

Chapter 3

Experimental

3.1 Instrumentation

Melting points of the monomers, and transitions in the polymers, were determined using a Perkin-Elmer Pyrus 1 differential scanning calorimeter (DSC). High performance liquid chromatography (HPLC) was used to determine monomer purity, with a Perkin-Elmer HPLC, Model 410. UV/VIS spectroscopy was performed using a Lambda 40 UV/VIS spectrometer. Monomer samples were submitted to Galbraith Laboratories for elemental analysis.

One and two dimensional ^1H NMR spectra of the intermediates and monomers were obtained on Varian 300 MHz and 400 MHz spectrometers using 5 mm o.d. tubes. ^{13}C noise decoupled NMR spectroscopy was performed on a Varian 400 MHz spectrometer using 10 mm o.d. tubes. Commercial PMMA was obtained from Aldrich ($M_w \sim 120,000$ g/mole). Samples were analyzed in CDCl_3 .

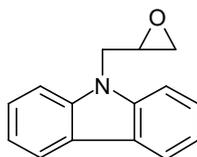
FTIR spectra were obtained using a Nicolet FTIR spectrometer. *In-situ* FTIR experiments were performed using an ASI-FTIR ReactIR™, Model 1000. Photo-DSC experiments were performed using a Perkin-Elmer Pyrus 7 DSC coupled with a double beam photocalorimetric accessory (DPA) and a xenon lamp as the irradiation source. Additional 7.0 mm diameter quartz windows were fitted directly on top of the sample pans to reduce solvent evaporation.

Gel permeation chromatography (GPC) was used to analyze linear polymers using a Perkin-Elmer GPC, Model 200, with a HT 2+4+5 column, and 0.02 M P_2O_5 in N-methyl pyrrolidinone (NMP) as solvent. Thermal gravimetric analysis (TGA) of the polymers under nitrogen were determined using a Perkin-Elmer TGA 7. Ground state minimum energy configurations were determined using Gaussian 98 molecular modeling software.

Refractive indices and birefringences of the solvent cast polymer films were measured using a Metricon Prism Coupler Instrument, Model 2010.

3.2 Novel Carbazole Based Monomer Syntheses

3.2.1 Carbazole Epoxide



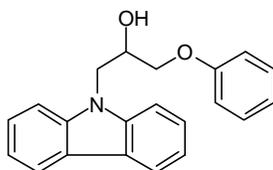
Carbazole epoxide
 $C_{15}H_{13}NO$
FW = 223 g/mole

Carbazole epoxide (9-(2,3-epoxypropyl)-carbazole) was prepared by first dissolving 40 g carbazole (239 mmole) (Aldrich, purified by dilute HCl wash, followed by recrystallization in methanol) with 500 ml dry, distilled THF, in a one liter 3-neck round bottom flask equipped with mechanical stirrer, nitrogen inlet, condenser, and addition funnel. Next, 131 ml epichlorohydrin (1.67 mole; 7-fold molar excess) (Aldrich, used as received) was added to the reaction flask slowly by addition funnel, with rapid stirring. KOH (34 g, 598 mmole; 2.5-fold molar excess) (Fisher, used as received) was then added slowly. After the addition of KOH, the reaction solution changed from clear to turbid. The reaction was allowed to proceed under nitrogen, at 80°C to 90°C (oil bath), for 12 to 14 hours, completion of reaction was monitored by TLC (25 % ether in hexane). The turbid reaction mixture was passed through a Büchner funnel to remove salts, and the salt mass was rinsed with THF and acetone. Solvent was removed from the filtered solution, producing a yellowish white mass. The solid was dissolved in methylene chloride, washed with water, dried again, and recrystallized from methanol. About 45 g of white, pure carbazole epoxide was obtained (85.0 % yield), which had a sharp melting point of 111°C was determined by DSC (30°C to 120°C at 10°C/min.). By HPLC (C-18 reverse phase column, 60/40 acetonitrile/water), the carbazole epoxide was 98.7 % pure. The 1H NMR spectrum had peaks at 2.57, 2.81, 3.34, 4.40, 4.62, 7.23, 7.49, and 8.10 ppm, with

expected integration ratios. The results of elemental analysis were 80.12 % carbon, 5.91 % hydrogen, 6.22 % nitrogen, and 7.54 % oxygen, which compared well with theoretical values 80.72 % carbon, 5.83 % hydrogen, 6.28 % nitrogen, and 7.17 % oxygen.

