Poly(aryl ether-azines)

Kenneth R. Carter* and James L. Hedrick

IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099

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Introduction

Polyazines and polymers containing the azino functionality, -(H)C=NN=C(H)-, represent an interesting class of materials. The first reported polyazines were reported in 1950 and were obtained as the condensation product from the reaction of dialdehydes or diketones with hydrazine.[1] In these reactions the azino group was generated as the polymer-forming reaction. A review of polyazines produced in this manner showed that they were generally crystalline, intractable solids with molecular weights ranging from 500 to 1000.[2] One reason for the poor properties of these systems was the low solubility of the condensation products in the reaction medium, resulting in low molecular weight. Polyazines with improved solubility had been achieved, to a limited extent, by incorporating long-chain alkyl groups into monomer precursors. This was shown to yield soluble polyazines, but the molecular weight (i.e., the degree of polymerization) of these materials was still quite low.[3] Alternatively, the azino functionality can be incorporated into a polymer system, preformed, as one of the monomers. Goldberry et al. reported the melt condsenation of hydroxy-substituted phenyl azines and dianilinodiphenylsilane, yielding soluble poly(diphenylsiloxy)aryl azines with molecular weights as high as 38 000.[4] Recent work by Weiss and co-workers showed that hydroxy-substituted phenyl azines could likewise be reacted with acid chloride and dibromoalkanes to give azine-polyesters[5] and azine-ethers,[6] the later materials being insoluble in common organic solvents.

It has been demonstrated that the introduction of aryl ether linkages can improve the solubility of a number of otherwise insoluble polymer systems such as imides,[7] phenylquinoxalines,[8] benzoxazoles,[9] and triazoles[10,11] to name but a few. In these polymerizations the aryl ether linkage is created in the polymer-forming reaction while the heterocycle is incorporated as one of the monomers, either a bisphenol or an activated halide. Conventionally, the activating groups for these nucleophilic aromatic substitution reactions have been electron-withdrawing substituents such as ketones, sulfones,[12] and phosphine oxides.[13] Our research group has been exploring the use of alternative activating groups such as heterocyclic rings in these types of reactions.[14,15] It has also been observed that other functional groups meet the criteria for activation of aryl fluorides, such as the azino group.[16] We now report the successful incorporation of an azino group into a poly(aryl ether) system via nucleophilic aromatic substitution polymerization, yielding new poly(aryl ether-azines).

Experimental Section

Materials. The monomers, 1,4-bis(4'-fluorophenyl)-2,3-diaza-1,3-butadiene (1) and 1,4-bis(4'-hydroxyphenyl)-2,3-diaza-1,3-butadiene (2), were prepared by previously described methods.[10,17] 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone(*N*,*N*'-dimethylpropyleneurea, DMPU; Aldrich) was vacuum distilled over calcium hydride. The monomer 2,2-bis(4'-hydroxyphenyl)-propane (Bisphenol A, **4a**; Aldrich), was recrystallized from toluene, and 2,2-bis(4'-hydroxyphenyl)hexafluoropropane (Bisphenol AF, **4b**; Aldrich) was purified by recrystallization from toluene/ethyl acetate (95:5). 4,4'-Difluorobenzophenone (**4d**) and 4,4'-difluorophenyl sulfone (**4e**) were recrystallized from toluene. All other materials were commercially available and used as received unless otherwise noted.

Analyses and Instrumentation. NMR spectra were recorded on either a IBM WP 250 spectrometer operating at 250.1 MHz (^{1}H) or a IBM WP 300 spectrometer operating at 282.3 MHz (^{19}F). Tetramethylsilane (Me_4Si) was used as a reference for ^{1}H measurements, while $CFCl_3$ was used as an internal standard for the ^{19}F NMR measurements, with the reference peaks being assigned at 0.0 ppm. Chemical shifts upfield of the reference are assigned a negative sign and are reported in ppm, while the coupling constants are reported in hertz. Elemental analysis and mass spectra were performed by Oneida Research Services. Glass transition temperatures, taken as the midpoint of the change in slope of the base line, were measured on a DuPont DSC 1090 instrument at a heating rate of 10 °C/min. Thermal gravimetric analyses (TGA) on the polymer samples were conducted at a heating rate of 10 °C/min in a nitrogen atmosphere. Intrinsic viscosity measurements were determined by using a Cannon-Ubbelohde dilution viscometer in *N*-methyl-2-pyrrolidinone (NMP; 25 °C). Gel permeation chromatography (GPC) was performed utilizing a Waters 150-C fitted with a Polymer Labs 10-μm column using THF as eluent. GPC molecular weights are reported versus polystyrene standards.

