Macromolecules **2005,** *38,* 2159−2166

Novel Poly(*p*-phenylene)s via Nucleophilic Aromatic Substitution of Poly(4′-fluoro-2,5-benzophenone)

Paul D. Bloom, Charles A. Jones III, and Valerie V. Sheares*

Department of Chemistry, University of North Carolina at Chapel Hill, CB#3290, Venable Hall, Chapel Hill, North Carolina 27599-3290

Received April 29, 2004; Revised Manuscript Received November 18, 2004

ABSTRACT: Poly(4′-fluoro-2,5-benzophenone) was synthesized by Ni(0) catalytic coupling and was reacted with various nucleophiles by aromatic substitution (S_NAr) to produce substituted poly(*p*-phenylene) thermoplastics. Substitution by the nucleophiles was determined in most cases to be nearly quantitative by gel permeation chromatography, ^{1}H NMR, and ^{19}F NMR. The number-average molar masses of the derivatized polymers by gel permeation chromatography and multiangle laser light scattering ranged from 27.1×10^4 to 31.4×10^4 g/mol. The largest increase in the glass transition temperature, relative to that of poly(4′-fluoro-2,5-benzophenone) was from 167 to 225 °C after displacement of fluoride by piperidine to give poly(4′-piperidino-2,5-benzophenone). The storage modulus of poly(4′-fluoro-2,5-benzophenone) was determined to be approximately 7.4 GPa at 50 °C by dynamic mechanical analysis, while the storage modulus of the improved film-forming 4-*tert*-butylphenoxy derivative ($T_g = 170$ °C) was 6.4 GPa at 50 °C.

Introduction

Poly(*p*-phenylene)s (PPPs) continue to receive much attention due to their excellent thermal, mechanical, and electrical properties. The main obstacle in the solution polymerization of high molecular weight poly(1,4-phenylene) is the low solubility of the growing rigid rod chains during polymerization. This problem has been overcome with the addition of pendant groups to PPP monomers.[1] A variety of substituted, high molecular weight PPPs, with excellent solubility in polar, aprotic solvents such as tetrahydrofuran and *N,N*-dimethylacetamide, have been synthesized.[2] However, the addition of pendant groups often adversely affects the physical properties of the final polymer. For example, the presence of solubilizing alkyl groups on a PPP backbone imparts lower overall thermal stability in comparison to that of solubilizing benzoyl substituents.[3] Therefore, pendant groups that maximize molar mass and physical properties are desirable.

Specifically, poly(2,5-benzophenone) shows great promise as a high-performance engineering thermoplastic with a glass transition temperature of 206 °C and 5% weight loss temperatures in nitrogen and air near 500 °C.[4] In addition, the tensile modulus of poly(2,5-benzophenone) far exceeds those of other high-performance polymers, including poly(phenylene sulfide) and poly(ether ether ketone).[5] Commercial production of poly(2,5-benzophenone) derivatives, under the name Parmax, is currently under way.[6] These materials were previously known as Poly-X-1000 (poly(2,5-benzophenone)) and Poly-X-2000 (poly(4′-phenoxy-2,5-benzophenone)) produced by Maxdem, Inc.[1]

While the benzoyl group of poly(2,5-benzophenone) serves to solubilize the material, the inclusion of functionality on the pendant group leads to other important materials. Polymers such as poly(4′-diethylamino-2,5-benzophenone) show nonlinear optical (NLO) properties.[7] Functional pendant groups on a PPP backbone also serve as sites for further chemical modification, graft copolymerization, or cross-linking.[8] Unfortunately, the introduction of new functional groups along the backbone of poly(*p*-phenylene) presents several problems. Typically, significant time and resources are needed to develop tailor-made monomers for polymers with specific end uses. Moreover, complications during polymerization due to the incompatibility of new functional groups with the catalyst system chosen for polymerization must be considered.

One of the most attractive synthetic procedures for the production of PPPs, originally developed for synthesis of biphenyls, is the Ni(0) coupling of bis(aryl halide) monomers and, more specifically, bis(aryl chloride)s.[9] This catalyst system, with minor variations, is reported to yield high molar mass PPPs with good conversions.[2] However, the catalyst system is sensitive to sources of hydrogen in the reaction mixture and monomers containing functionality that may adversely coordinate with Ni(0).

To circumvent the need for extensive monomer development and alterations in the Ni(0) catalyst conditions, we have developed a new methodology to rapidly synthesize functionalized PPPs. Previously, we reported the synthesis of functional poly(*p*-phenylene)s via nucleophilic aromatic substitution of poly(4′-fluoro-2,5-diphenyl sulfone).[8] Aromatic fluoride does not participate in the Ni(0) catalytic aryl−aryl coupling reaction used to produce PPPs from bis(aryl halide)s. Therefore, when activated by an electron-withdrawing group, an aromatic carbon bearing a fluorine atom can be used as a reactive site for postpolymerization functionalization of PPPs synthesized via Ni(0) catalytic coupling. While poly(4′-fluoro-2,5-diphenyl sulfone) was limited to low molar mass ($\langle M_n \rangle = 1160$ g/mol, $\langle M_w \rangle = 1660$ g/mol), it served as a model for the substitution chemistry. In addition, the ability to produce PPP graft copolymers and thermosets was demonstrated.

To extend this methodology to higher molecular weight PPP analogues, we report the synthesis and functionalization of poly(4′-fluoro-2,5-benzophenone). Poly(4′-fluoro-2,5-benzophenone) is synthesized via Ni(0) catalytic coupling of 2,5-dichloro-4′-fluorobenzophenone. Nucleophilic aromatic substitution of high

10.1021/ma0491560 CCC: $30.25

molar mass poly(4′-fluoro-2,5-benzophenone) is used to significantly increase the molecular weight, improve the processability, and alter the solubility and film-forming ability of PPP derivatives. In addition, our method is used to introduce NLO pendant groups along the rigid rod backbone. These unique high molecular weight PPP-based materials may find applications as high-performance engineering thermoplastics and as cure agents for epoxy-based thermosets. The details of these substitution reactions and the final polymer properties are described herein.

