond. Loss of the doublet at 165.45 ppm in the ^{13}C NMR of **1** was observed in all substitutions.

In addition to molecular weight and spectroscopic evidence of substitution, glass transition temperatures of the PPP derivatives were investigated by DSC to obtain the structure–property relationship for each

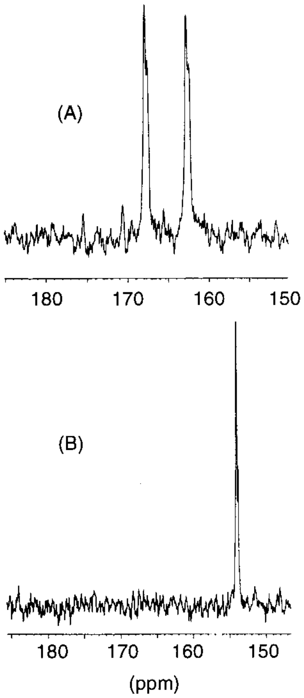


Figure 2. Displacement of fluoride from poly(4′-fluoro-2,5-diphenyl sulfone) (A) by morpholine (B) shown by ^{13}C NMR.

nucleophile. The effect of the substituent −R on the glass transition temperature is shown in Table 1. As expected, the glass transition temperature of **1** was readily modified by the nature of the nucleophile used for substitution. These glass transition shifts followed similar trends observed with the modification of main chain flexibility. Ueda and Ito[17] have shown the decrease in glass transition temperature with increasing flexibility in the backbone of poly(ether sulfone)s synthesized via Ni(0) catalysis. Poly(ether sulfone)s derived from monomers 1,1′-oxybis[4-(4-chlorophenylsulfonyl)-benzene] and 1,1′-sulfonylbis[4-(4-chlorophenoxy)benzene] showed a decrease in the glass transition temperature, determined by differential scanning calorimetery, from 269 to 190 °C, respectively. Similarly, the decrease in T_g of **8** and **9** compared to poly(4′-fluoro-2,5-diphenylsulfone) was related to an increase in flexibility due to the aromatic ether linkages. In addition, the elevated glass transition temperatures of para-substituted aromatic ether derivatives, **2** and **10**, over meta-substituted derivatives **8** and **9** was attributed to the increased chain packing in the para derivatives. Substitution of **1** with 4-aminophenol to give **7** allowed for incorporation of both flexible ether linkage and reactive aromatic amine functionality. The elevated T_g of **7** was evidence that the hydrogen bonding due to the aromatic amine was the dominant influence on the glass transition temperature compared with the flexibility of the aromatic ether. Morpholine and piperidine derivatives, **5** and **6**, gave the most significant increase in T_g at 189 and 186 °C, respectively (Figure 3). Addition of the six-membered aliphatic ring in **5** and **6** was thought to decrease the free volume by better chain packing and increase rigidity. Addition of linear aliphatic substituents in derivatives **4** and **3** caused a decrease in T_g to 85 and 132 °C, respectively. This decrease was attributed to the flexible nature of the long alkyl chain in **4** and the flexible sulfide in **3**. Similarly, the glass transition temperatures of PPPs with flexible substituents, such as poly(2-octoxycarbonyl-1,4-phenylene), show a decrease of 130 °C over that of the more rigid poly(2,5-benzophenone).[18] In addition to the ability to selectively control glass transition temperature, the thermal stability of **1** could be altered using the substitution methodology.

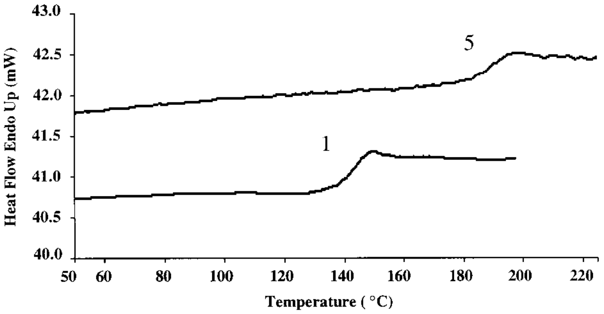


Figure 3. DSC data for polymers **1** and **5**. The glass transition temperature of **5** increased 45 °C over **1**.