The molar ratio for this reaction was 1 mole carbazole: 7 mole epichlorohydrin: 2.5 moles KOH. These ratios were maintained for both small and scaled up reactions.

3.2.2 Carbazole-Phenoxy Intermediate

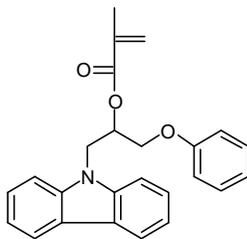


Carbazole-phenoxy intermediate
 $C_{21}H_{19}NO_2$
FW = 317 g/mole

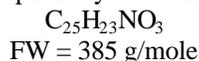
The carbazole-phenoxy based intermediate was produced by reacting 16.6 g (74.5 mmole) carbazole epoxide with 21 g phenol (224 mmole; 3-fold molar excess) (Aldrich, used as received), and 98 mg triphenylphosphine (372 μ mole) (Aldrich, used as received), neat, under nitrogen, at 120°C for 14 to 19 hours. Completion of reaction was monitored by TLC (25 % ether in hexane). The excess phenol was removed with good vacuum and slight heat. The final product was a slightly tan solid, which was pulverized into small pieces and vacuum dried further. The carbazole-phenol intermediate was obtained in 21.4 g (90.7 % yield). The 1H NMR spectrum had peaks at 2.42, 3.98, 4.52, 4.61, 6.85, 6.99, 7.28, 7.49, and 8.10 ppm, with expected integration ratios.

The molar ratio for this reaction was 1 mole carbazole epoxide: 2.5 moles phenol: 0.005 moles triphenylphosphine. These ratios were maintained for small and scaled up reactions.

3.2.3 Carbazole-Phenoxy Based Methacrylate



Carbazole-phenoxy based methacrylate

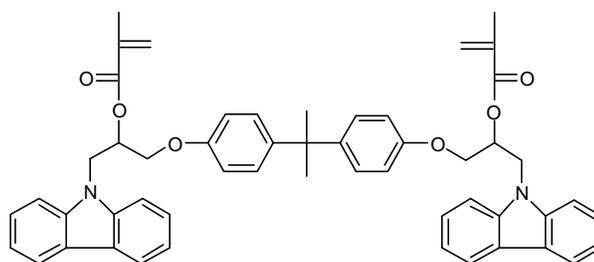


Carbazole-phenoxy based methacrylate was produced by dissolving 11.8 g (37.3 mmole) of the carbazole-phenoxy intermediate in 100 ml dry, distilled methylene chloride, in a 2-neck 250 ml round bottom flask equipped with a mechanical stirrer, nitrogen inlet, and rubber septum. The reaction flask was cooled in an ice/NaCl salt bath under nitrogen. 10.4 ml of triethylamine (TEA) (74.6 mmole, 2-fold molar excess) (Aldrich, used as received) was added by syringe. Methacrylic anhydride (11.12 ml, 174.6 mmole, 2-fold molar excess) (Aldrich, used as received) was added slowly, drop wise, maintaining temperature below 30°C throughout the addition. Methacryloyl chloride may also be used rather than methacrylic anhydride. Dimethylaminopyridine (DMAP) (1.86 mmole) (228 mg, Aldrich, used as received) was then added to catalyze the reaction. The reaction proceeded at room temperature for 3 to 4 hours. Completion of reaction was monitored by TLC (25 % ether in hexane). The contents of the reaction flask were washed with distilled, deionized (DD) water, dilute HCL, dilute NaHCO₃, then DD water. The solvent was removed from the organic layer, leaving a very viscous orange liquid. The product was recrystallized with methanol to afford 12.23 g of carbazole-phenoxy methacrylate (85.2 % yield). The final product was white, powdery material with no detectable odor. The carbazole-phenol based methacrylate was 100 % pure by HPLC (C-18 reverse phase column, 80/20 acetonitrile/water). The ¹H NMR spectrum had peaks at 1.89, 4.08, 4.65, 4.79, 5.61, 6.08, 6.92, 7.42, 7.58, and 8.08 ppm, with expected integration ratios. Two dimensional noise decoupled ¹H correlated spectroscopy (COSY) was used to help resolve peak assignments. A sharp melting point

of 92°C was determined by DSC (30°C to 120°C at 10°C/min). The results of elemental analysis were 77.31 % carbon, 6.07 % hydrogen, 3.57 % nitrogen, and 12.75 % oxygen, which compared well to theoretical values of 77.92 % carbon, 5.97 % hydrogen, 3.64 % nitrogen, and 12.47 % oxygen.