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′-Bipyridyl and triphenylphosphine were purified by recrystallization from ethanol and *n*-heptane, respectively. 4-Hydroxybiphenyl and 3-hydroxybenzotrifluoride were purchased from AlfaAESAR and used as received. 4′-Fluoro-2,5-dichlorobenzophenone was recrystallized twice (+99% by GC/MS) before polymerization. The Dow Chemical Co. provided the novolac epoxy resin DEN 431. Anhydrous nickel(II) chloride (99.99%) and zinc powder (−100 mesh, 99.998%) were 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 ^{13}C NMR polymer spectra were acquired using a Bruker AC-200 (50.3 MHz). Molecular weights were determined using a Waters gel permeation chromatography (GPC) system consisting of a Waters 510 pump, a Waters 717 autosampler, and an Optilab (Wyatt Corp.) refractive index detector coupled with a Wyatt 18-angle detector (DAWN EOS, Wyatt Corp.). The system was equipped with four PLgel columns (100, 500, 10^4, and 10^5 Å, Polymer Laboratories) 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 with a heating rate of 20 °C/min. Thermogravimetric analysis was carried out using a Perkin-Elmer TGA 7 at a heating rate of 10 °C/ min. Mechanical testing was performed using three-point-bending tests on a dynamic mechanical analyzer (Perkin-Elmer DMA7e). Samples were machined into bars approximately 1.5 mm in height and 3 mm in width. They were subjected to a 110 mN static force and 100 mN oscillatory dynamic force (frequency 1 Hz). The samples were examined at a scan rate of 5 °C/min. The storage modulus (E', Pa) and tan δ [E''/E' or ratio of the loss modulus (E'') to the storage modulus (E')] were used to compare the mechanical strength of the materials.

Monomer Synthesis. 4′-Fluoro-2,5-dichlorobenzophenone. 2,5-Dichlorobenzoyl chloride was prepared according to the literature procedure.[10] The excess thionyl chloride and 1,2-dichloroethane were removed under vacuum, and the acid chloride was used without further purification. 2,5-Dichlorobenzoyl chloride (14.6 g, 69.7 mmol) was added via syringe to a solution of anhydrous aluminum chloride (9.30 g, 69.7 mmol), excess fluorobenzene (13.4 g, 0.139 mol), and nitromethane at 0 °C in a round-bottom flask. The solution was warmed to room temperature and stirred for 24 h. The hydrogen chloride that evolved was collected in a water gas trap. 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 *n*-heptane/ethyl acetate (4:1) to give white crystals in 78.9% yield (14.8 g, 55.0 mmol). Mp: 87.2 °C (differential scanning calorimetry (DSC)). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.83 (ddd, $J_{\text{ortho}} = 8.8$ Hz, $J_{\text{meta F}} = 5.0$, $J_{\text{meta}} = 2.1$, 2H), 7.41 (m, 2H), 7.35 (dd, $J_{\text{ortho}} = 0.6$ Hz, $J_{\text{meta}} = 0.9$ Hz, 1H), 7.15 (ddd, $J_{\text{ortho}} = 8.7$, $J_{\text{ortho F}} = 6.9$, $J_{\text{meta}} = 2.1$, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 192.1, 166.3 (d, $^1J_{\text{C-F}} = 257.2$ Hz), 139.6, 133.0, 132.8 (d, $^3J_{\text{C-F}} = 9.7$ Hz), 132.3 (d, $^4J_{\text{C-F}} = 2.7$ Hz), 131.3, 131.2, 129.4, 128.8, 116.0 (d, $^2J_{\text{C-F}} = 22.1$ Hz). Anal. Calcd: C, 58.02; H, 2.62. Found: C, 58.07; H, 2.79.

Polymer Synthesis. Poly(4′-fluoro-2,5-benzophenone). To a previously flame-dried 100 mL two-neck, pear-shaped flask, equipped with an overhead stirrer, were added zinc (2.00 g, 30.6 mmol), nickel(II) chloride (0.150 g, 1.16 mmol), 2,2′-bipyridyl (0.180 g, 1.15 mmol), and triphenylphosphine (1.50 g, 5.72 mmol). Additions of the catalyst mixture to the reaction flask were made in a drybox under a nitrogen atmosphere. The flask was sealed with a septum and 10 mL of anhydrous *N*,*N*-dimethylacetamide (DMAc) added via syringe. The stirred mixture was heated in an oil bath to 80 °C under nitrogen. Once the catalyst mixture color changed from yellow-brown to deep red, 4′-fluoro-2,5-benzophenone (9.60 g, 35.7 mmol) dissolved in 10 mL of anhydrous DMAc was added via syringe. The reaction was allowed to proceed for 3 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 dissolved in chloroform, precipitated into methanol, stirred for an additional 24 h, filtered, and dried in a vacuum oven to give 7.06 g (99.8% yield) of *partially reduced* poly(4′-fluoro-2,5-benzophenone) **1**. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.68−6.70 (m), 3.49−3.24. ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 196.8−195.5, 168.6, 163.6, 160.0, 139.2, 134.1, 132.9, 130.7, 129.7, 127.3, 128.0, 125.3, 115.8, 114.0, 81.0. ^{19}F NMR (376 MHz, CD_2Cl_2 with PhF): δ −98.4 (m, 3.6 F), −108.7 (m, 1F). Partially reduced poly(4′-fluoro-2,5-benzophenone) **1** (6.00 g, 30.3 mmol) was dissolved in dichloromethane (250 mL) in a round-bottom flask equipped with a magnetic stirrer. Pyridinium chlorochromate (PCC) (7.50 g) was ground to a fine powder and added to the solution at room temperature, and the resulting solution was allowed to stir for 3 h. (*Caution: PCC should be handled with care as it is a known carcinogen!*) The solution was then poured into methanol/HCl (65:35) and the poly(4′-fluoro-2,5-benzophenone) **2** precipitate collected by suction filtration. The precipitate was vacuum-dried, dissolved in methylene chloride, and precipitated into methanol/HCl (65:35) to further remove residual impurities to give 5.91 g (98.5% recovered) of poly(4′-fluoro-2,5-benzophenone). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.67−6.95 (m). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 196.4−195.8, 166.2 (d, $J_{\text{C-F}} = 257$ Hz), 139.2, 132.8, 131.4, 130.7, 129.7, 128.0, 115.8. ^{19}F NMR (376 MHz, CD_2Cl_2 with PhF): δ −98.4 (m, 129 F), −108.7 (m, 1F). Anal. Calcd: C, 78.78; H, 3.56. Found: C, 78.77; H, 4.03. Refractive index (in THF): d*n*/d*c* = 0.221.