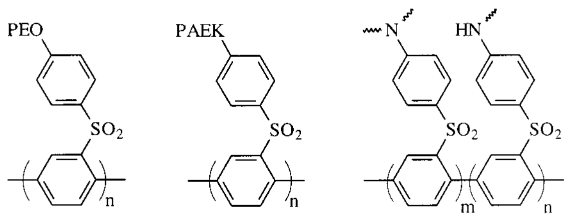
The influence of the substituent on the structure−property relationship was observed by thermogravimetric analysis. The results from thermogravimetric analysis in Table 1 showed that derivative **3** had the lowest thermal stability with 5% and 10% weight loss values in air and nitrogen less than 410 °C. The aliphatic amines displayed lower weight loss temperatures than the aromatic ethers. This was especially true for the 10% weight loss values in air. Substitution with 4-hydroxybiphenyl (**2**), to produce an extended aromatic ether, showed the greatest improvement in thermooxidative stability with the 5% weight loss temperature in air increasing 61 °C over poly(4′-fluoro-2,5-diphenylsulfone) to 498 °C. The fluorinated derivative **9** had a higher 10 wt % loss temperature in air of 492 °C than its nonfluorinated counterpart **8** at 454 °C. Thermooxidative stability and glass transition temperatures were increased over **1** for several derivatives. Following the model study, it remained to be seen if the trends in thermal properties of the oligomeric materials would be observed with higher molecular weight PPPs such as poly(4′-fluoro-2,5-benzophenone).

Macromonomer Substitution. Substitution of **1** with nucleophilic macromonomers to produce graft copolymers was carried out to obtain higher molecular weight polymer, alter solubility and improve film-forming ability. Graft copolymers are commonly synthesized through polymerization of a monomer from a polymer backbone by chain transfer or functional group initiation. The reaction of two separate well-defined polymers containing proper functionality can also facilitate grafting.[19] These methods have led to new materials with unique morphologies that have found important applications as blend compatiblilizers.[20] Poly(ethylene oxide) ($\langle M_n \rangle = 2.41 \times 10^3$, PDI = 1.30) containing one terminal hydroxyl group per chain was reacted with **1** to produce **11** (Figure 4), a PPP soluble in water and polar, aprotic solvents. Stoichiometry, based on repeat units of **1**, was held at a 0.8:1.0 ratio of PEO to **1**. At equivalent stoichiometry, the PEO−PPP contained approximately 20% unreacted PEO. Therefore, the 0.8:1.0 ratio of PEO to **1** was used to maximize conversion. The number-average molecular weight of the resulting PPP−PEO graft was $\langle M_n \rangle = 1.07 \times 10^4$. The PDI was 1.40 by GPC, relative to polystyrene standards. Substitution of the PEO was determined to be 80% and 78% by GPC and ^{1}H NMR, respectively. Given the ratio of starting materials, this corresponded

Table 2. Characterization of Graft Copolymers

					TGA results			
sample	$\langle M_n\rangle^a$ g/mol	PDI^a	T_g (°C)^b	T_m (°C)^b	5% N_2 (°C)^c	5% air (°C)^c	10% N_2 (°C)^c	10% air (°C)^c
PEO	2410	1.30		54	368	272	380	291
PAEK	4100	1.97	136		415	422	428	432
11 (PPP−PEO)	10 700	1.40		54	357	253	369	295
12 (PPP−PAEK)	11 600	3.66	158		510	513	523	523

[a] Data obtained by GPC. [b] Data obtained by DSC. Subambiant temperature DSC was not performed. No T_m was observed for PAEK and PPP−PAEK. [c] Weight loss temperatures obtained by TGA.



11 **12** **14**

Figure 4. Structures of graft copolymers **11** and **12** and thermoset **14**.

to nearly quantitative conversion. Following the example in Figure 2, ^{13}C NMR results showed the displacement of fluoride by oxygen with a new signal at 162.9 ppm, corresponding to the 4′-ipso carbon involved in the nucleophilic substitution. Most importantly, the PPP−PEO graft copolymer was soluble in water and polar, aprotic solvents such as THF and DMAc. Furthermore, the same T_m of 54 °C was found for PEO and the PPP−PEO graft. The PEO−PPP graft showed comparable thermooxidative stability in air and nitrogen to poly(ethylene oxide) (Table 2).

Major improvements in polymer film qualities were achieved via substitution with reactive macromonomers. Polyparaphenylenes, in general, form very brittle films. Even amorphous, high molecular weight poly(2,5-benzophenone)s suffer from this problem.[10] The inability to form flexible films is a major barrier in the testing and development of PPP-based gas separation membranes, low dielectric constant materials, etc. In addition to PEO substitution to alter solubility, low molecular weight PAEK ($\langle M_n\rangle = 4.10 \times 10^3$, PDI = 1.97) was substituted on poly(4′-fluoro-2,5-diphenyl sulfone) to give poly(4′-fluoro-2,5-diphenylsulfone)-*graft*-poly(arylene ether ketone) (Figure 4, **12**). The chosen PAEK is an amorphous thermoplastic that has excellent flexible film-forming properties at high molecular weights. It should be noted that neither the low molecular weight PAEK used nor **1** alone was capable of forming flexible films. The resulting PPP−PAEK had an $\langle M_n\rangle$ of 1.16×10^4 and a PDI of 3.66 (Figure 5). Flexible, transparent, creasable films were cast from a solution of **12** in chloroform. Thermooxidative stability of **12** was improved over the starting prepolymers with the 5% weight loss temperatures in air increasing 76 and 91 °C over **1** and the PAEK macromonomer, respectively (Table 2). As expected, branching of the PPP−PAEK occurred at longer reaction times and for equivalent amounts of PAEK and PPP, based on functionalities of 2 and 5, respectively. Cross-linking was evidenced during these reactions by a growing high molecular weight shoulder in the GPC, increasing PDI and finally, precipitation of insoluble material from the reaction mixture. Therefore, the structure of **12** likely contains, in addition to the graft structure, a small amount of highly branched PPP−PAEK copolymer.