The molar ratio for this reaction was 1 mole carbazole-phenoxy intermediate: 2 moles methacrylic anhydride: 2 moles TEA: 0.05 mole DMAP. These ratios were maintained for small and scaled up reactions.

3.2.4 Carbazole-Bisphenol A Based Dimethacrylate



Carbazole-bisphenol A based dimethacrylate

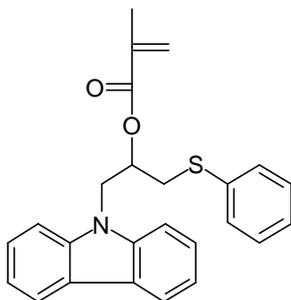
$C_{53}H_{50}N_2O_6$
FW = 810 g/mole

Carbazole-bisphenol A based dimethacrylate was produced by first synthesizing the carbazole-bisphenol A intermediate under conditions similar to the carbazole-phenoxy intermediate synthesis. Bisphenol A (Dow Chemical) was recrystallized from toluene. In the presence of triphenylphosphine catalyst, 20 g of carbazole epoxide (89.7 mmole) was reacted, neat, with 10.5 g bisphenol A (44.8 mmole), which was a ratio of two moles carbazole epoxide to one mole of bisphenol A. The carbazole-bisphenol A intermediate was obtained in 28.05 g (94.9 % yield), and was an orange, glassy, brittle material. The intermediate was reacted with a 3-fold molar excess of TEA and methacrylic anhydride, using the same reaction conditions and purification as for the carbazole-phenol based methacrylate. About 21 g of the carbazole-bisphenol A based dimethacrylate was obtained (72.7% yield), which was a tannish white material. By HPLC (C-18 reverse

phase column, 80/20 acetonitrile/water), the carbazole-bisphenol A based dimethacrylate was 100 % pure. The ^1H NMR spectrum had peaks at 4.08, 4.72, 5.62, 5.84, 6.13, 6.40, 6.85, 6.97, 7.23, 7.40, 7.55, and 8.11 ppm, with expected integration ratios. A sharp melting point of 65°C was determined using DSC (30°C to 120°C at $10^\circ\text{C}/\text{min}$). The results of elemental analysis were 77.86 % carbon, 6.26 % hydrogen, 3.20 % nitrogen, and 12.71 % oxygen, which compared well with theoretical values of 78.52 % carbon, 6.17 % hydrogen, 3.46 % nitrogen, and 11.85 % oxygen.

The molar ratio for the first reaction was 1 mole carbazole epoxide: 0.5 moles bisphenol A: 0.005 triphenylphosphine. The molar ratio for the second reaction was 1 mole carbazole-bisphenol A intermediate: 3.0 moles methacrylic anhydride: 3.0 moles TEA: 0.05 moles DMAP.

3.2.5 Carbazole-Benzene Thiol Based Methacrylate



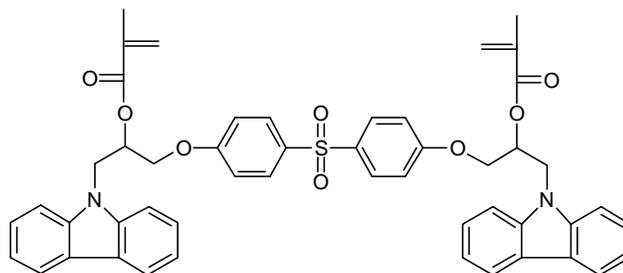
Carbazole-benzene thiol based methacrylate
 $\text{C}_{25}\text{H}_{23}\text{NO}_2\text{S}$
FW = 401 g/mole