Pendant Group Substitution. 3-Hydroxybenzotriflouride (3). Poly(4′-fluoro-2,5-benzophenone) (0.15 g, 7.6×10^{-4} mol), 3-hydroxybenzotrifluoride (0.37 g, 2.3×10^{-3} mol), and anhydrous potassium carbonate (0.15 g, 1.1×10^{-3} mol) were added to a 15 mL round-bottom flask, equipped with a magnetic stir bar and rubber septum. The flask was previously flame-dried and kept under a constant flow of N_2 at all times. *N*,*N*-Dimethylacetamide (5 mL) was added to the flask by syringe, and the flask immersed in an oil bath preheated to 145 °C. The reaction was carried out at 145 °C for 12 h. The solution was poured into 100 mL of methanol, acidified with HCl to remove K_2CO_3, and stirred for 2 h. The white precipitate was collected by suction filtration and vacuum-dried to give an overall yield of 99.7%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.73−6.87 (m). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 196.8−195.7, 161.4, 156.4, 140.1−138.9, 133.2−128.2, 125.5, 124.7, 123.6, 122.8, 121.6, 120.1, 117.9. ^{19}F NMR (376 MHz, CD_2Cl_2 with PhF): δ −55.6. Similar procedures were used for the nucleophilic aromatic substitution of poly(4′-fluoro-2,5-benzophenone) with 4-*tert*-butylphenol, 4-hydroxybiphenyl, 2,2,3,3,4,4,4-heptafluoro-1-butanol, piperidine, *n*-butylamine, *n*-hexylamine, and *n*-octylamine. Substitution of poly(4′-fluoro-2,5-benzophenone) with diethylamine was performed in anhydrous DMSO in a sealed ampule at 80 °C for 24 h.

4-*tert*-Butylphenol (4). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.64−6.79 (m, 11H), 1.31−1.29 (m, 9H). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 195.6, 162.9, 153.3, 148.3, 139.8, 133.3, 132.7−127.5, 120.3, 117.2, 34.9, 31.7. Yield (recovered): 93.4%.

4-Hydroxybiphenyl (5). Derivative **5** was synthesized on a larger scale from **2** (2.00 g, 1.01×10^{-2} mol) and 4-hydroxybiphenyl (5.16 g, 3.03×10^{-2} mol). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.67−7.30, 7.05, 6.84. ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 196.6−195.5, 161.9, 154.7, 140.1, 139.0, 137.7, 132.2, 131.6, 128.8, 127.3, 126.9, 120.4, 116.9. Yield (recovered): 94.8%.

2,2,3,3,4,4-Heptafluoro-1-butanol (6). ^{1}H NMR (300 MHz, *N,N*-dimethylformamide-d_7): δ 7.76−6.84 (m, 4.1 H), 4.87 (m, 1H). ^{13}C NMR (50.3 MHz, *N,N*-dimethylformamide-d_7): δ 196.6, 139.9, 133.1−127.9, 121.9, 116.1, 111.0. ^{19}F NMR (376 MHz, CD_2Cl_2 with PhF): δ $\angle 73.5$ (3F), −112.6 (2F), −119.8 (2F). Yield (recovered): 92.1%.

Diethylamine (7). ^{1}H NMR (300 MHz, CD_2Cl_2): 7.58−6.48 (2.4 H), 3.36 (1H), 1.13 (1.5). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 195.4, 151.8, 139.1, 131.2−124.7, 115.6, 110.5, 45.0, 12.8. Yield (recovered): 86.8%.

Piperidine (8). ^{1}H NMR (300 MHz, CD_2Cl_2): 7.60−7.18, 6.68 (7H), 3.31 (4H), 1.63 (6H). ^{13}C NMR (50.3 MHz, $CDCl_3$): 195.7, 154.2, 138.1, 132.7−126.3, 112.7, 48.4, 25.3, 24.4. Yield (recovered): 96.0%.

***n*-Butylamine (9).** ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.47−7.29 (5H), 6.64 (1H), 6.40 (2H), 3.00 (2H), 1.45−1.32 (4H), 0.85 (3H). ^{13}C NMR (50.3 MHz, DMSO-d_6) δ 193.3, 152.9, 140.3, 137.3, 131.6−124.1, 110.3, 41.7, 30.3, 19.3, 13.1. Yield (recovered): 95.5%.

***n*-Hexylamine (10).** ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.60−7.26, 6.40 (7H), 4.26 (1H), 3.10 (2H), 1.57 (2H), 1.31 (6H), 0.88 (3H). ^{13}C NMR (50.3 MHz, DMSO-d_6) δ 193.1, 152.7, 140.2, 139.3, 137.3, 131.5−124.0, 110.2, 42.0, 30.4, 28.1, 25.6, 21.4, 13.1. Yield (recovered): 95.8%.

***n*-Octylamine (11).** ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.61−7.27, 6.40 (7H), 4.25 (1H), 3.05 (2H), 1.6 (2H), 1.29 (10H), 0.89 (3H). ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ 195.7, 153.0, 138.9, 133.2−126.5, 43.8, 32.4, 29.8, 27.6, 23.2, 14.4. Yield (recovered): 91.4%.

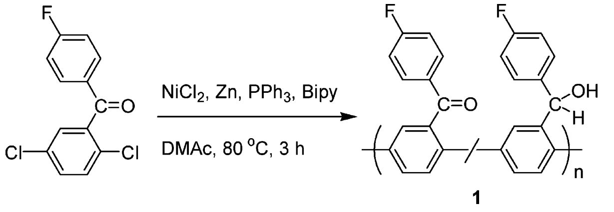
Thermoset Synthesis. Reaction of DEN 431 Novolac Epoxy with 11. Derivative **11** was calculated to have an amine equivalent weight (molecular weight of the amine/number of active hydrogens) of 307. Dow Chemical resin DEN 431 (1.5 g) with an epoxy equivalent weight of 179 was mixed with 1.2 g of **11** at room temperature. The pastelike material was then placed in a die mold, pressed into a compact pellet, and heated at 100 °C for 12 h and at 160 °C for an additional 4 h. The cured, tan-colored sample was removed from the mold and machined into DMA test samples. The poly(*p*-phenylene) cure agent was miscible with the epoxy resin, resulting in the homogeneous appearance of the final product.

Results and Discussion

Monomer Synthesis. The polymer chosen for the nucleophilic aromatic substitution approach required the synthesis of 2,5-dichloro-4′-fluorobenzophenone. Friedel−Crafts acylation of fluorobenzene with 2,5-dichlorobenzoyl chloride gave 2,5-dichloro-4′-fluorobenzophenone in 78.9% yield. As previously stated, fluorinated aromatics do not undergo Ni(0) catalytic aryl−aryl coupling, allowing their use as reactive sites in the resulting polymers.[8] Furthermore, 2,5-dichloro-4′-fluorobenzophenone cannot be functionalized by nucleophilic aromatic substitution before polymerization due to the concurrent displacement of chloride from the 2 position.