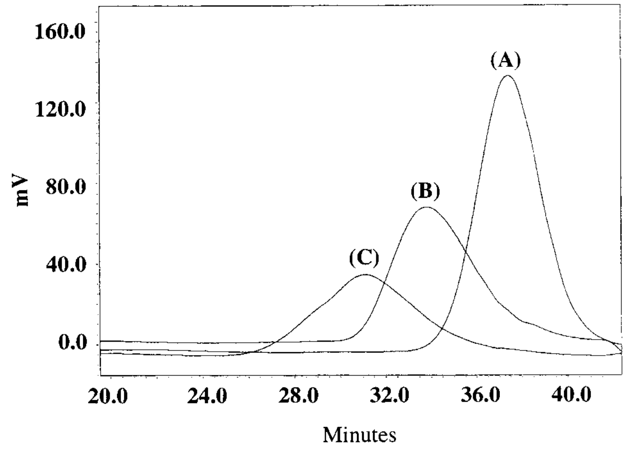


Figure 5. GPC chromatograms of (A) **1**, (B) low molecular weight PAEK, and (C) **12** (PPP-*g*-PAEK).

Thermosets. Another key consideration associated with the use of amorphous PPPs as potential engineering materials, is their high solubility in most polar, aprotic solvents such as THF. Solubility is an attribute during polymer synthesis, but a major drawback when solvent resistance of the final polymer is needed. The desired solvent resistance can be achieved by cross-linking of these thermoplastic materials. To address this point, nucleophilic aromatic substitution was used to produce thermosetting PPP materials from **1**. The epoxy cure agent **7** was synthesized via nucleophilic aromatic substitution of **1** with 4-aminophenol. This PPP-based epoxy cure agent was reacted with Dow liquid novolac epoxy D.E.N. 431 at equivalent stoichiometry to produce **13**. Excellent solvent resistance to DMAc, *m*-cresol, and THF, with no weight gain after a 24 h immersion period in each solvent, was seen for the resulting cross-linked material. Analysis of **13** by differential scanning calorimetry showed a glass transition temperature of 175 °C. Thermogravimetric analysis of **13** was similar to D.E.N. 431 cured with 4,4′-diaminodiphenyl sulfone with 5 and 10% weight loss values in air of 392 and 408 °C, respectively.

Nucleophilic aromatic substitution was also used to directly cross-link **1** with a multifunctional nucleophile, diethylenetriamine (DETA). A viscous solution, near the gel point, was first produced by reacting **1** with DETA in DMAc. This solution was then cast into a thin film and allowed to further react in a heated vacuum oven to produce semitransparent cross-linked PPP films (**14**). Because of the synthesis of secondary aromatic amines during cross-linking, which are unreactive to further substitution, diethylenetriamine was assigned a functionality of 3 for nucleophilic aromatic substitution. In contrast, diethylenetriamine has a functionality of 5 for epoxy cure. The cross-linked material was insoluble in polar, aprotic solvents with excellent solvent resistance. After immersion in THF, *m*-cresol and DMAc for 24 h, the cross-linked PPP increased in weight by 0.0, 0.9, and 5.6%, respectively. The higher value for DMAc was expected, due to its use as the solvent during thermoset synthesis. The high glass transition temperature of 240 °C for thermoset **14** was attributed to the formation of a highly cross-linked network. This high T_g PPP was more flexible than **1**; however, it did not form a creasable film.

Conclusions

Pendant groups of poly(4′-fluoro-2,5-diphenyl sulfone) were derivatized via nucleophilic aromatic substitution. Nearly quantitative substitution of poly(4′-fluoro-2,5-diphenyl sulfone), indicated by GPC and ^{1}H NMR, was accomplished using various nucleophiles under basic conditions in polar, aprotic solvents such as DMAc and DMSO. This versatile method of pendant group substitution via nucleophilic aromatic substitution allowed for the rapid synthesis of many functionalized high performance materials from a single precursor. The change in physical properties of the modified polymers compared to the unsubstituted poly(4′-fluoro-2,5-diphenyl sulfone) was a direct result of the selected nucleophile. The glass transition temperatures of poly(4′-fluoro-2,5-diphenyl sulfone) derivatives could be tuned from 85 to 189 °C. Thermooxidative stability of poly(4′-fluoro-2,5-diphenylsulfone) was improved by substitution of 4-hydroxybiphenyl.