1,4-Bis[4'-(4-methylphenoxy)phenyl]-2,3-diaza-1,3-butadiene (3). A 15-mL, three-necked flask equipped with a nitrogen inlet, mechanical stirrer, and Dean-Stark trap fitted with a condenser was charged with 1.12 g (4.57 mmol) of **1** and 0.99 (9.15 mmol) of *p*-cresol. The reactants were carefully washed into the flask with 8.0 mL of DMPU. An excess of K_2CO_3 (2.85 g, 20.6 mmol) and approximately 6 mL of dry toluene were added. The reaction mixture was heated to 145 °C, at which point the toluene began to reflux. Collected toluene was removed from the Dean-Stark trap, and more deoxygenated toluene was periodically added and then subsequently collected and drained from the trap. The reaction mixture was maintained at this temperature for 4-6 h to ensure complete dehydration of the system. The temperature was increased to 170 °C, and the mixture was allowed to react for approximately 15 h. The reaction mixture was extracted into CH_2Cl_2, washed (3×) with water, filtered, dried, and recrystallized from hexane/ethyl acetate to yield 500 mg of yellow crystals of **3**. HPLC analysis of the crude reaction mixture showed complete conversion to product with no other peaks present in the chromatogram: mp 198-199 °C; ^{1}H NMR ($CDCl_3$) δ 8.63 (s, 2H), 7.78 (d, 4H), 7.18 (d, 4H), 6.99 (m, 8H), 2.37 (s, 6H). Anal. Calcd for $C_{28}H_{24}N_2O_2$: C, 79.97; H, 5.75; N, 6.66. Found: C, 78.76; H, 5.55; N, 6.49.

Polymer Synthesis. The various poly(aryl ether) syntheses were conducted in a manner similar to that described here for the poly(aryl ether) derived from **1** and Bisphenol A, **4a**. A 15-mL, three-necked flask equipped with a nitrogen inlet, mechanical stirrer, and Dean-Stark trap fitted with a condenser was charged with 0.8826 g (3.614 mmol) of **1** and 0.8246 (3.612 mmol) of **4a**. The monomers were carefully washed into the flask with 8.0 mL of DMPU. An excess of K_2CO_3 (2.00 g, 14.4 mmol) and approximately 6 mL of dry toluene were added. The reaction mixture was heated to 145 °C, at which point the toluene began to reflux. Collected toluene was removed from the Dean-Stark trap, and more deoxygenated toluene was periodically added and then subsequently collected and drained from the trap. The reaction mixture was maintained at this temperature for 4-6 h to ensure complete dehydration of the system. The temperature was increased to 180 °C, and the mixture was allowed to react for approximately 35 h. Completion or near completion was qualitatively estimated by the point where the reaction mixture viscosity increased dramatically. The polymer was precipitated into 500 mL of a methanol/water (1:1) solution, followed with vigorous stirring prior to filtering. The precipitated polymer, **5a**, was washed several times with methanol and vacuum dried to constant weight, 1.22 g (>99% yield). The yields were essentially quantitative for all of the polymerizations.

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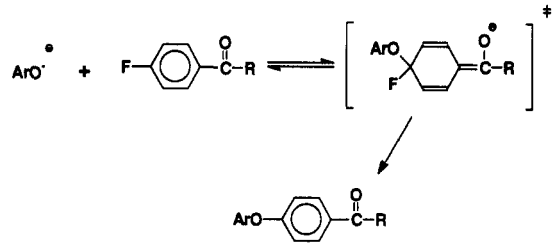
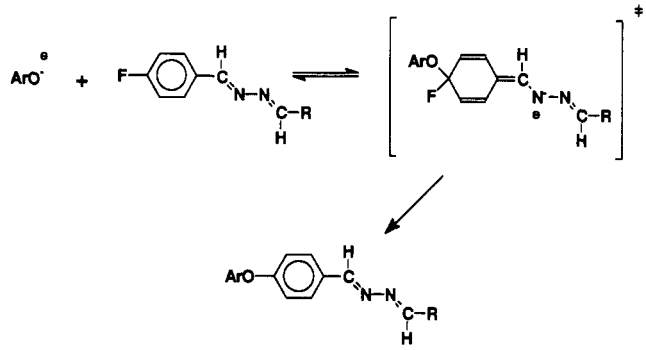
Scheme 1