Polymer Synthesis. Polymerization of 2,5-dichlorobenzophenone[2,4,11] and alkyl-substituted 2,5-dichlorobenzophenones[10] via Ni(0) coupling has been studied. In all cases, high yields of high molar mass polymers were achieved. Poly(4′-fluoro-2,5-benzophenone) **1** was prepared by Ni(0) catalytic coupling of 4′-fluoro-2,5-dichlorobenzophenone in DMAc (Scheme 1) with nearly quantitative yield (99.8%). By GPC analysis, the number-average molar mass was determined to be 2.25×10^4 g/mol (relative to polystyrene standards) with a polydispersity of 2.60 (Table 1).

Scheme 1. Synthesis of Partially Reduced Poly(4′-fluoro-2,5-benzophenone) 1



Previously, the Sheares group reported the partial reduction of poly(benzophenone) carbonyl moieties to the corresponding secondary alcohols during Ni(0)-catalyzed polymerization.[10] Similar reduction of the carbonyl moiety was observed during the polymerization of 4′-fluoro-2,5-dichlorobenzophenone. This side reaction was an obstacle to the planned S_NAr chemistry, as the carbonyl group was required as the electron-withdrawing activating group in nucleophilic aromatic substitution. Therefore, partially reduced **1** was oxidized to the desired poly(4′-fluoro-2,5-benzophenone) **2** by treating it with 3−5 equiv of PCC in 1,2-dichloroethane as shown in Scheme 2. The number-average molar mass of **2** (2.11×10^4 g/mol, polydispersity 2.77 by GPC relative to polystyrene standards) remained close to that determined for **1** (Table 1). The ^{19}F NMR spectrum of **1** showed two signals at −98.4 and −108.7 ppm that were identified as the aromatic fluorides on the carbonyl and alcohol pendant groups, respectively (Figure 1). Integration of these signals indicated that approximately 22% of the carbonyl groups were reduced to secondary alcohols during polymerization. After oxidation of **1** with PCC to give **2**, the signal at −108.7 ppm almost completely disappeared. The ^{13}C NMR spectrum of **1** contained a signal at 81.0 ppm, due to partial reduction of the carbonyl group. This peak was absent in the ^{13}C NMR spectrum of **2**. In addition, the FT-IR spectrum of **1** showed a broad OH absorption band at 3471 cm^{-1}, C−H sp^2 stretching modes at 3104, 3069, and 3029 cm^{-1}, and C−H sp^3 stretching modes at 2975 and 2872 cm^{-1}. The OH and CH sp^3 bands were barely visible in the FT-IR spectrum of **2** (Figure 2). Polymer **2**, which contained less than 0.8% reduced carbonyl repeat units, was now better suited than **1** for functionalization by nucleophilic aromatic substitution.

The mechanism of carbonyl reduction during Ni(0)-catalyzed polymerization and the source of hydrogen in the reaction mixture were not apparent. Residual moisture in the polymerization solvent, DMAc, or other reaction components was an unlikely source of hydrogen. Colon et al. demonstrated that small amounts of water, added to Ni(0) coupling reactions, result in the displacement of halide ions by hydrogens.[9] If trace amounts of water were the source of hydrogen, polymer termination would likely be observed. However, the high yield of **1** (+99%) suggests little termination of the reaction before complete conversion of monomer. Furthermore, the relatively large amount of reduced benzoyl pendant groups (22% or 7.8 mmol of repeat units) due to trace amounts of water was unlikely. The reduction was observed in NMP and in DMAc.

The secondary alcohol pendant groups present in **1** had a drastic influence on the polymer physical properties. Films of **1** cast from tetrahydrofuran were opaque and brittle. In contrast, films of **2** prepared in the same

Table 1. Characterization of Poly(4′-fluoro-2,5-benzophenone)s

				TGA results (weight loss)[c]			
polymer	$\langle M_n \rangle^a$ (10^4 g/mol)	$\langle M_w \rangle^a$ (10^4 g/mol)	T_g^b	5% in N_2 (°C)	5% in air (°C)	10% in N_2 (°C)	10% in air (°C)
1	2.25	5.85	195	386	486	567	558
2	2.11	5.85	167	576	536	611	566

[a] Data obtained by GPC in THF, relative to polystyrene standards. [b] Data obtained by DSC at 20 °C/min. [c] Weight loss temperatures obtained by TGA at 10 °C/min.

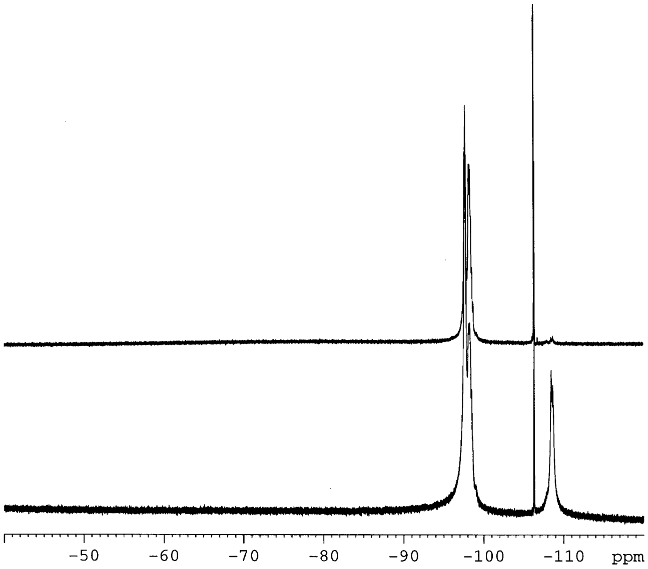
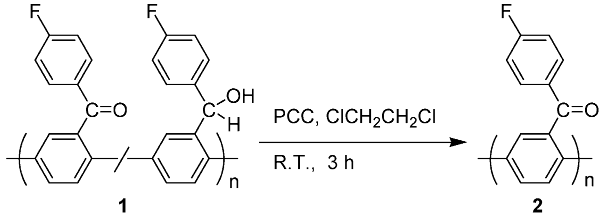


Figure 1. ^{19}F NMR of poly(4′-fluoro-2,5-benzophenone) **2** after treatment with PCC (top) and partially reduced poly(4′-fluoro-2,5-benzophenone) **1** (bottom). Fluorobenzene (−106.5 ppm) was added as a reference.