Carbazole-benzene thiol based methacrylate was produced using synthetic methods similar to the carbazole-phenoxy based methacrylate. Carbazole epoxide (15 g, 67.3 mmole) was reacted, neat, with 20 g of benzene thiol (181.5 mmole, 2.7-fold molar excess), in the presence of triphenylphosphine catalyst. The carbazole-benzene thiol based intermediate was obtained in 13.54 g (60 % yield), and was a white, powdery material. To 10 g of the carbazole-benzene thiol based intermediate (30 mmole), a 2.5-fold molar excess of the TEA and methacrylic anhydride were added, with a catalytic

amount of DMAP. Because benzene thiol is fairly volatile and has a strong stench reminiscent of skunk oil, cold traps were placed in line, with respect to nitrogen flow, before and after the reaction. The carbazole-benzene thiol based methacrylate was obtained in 8.22 g (68.3 % yield), and was a white, powdery material. Purification of this material was similar to the carbazole-phenoxy based methacrylate, except that the product was suspended (rather than recrystallized) in hot methanol, then filtered, and dried. All glassware, including cold traps, were cleaned with bleach to remove stench. Solubility was an issue; this material was insoluble all common solvents, and could not be analyzed using HPLC nor NMR spectroscopy. From TLC (25 % acetone in hexane), both the intermediate and the final methacrylated product were observed to have one clean spot. The intermediate had an R_f of 0.47, and the product had an R_f of 0.55. A melting point of 114°C for the carbazole-benzene thiol based methacrylate was determined using DSC (30°C to 120°C at 10°C/min). The results of elemental analysis were 58.14 % carbon, 7.27 % hydrogen, 0.53 % nitrogen, 31.09 % oxygen, and 3.35 % sulfur, which compared with theoretical values of 74.81 % carbon, 5.74 % hydrogen, 3.49 % nitrogen, 7.98 % oxygen, and 7.98 % sulfur.

The molar ratio for the first reaction was 1 mole carbazole epoxide: 2.7 moles benzene thiol: 0.005 moles triphenylphosphine. The molar ratio for the second reaction was 1 mole carbazole-benzene thiol intermediate: 2.5 moles methacrylic anhydride: 2.5 moles TEA: 0.05 moles DMAP.

3.2.6 Carbazole-4,4'-Sulfonyldiphenol Based Dimethacrylate



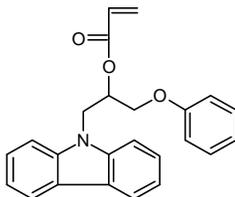
Carbazole-4,4'-sulfonyldiphenol based dimethacrylate
 $C_{50}H_{44}N_2O_8S$
FW = 832 g/mole

Carbazole-4,4'-sulfonyldiphenol based dimethacrylate was produced using synthetic methods similar to the carbazole-bisphenol A based dimethacrylate. In the presence of triphenylphosphine catalyst, an exact molar ratio of 2 moles carbazole epoxide were reacted, neat, with one mole of 4,4'-sulfonyldiphenol, to form the intermediate in a 70.5% yield. A 3-fold molar excess of TEA and methacrylic anhydride, with a catalytic amount of DMAP, was added the intermediate. The carbazole-sulfonyldiphenol based dimethacrylate was obtained in 10.2 g (85.2 % yield), and was a white, powdery material. Purification of this material was similar to the carbazole-bisphenol A based dimethacrylate, except that the product was suspended (rather than recrystallized) in hot methanol, then filtered, and dried. Solubility was an issue. This material was insoluble all common solvents, and was not analyzed using HPLC nor NMR spectroscopy. From TLC (25 % acetone in hexane), both the intermediate and the final methacrylated product had one clean spot. The intermediate had an R_f of 0.16, and the product had an R_f of 0.31. A melting point of 81°C for the carbazole-sulfonyl diphenol based dimethacrylate was determined using DSC (30°C to 120°C at 10°C/min). The results of elemental analysis were 63.53 % carbon, 5.26 % hydrogen, 2.87 % nitrogen, 16.89 % oxygen, and 3.10 % sulfur, which compared with theoretical values of 72.11 % carbon, 5.29 % hydrogen, 3.37 % nitrogen, 15.38 % oxygen, and 3.85 % sulfur.

The molar ratio for the first reaction was 1 mole carbazole epoxide: 0.5 moles sulfonyldiphenol: 0.005 moles triphenylphosphine. The molar ratio for the second

reaction was 1 mole carbazole-sulfonyldiphenol intermediate: 3 moles methacrylic anhydride: 3 moles TEA: 0.10 moles DMAP.