Graft copolymers were also synthesized via nucleophilic aromatic substitution from low molecular weight PAEK and PEO with poly(4′-fluoro-2,5-diphenylsulfone). Poly(4′-fluoro-2,5-diphenylsulfone)-*graft*-poly(ethylene oxide) (**11**) was soluble both in polar, aprotic, organic solvents and in water. Poly(4′-fluoro-2,5-diphenylsulfone)-*graft*-poly(arylene ether ketone) (**12**) was achieved with an excess of PAEK. Thermal properties of the PPP−PAEK graft were improved over **1**, with elevated 5% weight loss temperatures in nitrogen and air of 510 and 513 °C, respectively. Furthermore, poly(4′-fluoro-2,5-diphenylsulfone)-*graft*-PAEK formed transparent, creasable films in contrast to its starting materials.

In addition to soluble PPP materials, high T_g thermosets have been produced via nucleophilic aromatic substitution. The 4-aminophenol derivative **5** of poly(4′-fluoro-2,5-diphenyl sulfone) was used to cure Dow novolac epoxy resins. A semiflexible, semitransparent film (**14**) was produced from the reaction of **1** with DETA. The glass transition temperature of the DETA thermoset was 240 °C. Both materials showed excellent solvent resistance to polar, aprotic solvents.

In future efforts, we will first extend this small molecule substitution and grafting chemistry to other high performance materials such as poly[3-(*p*-fluoro)benzoyl-2,5-thiophene] and poly(4′-fluoro-2,5-benzophenone). In addition to the use of monofunctional nucleophiles, the use of multifunctional nucleophiles will be expanded to improve the flexibility of film-forming PPP thermosets. Finally, we will examine the addition of 4′-fluoro-2,5-dichlorodiphenyl sulfone and/or 4′-fluoro-2,5-dichlorobenzophenone as comomomers with other bis(aryl halide)s to further expand options for cross-linking or extending the applications for high performance PPP materials.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Material Sciences Division, U.S. Department of Energy, under Contracts No. DE-AC03-765F00098 and W-405-Eng-82, and Iowa State University.

References and Notes

(1) Colon, I.; Kelsey, D. R. *J. Org. Chem.* **1986**, *51*, 2627.
(2) Ueda, M.; Miyaji, Y.; Ito, T. *Macromolecules* **1991**, *24*, 2694.
(3) Wang, J.; Sheares, V. V. *Macromolecules* **1998**, *31*, 6769.
(4) Marrocco, M.; Gange, R. R. U.S. Patent 5,227,457, 1993.
(5) Phillips, R. W.; Sheares, V. V.; Samulski, E. T.; DeSimone, J. M. *Macromolecules* **1994**, *27*, 2354.
(6) Quirk, R. P.; Wang, Y. *Macromolecules* **1995**, *28*, 3495.
(7) Percec, V.; Zhao, M.; Bae, J.; Hill, D. *Macromolecules* **1996**, *29*, 3727.
(8) Pasquale, A. J.; Vonhof, T. K.; Sheares, V. V. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1997**, *38* (1), 170.
(9) Pasquale, A. J.; Sheares, V. V. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1998**, *39* (1), 331.
(10) Pasquale, A. J.; Sheares, V. V. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 2611.
(11) Gagne, R. R.; Marrocco, M.; Trimmer, M. S.; Hendricks, N. H. U.S. Patent 5,869,592, 1999.
(12) Bader, H.; Hansen, A. R.; McCarty, F. J. *J. Org. Chem.* **1966**, *31*, 2319.
(13) Poly(4′-fluoro-2,5-diphenyl sulfone) has one functional group (−F) per repeat unit and therefore, equivalent functional groups for 0.50 g of polymer are calculated by (grams polymer/molecular weight of repeat unit). For 0.50 g of **1**, there was 2.14×10^{-3} mol of reactive fluoride groups for nucleophilic aromatic substitution.
(14) Reference to unpublished work.
(15) Percec, V.; Bae, J. Y.; Zhao, M.; Hill, D. H. *J. Org. Chem.* **1995**, *60*, 176.
(16) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry Part A*, 3rd ed.; Plenum Press: New York, 1990; p 589.
(17) Ueda, M.; Ito, T. *Polym. J.* **1990**, *23*, 297.
(18) Quirk, R. P.; Yu, W. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **2000**, *41* (1), 837.
(19) Stevens, M. P. *Polymer Chemistry An Introduction*, 3rd. ed.; Oxford University Press: New York, 1999; pp 273−276.
(20) Rudin, A. *The Elements of Polymer Science and Engineering*, 2nd ed.; Academic Press: San Diego, CA, 1999; p 472.

MA0011791