Scheme 2. PCC Oxidation of Partially Reduced Poly(4′-fluoro-2,5-benzophenone)



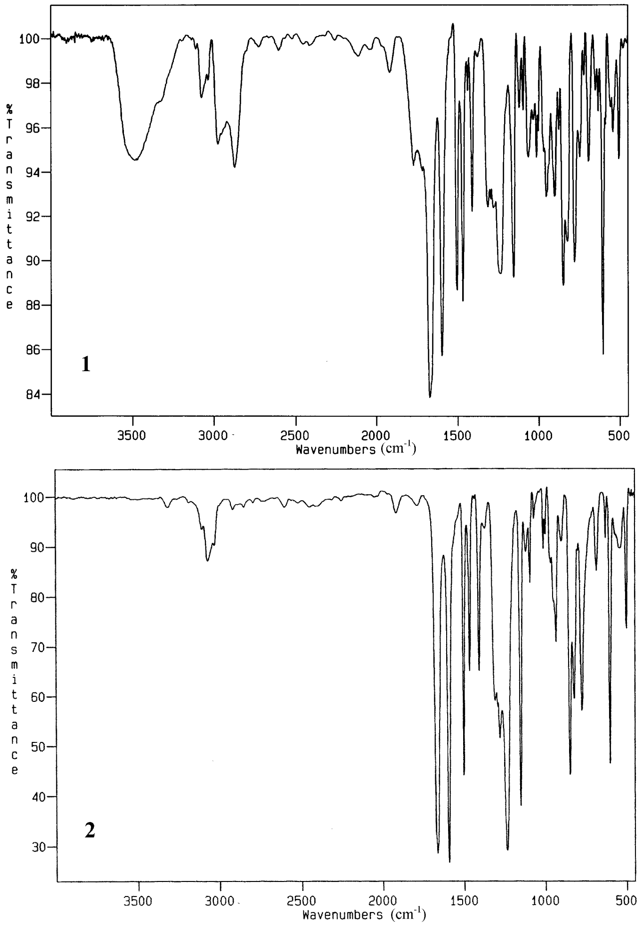


Figure 2. FT-IR spectra of polymers **1** and **2**.

manner were completely transparent and had improved flexibility. The thermal properties of **1** and **2** are summarized in Table 1. The higher glass transition temperature (T_g) of **1** (195 °C) compared to **2** (167 °C) was attributed to the hydrogen bonding of hydroxy groups not present in **2**. Polymer **2** had higher 5% and 10% weight loss temperatures in nitrogen and air compared to **1**, presumably due to the fully aromatic structure of **2** extending through the backbone and pendant groups.

Polymer Substitution. Recently, oligomeric poly(4′-fluoro-2,5-diphenyl sulfone) was shown to be a prime substrate for functionalization via nucleophilic aromatic substitution.[8] This model study was conducted to determine the feasibility of substitution reactions and the resulting polymer properties. The results showed that high degrees of substitution (91−100%) were achieved with various nucleophiles. The strong electron-withdrawing nature of the sulfonyl group in low molecular weight poly(4′-fluoro-2,5-diphenyl sulfone) activated nucleophilic aromatic substitution.

Similarly, the electron-withdrawing ability of the carbonyl groups can be used to facilitate nucleophilic aromatic substitution. These substitution reactions are known to be nearly quantitative as evidenced by the synthesis of high molar mass poly(arylene ether ketone)s from 4,4′-difluorobenzophenone and various bisphenols under basic conditions in polar, aprotic solvents.[12] After partially reduced poly(4′-fluoro-2,5-benzophenone) **1** was oxidized with PCC to give **2**, substitution reactions could be performed and resulting polymer properties determined. Nucleophilic substitution of poly(4′-fluoro-2,5-benzophenone) **2** was carried out as shown in Scheme 3. Excess nucleophile (approximately 3 equiv) used to drive the substitution reaction was removed during the precipitation stage of polymer recovery.[13]

Because rigid rod PPPs have inaccurate correlation with polystyrene standards,[14] absolute molecular weight characterization of our PPP derivatives was performed using a Wyatt DAWN EOS multiangle laser light scattering (MALLS) detector, as MALLS does not rely on a relative calibration to determine molar mass. Molar masses for **2**−**6** determined by GPC−MALLS are given in Table 2. Theoretical molar masses for derivatives **3**−**6** were calculated on the basis of 100% substitution. While

Scheme 3. Nucleophilic Aromatic Substitution of Poly(4′-fluoro-2,5-benzophenone) with Various Nucleophiles

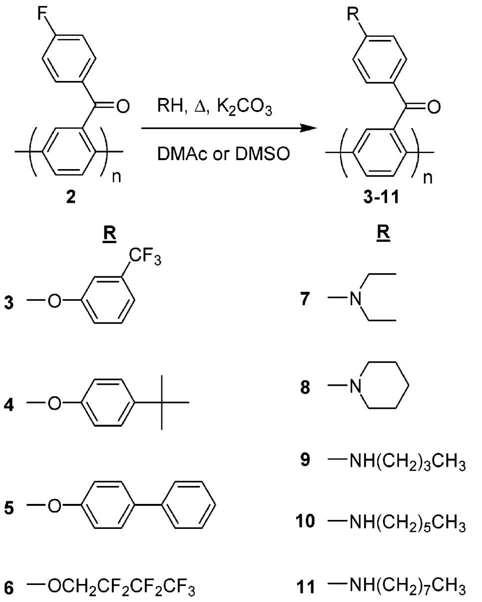


Table 2. Molar Mass Analysis of PPP Derivatives by GPC−MALLS[a]

polymer	theoretical ⟨M_n⟩ (10^4 g/mol)	⟨M_n⟩ (10^4 g/mol)	⟨M_w⟩ (10^4 g/ mol)	PDI
2 unsubstituted		1.66	2.64	1.59
3	2.86	2.71	3.56	1.31
4	2.76	2.66	4.06	1.53
5	2.93	2.89	5.12	1.77
6	3.18	3.14	4.55	1.45

[a] Using a DP_n of 84 for **2**, theoretical number-average molar masses were calculated on the basis of 100% substitution. M_r for **3**, **4**, **5**, and **6** is 340.30, 328.41, 348.4, and 378.24, respectively.

the number-average molar mass of **2** was lower than that determined relative to polystyrene standards (2.11 × 10^4 g/mol), there was a good correlation of the molar masses for **3**−**6** determined by MALLS with their expected number-average molar masses based on 100% substitution of **2**. Analyses of amine-substituted derivatives by MALLS were not reproducible and showed polydispersities close to 1.00. These results suggested that aggregation of **7**−**11** was occurring in THF. In addition, unexplained peaks were observed in GPC chromatograms obtained following the analysis of amine-substituted PPP derivatives. Coupled with their long retention times, these derivatives appear to have poor separation and throughput in the GPC system with THF as the mobile phase.