3.2.7 Carbazole-Phenoxy Based Acrylate



Carbazole-phenoxy based acrylate

$C_{24}H_{21}O_3N$
FW = 371 g/mole

Carbazole-phenoxy based acrylate was synthesized in an analogous fashion as the carbazole-phenoxy based methacrylate, except that acryloyl chloride was added to the carbazole-phenoxy based intermediate, instead of methacryloyl chloride or methacrylic anhydride. Carbazole epoxide (10 g, 31.5 mmole) was dissolved in 30 mL dry, distilled methylene chloride, in a 2-neck 250 ml round bottom flask equipped with a mechanical stirrer, nitrogen inlet, and rubber septum. The reaction flask was cooled in an ice/NaCl salt bath under nitrogen. TEA (8.8 mL, 63 mmole) (Aldrich, used as received) was added by syringe. Acryloyl chloride (5.38 mL, 66 mmole) (Aldrich, used as received) was added extremely slowly to the chilled reaction mixture, because the acrylating reaction produced a strong exothermic reaction. DMAP (193 mg, 1.58 mmole) was added to the reaction mix. Immediately after the addition of the acryloyl chloride, the reaction mixture turned a bright lemon yellow color. The reaction proceeded for 3 hours at room temperature. Completion of reaction was monitored by TLC (25 % ether in hexane). Vacuum, with double traps including a base trap, was used to remove solvent and excess volatile reagents. After precipitating the monomer in chilled methanol/water mixture (50/50), filtering, and vacuum drying, the carbazole-phenoxy based acrylate was a whitish, gummy solid with a slight yellow color (56.0 % yield). From TLC (25 % acetone in hexane), both the intermediate and the final acrylate product had one clean spot. The intermediate had an R_f of 0.16, and the product had an R_f of 0.45. A melting

point of 78°C for the carbazole-phenoxy based acrylate was determined using DSC (30°C to 120°C at 10°C/min). The results of elemental analysis were 70.92 % carbon, 5.68 % hydrogen, 3.14 % nitrogen, and 15.67 % oxygen, which compared with theoretical values of 77.62 % carbon, 5.66 % hydrogen, 3.77 % nitrogen, and 12.94 % oxygen.

The molar ratio for the acrylate reaction was 1 mole carbazole-phenoxy intermediate: 2 moles acryloyl chloride: 2 moles TEA: 0.05 mole DMAP.

3.3 Novel Carbazole Containing Homopolymers and Copolymers

The carbazole-phenoxy based methacrylate polymerization was investigated using four different techniques; UV photo-polymerization, solution free radical polymerization, free radical polymerization in the melt, and modified suspension free radical polymerization. All polymerization solvents were vacuum purged, then well purged with nitrogen, several times, or distilled under nitrogen.

Carbazole based dimethacrylate polymer and copolymer films were produced by photopolymerization. Copolymers of carbazole-phenoxy based methacrylate and methyl methacrylate were produced by photopolymerization and solution polymerization.

A Perkin-Elmer, Model 200 GPC (HT 2+4+5 column, 0.02 M P₂O₅ in NMP) was used to analyze the linear polymers. FTIR, ¹H NMR, ¹³C NMR, DSC, and TGA were used to analyze the polymers. Refractive index and birefringence was determined on films using a Metricon Prism Coupler, Model 2010. Birefringence was observed using a Nikon Optiphot-Pol Polarizing Microscope, with a first order red-line (530 nm) filter. Refractive index was not determined on the sulfur containing methacrylates and dimethacrylates, because these polymers were very insoluble and powdery, and did not make good films.

3.3.1 Photopolymerization

Carbazole based methacrylate and dimethacrylate polymer films were produced by photo-induced polymerizations using UV irradiation (300 - 450 nm) with a suitable photo-initiator, such as 1-hydroxycyclohexyl phenyl ketone (Irgacure 184TM, Ciba Specialty Chemicals, used as received). Typically, 2 mole percent of photo-initiator was mixed with 1 to 3 g of methacrylated monomer, or mixtures of monomers, then dissolved in 2 to 5 mL of nitrogen purged DMF or DMAC. Films were cured in a custom built, mercury bulb, UV oven for 60 minutes. Copolymers of carbazole-phenoxy based methacrylate and methyl methacrylate were also produced using photopolymerization. Methyl methacrylate (Aldrich) was prepared by passing through either a basic alumina column or an inhibitor removal column (Aldrich).