To complement GPC−MALLS results, substitution was quantified by ^{1}H NMR and ^{19}F NMR. Given that the partially reduced carbonyl group was present in **2** at approximately 1%, as determined by ^{19}F NMR, the maximum substitution possible was 99%. The extent of substitution was easily calculated by ^{1}H NMR from the integration of aromatic to aliphatic protons after substitution. Calculation of percent substitution by ^{1}H NMR was accomplished for derivatives **4**, **6**, **7**, **8**, **9**, **10**, and **11** with aliphatic and aromatic protons (Table 3). For example, examination of the methyl groups of **4** by ^{1}H NMR integration (Figure 3) showed the proper ratio of aromatic to aliphatic protons (11:9) corresponding to completely substituted product (99%). Substitution of **5** could not be determined by NMR integration. However, the ^{13}C NMR of **5** showed complete replacement of the doublet at 166.2 ppm with a signal at 161.9 ppm due to the presence of the newly formed C−O bond.

The low boiling point of diethylamine made it difficult to achieve reaction temperatures necessary for substitution in DMAc without loss of the nucleophile. Typical substitutions in DMAc were 50%. Therefore, diethylamine, potassium carbonate, and **2** were mixed in DMSO in a sealed ampule and heated at 80 °C for 24 h. Although an improvement over the results in DMAc was seen, the diethyl-substituted derivative **7** had the lowest substitution conversion of 74%. Samulski and Taylor[7] reported the synthesis and NLO properties of poly(4′-diethylamino-2,5-benzophenone). In addition to the difficult monomer synthesis, the direct Ni(0) coupling synthetic approach from the 4′-diethylamino-2,5-dichlorobenzophenone monomer produced relatively low molar mass material ($M_n = 5.3 \times 10^3$ g/mol, PDI = 2.1). It has not been determined if our high molecular weight 74% diethylamine-substituted derivative displays similar NLO behavior.

^{19}F NMR was used to calculate the percent substitution for derivatives **3** and **6**. The ^{19}F NMR spectrum of **3** in Figure 4 shows only the presence of the trifluoromethyl group signal at −55.6 ppm. For the 2,2,3,3,4,4,4-heptafluoro-1-butanol-substituted derivative **6**, only three signals, which integrated in a ratio of 3:2:2, were observed. Typically, alkyl alcohols are not active nucleophiles in the presence of potassium carbonate under the conditions used for substitution. However, the inductive withdrawing effects of the fluorine in 2,2,3,3,4,4,4-heptafluoro-1-butanol sufficiently decrease its pK_a, allowing it to be converted to the potassium alkoxide under the reaction conditions used for nucleophilic aromatic substitution.

Thermal Analysis. 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 nucleophile. Our previous report on the substitution of oligomeric poly(4′-fluoro-2,5-diphenyl sulfone) showed that the effect of the substituent −R on the glass transition temperature was significant.[8] The glass transition temperatures for polymers **2**−**11** are shown in Table 4. A comparison of the effects of the substituent −R on the glass transition temperature for oligomeric PPPs from our previous study of poly(4′-fluoro-2,5-diphenyl sulfone)[8] and high molar mass PPPs synthesized here is shown in Table 5. As expected, the glass transition temperature of **2** was modified by the nature of the nucleophile used for substitution. The glass transition temperatures of 4-*tert*-butylphenol (**4**) and 4-hydroxybiphenyl (**5**) substituted PPPs were 170 and 168 °C, respectively. These substitutions produced little change in T_g compared to that of unsubstituted PPP **2** of 167 °C. These results were consistent with our findings for substitution of oligomeric poly(4′-fluoro-2,5-diphenyl sulfone) with 4-*tert*-butylphenol and 4-hydroxybiphenyl, which produced only a 2−3 °C change in the glass transition temperature compared to that of the unsubstituted material (Table 5). The T_g of the 3-hydroxybenzotrifluoride derivative **3** was found to decrease by 44 °C. This decrease is attributed to an increase in free volume between chains as a result of the size and the low intermolecular forces of the CF_3 group. Piperidine derivative **8** gave the most significant increase in T_g, reaching 225 °C. A large increase in T_g

Table 3. Percent Substitution for PPP Derivatives by ^{1}H and ^{19}F NMR

polymer	substitution determined by ^{1}H NMR[a] (%)	substitution determined by ^{19}F NMR[b] (%)	polymer	substitution determined by ^{1}H NMR[a] (%)	substitution determined by ^{19}F NMR[b] (%)
3	–	99	8	99	–
4	99	–	9	99	–
6	85	99	10	99	–
7	74	–	11	99	–

[a] Percent substitution calculated from ^{1}H NMR integration of the aliphatic proton signals from the nucleophile to the total aromatic proton signal. [b] Percent substitution calculated from ^{19}F NMR integration of the fluorine signals from the nucleophile to the fluorine signal at −98.4 ppm.

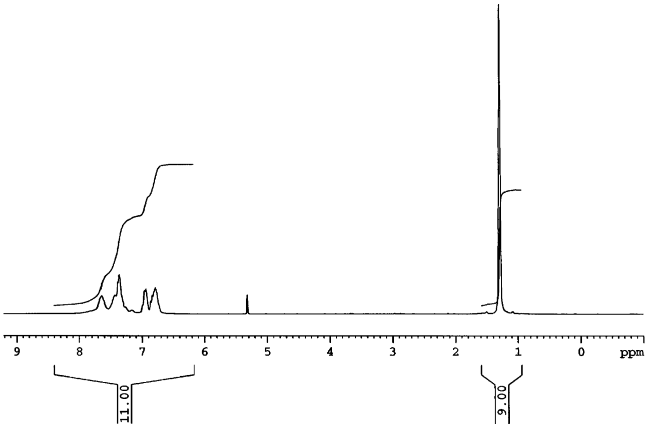


Figure 3. ^{1}H NMR spectrum of **4**. The ratio of aromatic to aliphatic protons is 11:9.

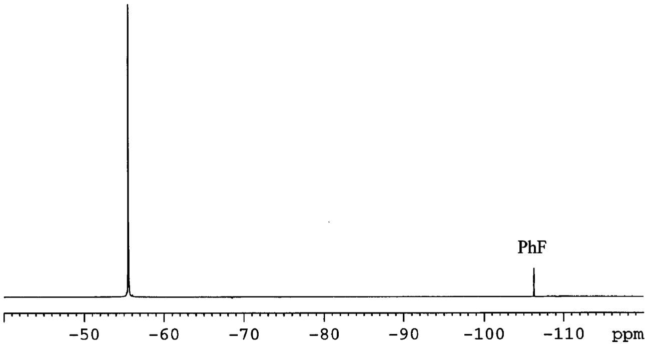


Figure 4. ^{19}F NMR spectrum of **3**. The trifluoromethyl group resonance was observed at −55.6 ppm.

Table 4. Thermal Properties of PPP Derivatives

		TGA results (weight loss)[b]			
polymer	T_g[a] (°C)	5% in N_2 (°C)	5% in air (°C)	10% in N_2 (°C)	10% in air (°C)
2	167	576	536	611	566
3	123	532	529	564	561
4	170	510	501	525	528
5	168	542	545	578	578
6	168 (T_m = 251)	401	367	478	441
7	141	462	396	488	476
8	225	444	373	483	424
9	164	306	302	438	400
10	145	441	271	470	316
11	128	444	398	466	440

[a] Determined by differential scanning calorimetry at 20 °C/min. [b] Determined by thermogravimetric analysis at 10 °C/min.

for the piperidine derivative of poly(4′-fluoro-2,5-diphenyl sulfone) was also seen.[8] Addition of linear aliphatic substituents in derivatives **9**−**11** caused decreases in T_g to 164, 145, and 128 °C, respectively. These decreases were attributed to the increased flexibility with longer alkyl chains. In addition, the diethylamine derivative **7** had a lower T_g, associated with the increased flexibility of its alkyl chains. The glass transition temperature of the 2,2,3,3,4,4,4-heptafluoro-1-butanol derivative showed little change. However, the DSC thermogram clearly showed the presence of a melt transition with an onset of 251 °C. Therefore, the presence of short perfluorinated alkyl pendant groups may result in side chain packing and induce some crystallization.[15]

The influence of the substituents on the thermal stability was observed by thermogravimetric analysis. The results in Table 4 show that derivative **5** had a slight improvement in thermooxidative stability with the 5% and 10% weight loss temperature increasing 9 and 12 °C over those of poly(4′-fluoro-2,5-benzophenone) to 545 and 578 °C, respectively. The aliphatic amines displayed lower weight loss temperatures than the aromatic ethers. These results were very similar to those reported in the model study based on poly(4′-fluoro-2,5-diphenyl sulfone). All derivatives showed a decrease in thermooxidative stability compared to **2** due to their nonaromatic components, with the exception of **5**, which produced an aromatic ether.

Processing and Mechanical Analysis. One of the main obstacles in the processing and fabrication of PPP components for applications is their brittle nature. As previously stated, partially reduced poly(4′-fluoro-2,5-benzophenone) **1** forms very brittle opaque films. Compression molding of **1** was also attempted. Polymer **1** was heated in a die mold under 7 MPa of pressure to 315 °C. After being cooled to room temperature, the sample was removed from the mold. The material was so brittle that the sample displayed major cracking during removal. In contrast polymer **2**, which formed flexible, transparent films, was easily molded and showed no cracking under similar conditions. In addition, **2** was easily machined into test samples for dynamic mechanical analysis (DMA). DMA of **2** (Figure 5) was performed in flexure mode with a three-point-bending apparatus. The storage modulus of **2** was high (approximately 7.4 GPa at 50 °C). As a comparison, the storage moduli of Nylon 6/6, poly(ether imide), and poly(ether ether ketone), recorded at 50 °C, are 2.5, 3.0, and 3.6 GPa, respectively.[16] Films produced by solution casting of substituted aryl ether derivatives **3**−**5** had increased flexibility over those of **2**. Derivative **4** was also compression molded and machined into samples for DMA. The DMA test for **4** is shown in Figure 6. The polymer had a storage modulus of 6.4 GPa at 50 °C. The lower modulus of **4** compared to **2** was attributed to the presence of the added aryl ether pendant groups. Nonetheless, polymer **4** is an example of a thermally stable, high modulus, high molecular weight, processable PPP. Due to its semicrystalline nature, derivative **6** produced white opaque films that were more brittle than those of **3**−**5**. All amine-substituted derivatives produced brittle films.

Thermosets. The synthesis of PPP cured thermosets was reported in our previous model study. The high

Table 5. Substituent Effect on the Glass Transition Temperature in Low and High Molecular Weight PPPs

substituent −R	ΔT_g (°C) for poly(4-fluoro-2,5-diphenyl sulfone)[a,8]	ΔT_g (°C) for poly(4-fluoro-2,5-benzophenone)[b]
4-*tert*-butylphenol (**4**)	+3	+3
4-hydroxybiphenyl (**5**)	−2	+1
3-hydroxybenzotrifluoride (**3**)	−35	−44
piperidine (**8**)	+42	+58
n-octylamine (**11**)		−39
n-nonylamine	−59	

[a] The T_g of poly(4′-fluoro-2,5-diphenyl sulfone) was 144 °C. [b] The T_g of poly(4′-fluoro-2,5-benzophenone) was 167 °C. Data for poly(4′-fluoro-2,5-diphenyl sulfone) from ref 8.

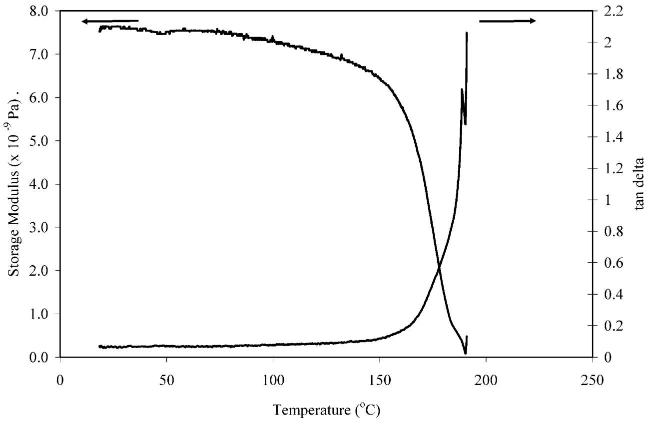


Figure 5. Dynamic mechanical analysis of **2** performed at 5 °C/min.