3.3.1.1 Photo-DSC

Modified crimped DSC pans were used for all photo-DSC experiments, without lids. To prevent volatiles from escaping, small quartz windows with a diameter of 7.0 mm, which was slightly larger than the pans yet smaller than the diameter of the sample holder for the pans, were placed on top of the sample and reference pans. The photo-DSC experiments were performed isothermally at 30°C, using a UV wavelength of 350 nm. A small quantity, 10 μ L of 0.826 M carbazole-phenoxy based methacrylate in DMF, with 2 mole % Irgacure 184TM, was placed in the sample using a micropipette. The first 3 minutes of the experiment kept the shutter closed. At 3 minutes, the shutter was opened, irradiating both the sample pan and empty reference pan with 350 nm UV light. The shutter was closed again at 30 minutes (so irradiation time for 27 minutes). A background sample was needed to take into account the absorption of the carbazole and phenoxy substituents. The experiment was repeated with 10 μ L of 0.826 M, with respect to repeat units, of polymerized carbazole-phenoxy based methacrylate in DMF. The DSC thermogram of the polymer was subtracted from the analogous DSC thermogram of the monomer. The corrected ΔH for the carbazole-phenoxy based methacrylate obtained was -382.907 mJ/mole, which converted to -39.4 kJ/mole.

3.3.2 Solution Polymerization

Polymers of carbazole-phenoxy based methacrylate were polymerized in nitrogen purged DMAC. Typically, several grams of monomer were mixed with 1 or 2 mole % of AIBN. Enough DMAC was added to dissolve the monomer, typically 5 to 10 mL of nitrogen purged DMAC. The polymerization was performed with rapid stirring in a round bottom flask equipped with a nitrogen inlet between 85 to 95°C (hot water bath), for 2 hours. The polymerization was allowed to cool slowly to room temperature. Some solution polymerizations were also performed in nitrogen purged DMF, with similar results.

Copolymers of carbazole-phenoxy based methacrylate and methyl methacrylate were also produced, in 25/75, 50/50, 72/25 mole % and weight % ratios. Polymer films were produced by solvent casting from chloroform or methylene chloride, with a 30 weight percent polymer to solvent ratio. Films were dried slowly, then vacuum dried at temperatures slightly above their respective glass transition temperatures.

The carbazole-phenoxy based acrylate was solution polymerized in an analogous fashion (1 mole % AIBN, DMAC, 90°C, under nitrogen for 2 hours). Carbazole-phenoxy based acrylate polymer films were solvent cast from methylene chloride, with a 30 weight percent polymer to solvent ratio.

3.3.2.1 *In situ* FTIR Solution Polymerization

In situ FTIR was used to follow the free radical, solution polymerization of the carbazole-phenoxy based methacrylate. To the reaction flask, 9 g of carbazole-phenoxy based methacrylate (23.4 mmole) was mixed with 76.8 mg AIBN (468 μ mole, 2 mole %), and dissolved in 30 mL nitrogen purged DMAC (30 weight % solids). The reaction was performed at 90 to 91°C (hot oil bath), under nitrogen, for 90 minutes. From the *in situ* FTIR experiment, the solution free radical polymerization was completed within 40 minutes.

3.3.3 Melt Polymerization

A small amount (1 g, 26.0 mmole) of carbazole-phenoxy based methacrylate was mixed with 9.5 μ L (52 μ mole, 2 mole %) t-butyl peroxide (Aldrich, used as received), and heated to 118°C, neat, under nitrogen, for less than 10 minutes. The mixture melted quickly, then became very viscous and impossible to stir within minutes. The resulting polymer was insoluble in common solvents, including NMP at 60°C, and was probably cross-linked, via undetermined free radical side chain processes.

3.3.4 Modified Suspension Polymerization

A small amount of polyvinyl alcohol (41.3 mg, Aldrich, $M_n = 85,000 - 146,000$, 87 to 89 % hydrolyzed) was dissolved in 15 mL oxygen free water. Then 2.98 g carbazole-phenoxy based methacrylate (7.74 mmole) was dissolved in 10 mL oxygen free toluene, followed by 21.5 mg benzoyl peroxide (88.7 mmole, 1 mole %) (Aldrich, used as received) was added to the organic solution. The monomer/initiator/toluene phase was added to the aqueous phase, with rapid stirring, under nitrogen. The polymerization proceeded at 90 to 98°C with rapid stirring for over 14 hours, with aliquots taken periodically. The polymer produced was difficult to solubilize into common solvents, and had a high molecular weight ($\langle M_n \rangle = 158,500$ g/mole), with a high polydispersity ($\langle M_w \rangle / \langle M_n \rangle = 8.13$), probably because of branching and partial cross-linking.