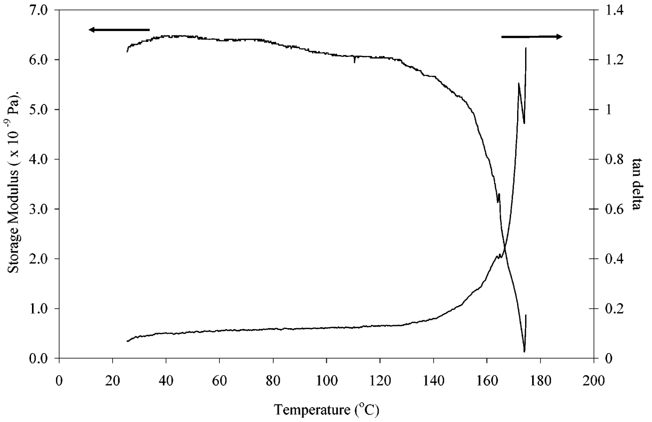


Figure 6. Dynamic mechanical analysis of **5** performed at 5 °C/min.

solubility of substituted PPPs in most polar, aprotic solvents is a major drawback when solvent resistance of the final polymer is needed. Solvent resistance can be achieved by cross-linking of these thermoplastic materials. To address this point, nucleophilic substitution of **2** with primary aliphatic amines produced PPP derivatives **9**−**11** that contained active N−H groups for epoxy cross-linking. PPP-based epoxy cure agent **11** was mixed with Dow liquid novolac epoxy DEN 431 in a ratio of 1.2 g of PPP to 1.5 g of epoxy. This ratio was not based on epoxy and amine equivalent weight, but instead on the required amount of liquid epoxy needed to form a paste with the PPP powder. The mixture was compression molded and cured at 140 °C to give a homogeneous tan-colored sample. The material was completely insoluble in polar, aprotic organic solvents. The particles of PPP appeared to have completely dissolved in the epoxy resin during cure. The flexural modulus at 23 °C, determined according to ASTM standard D790M-92, was 2.75 GPa. The 5% weight loss temperatures in air and nitrogen, determined by thermogravimetric analysis, were 422 and 425 °C, respectively. This example was provided to show the ability to use amine-substituted PPP derivatives as epoxy cure agents, given their apparent good miscibility with novolac epoxy resins. For actual thermoset applications, the amino PPP derivatives could be used in combination with other amines as is typical for epoxy formulation. Our substituted materials should allow the radiation-resistant nature of PPPs[17] to be exploited in certain epoxy coating applications.

Conclusions

Poly(4′-fluoro-2,5-benzophenone) was derivatized via nucleophilic aromatic substitution. As was shown for oligomeric poly(4′-fluoro-2,5-diphenyl sulfone), nearly quantitative substitution, indicated by GPC and 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 demonstrated 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-benzophenone) was similar to that observed in the low molecular weight poly(4′-fluoro-2,5-diphenyl sulfone). The glass transition temperatures of poly(4′-fluoro-2,5-benzophenone) derivatives could be tuned from 123 to 225 °C. Thermooxidative stability of poly(4′-fluoro-2,5-benzophenone) was improved by substitution of 4-hydroxybiphenyl.

In addition to the modification of physical properties, PPPs with new applications have been produced via nucleophilic aromatic substitution. The *n*-octylamine derivative **11** of poly(4′-fluoro-2,5-benzophenone) was used to cure Dow novolac epoxy resins. Furthermore, NLO-active chromophores such as the diethylaminobenzoyl group were introduced by substitution with diethylamine. Future research will include a more detailed study of the synthesis of NLO materials via nucleophilic aromatic substitution of poly(4′-fluoro-2,5-benzophenone). Finally, we will extend our substitution chemistry to other high-performance materials such as poly(arylenephosphine oxide)s.[18]

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

References and Notes

(1) Nalwa, H. S., Ed.; *Handbook of Organic Conductive Molecules and Polymers*; John Wiley & Sons: New York, 1997; pp 213−219.

(2) Marrocco, M. L.; Gange, R. R. U.S. Patent 5,227,457, 1993.

(3) (a) Rehahn, M.; Schluter, A. D.; Wegner, G. *Makromol. Chem.* **1990**, *191*, 1991. (b) Miller, R. B.; Dugar, S. *Organometallics* **1984**, *3*, 1261.

(4) Phillips, R. W.; Sheares, V. V.; Samulski, E. T.; DeSimone, J. M. *Macromolecules* **1994**, *27*, 2354.

(5) Marrocco, M. L.; Gagne, R. R.; Trimmer, M. S.; Hsu, L. C. *Sampe Proc.* **1994**, *39*, 1063.

(6) Mississippi Polymer Technologies, Inc., Maxdem, Inc. (www.maxdem.com).

(7) Taylor, D. K.; Samulski, E. T. *Macromolecules* **2000**, *33*, 2355.

(8) Bloom, P. D.; Sheares, V. V. *Macromolecules* **2001**, *34*, 1627.

(9) Colon, I.; Kelsey, D. R. *J. Org. Chem*. **1986**, *51*, 2627.

(10) Pasquale, A. J.; Sheares, V. V. *J. Polym. Sci., Part A: Polym. Chem*. **1998**, *36*, 2611.

(11) Quirk, R. P.; Wang, Y. *Macromolecules* **1995**, *28*, 3495.

(12) Odian, G. *Principles of Polymerization*, 3rd ed.; Wiley-Interscience: New York, 1991; p 155.

(13) Obrecht, D.; Villalgordo, J. M. *Solid-Supported Combinatorial and Parallel Synthesis of Small-Molecular-Weight Compound Libraries*; Pergamon: The Netherlands, 1998; p 25.

(14) Lies, P.; Hensel, V.; Schluter, A. D. *Liebigs Ann*. **1996**, 1037.

(15) Sperling, L. H. *Introduction to Physical Polymer Science*; John Wiley and Sons: New York, 1992; p 171.

(16) Sepe, M. *Dynamic mechanical analysis for plastics engineering*; Plastics Design Library: Norwich, NY, 1998; pp 62−63, 100−101, and 102−103.

(17) Kovacic, P.; Marchionna, V. J.; Kovacic, J. P. *J. Polym. Sci., Part A: Gen. Pap.* **1965**, *3*, 4297.

(18) Salazar, L.; Bloom, P. D.; Sheares, V. V. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2001**, 42 (*2*).

MA0491560