Ketone activation



Azine activation

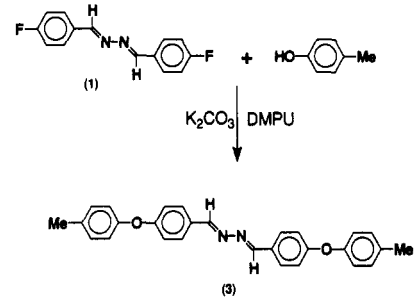


Results and Discussion

In nucleophilic aromatic substitution reactions an aryl halide (fluorides are more reactive than chlorides) is activated by an electron-withdrawing group (conventionally either a ketone or sulfone group) toward substitution by an anionic phenoxide nucleophile (Scheme 1). This activating group serves two purposes. First, the electron-withdrawing group decreases the electron density at the site of substitution and second, it lowers the energy of the transition state for the reaction by stabilizing the anionic intermediate. In this work, it was anticipated that the azino functional group would activate the aromatic ring toward substitution by functioning both as an electron-withdrawing substituent and as a stabilizing substituent for the anionic intermediate. NMR is a valuable tool for evaluating the electron-withdrawing effect of substituents in potential monomers. Fluorine nuclei (^{19}F) have proven to have been the most sensitive NMR probes of reactivity with a chemical shift range spanning 9 ppm (2500 Hz) between highly activated monomers (e.g., fluorophenyl sulfones ≈ -104 ppm) and nonactivated aryl fluorides (e.g., fluorobenzene ≈ -113 ppm). The magnitude of these ^{19}F NMR chemical shifts has been found to correlate with the actual reactivity of the monomers.[18] The ^{19}F shifts of the azine monomer were found to be in the range of other activated systems (-108 ppm), so it was anticipated that this monomer might be a good candidate for nucleophilic aromatic substitution polymerization with conventional bisphenols. It was also hoped that the azino group could also be incorporated by reacting the bis(hydroxy) azine monomer with conventional activated fluorides to give new poly(aryl ether–azines).

To survey the utility of the difluoro azine monomer in a nucleophilic substitution reaction, a model reaction between **1** and *p*-cresol was performed (Scheme 2). Both reactants were added in equimolar proportions and heated to 170 °C for 16 h in the presence of 100% molar excess of anhydrous K_2CO_3 in dimethylpropyleneurea (DMPU), with toluene being used in the early stages of the reaction to azeotropically dehydrate the system. The reaction led quantitatively to the formation of a single product identified as 1,4-bis[4′-(4-methylphenoxy)phenyl]-2,3-diaza-1,3-butadiene (**3**).

Scheme 2



Scheme 3

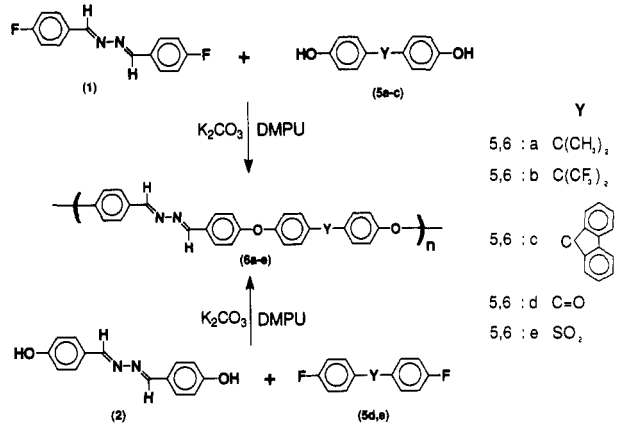


Table 1. Properties of Poly(aryl ethers–azines)

polymer	M_w[a] (°C)	[η] (dL/g)	T_g
5a	28 000	0.34	163
5b	14 000	0.14	162
5c	32 000	0.62	227
5d	*b*	*b*	179
5e	14 000	0.10	151

[a] GPC in THF. [b] Polymer precipitated from solution and did not redissolve.

Polymerizations of **1** with Bisphenol A (**4a**), Bisphenol AF (**4b**), and Bisphenol F (**4c**) led to the formation of the corresponding polymers **5a–c** (Scheme 3). The polymerizations were performed under the same conditions as the model reaction. The polymers were coagulated in a 1:1 methanol/water solution, and a small amount of glacial acetic acid was added to neutralize any unreacted end groups. The polymers were filtered and vacuum dried. The bis(hydroxy) monomer, **2**, was similarly polymerized with difluorobenzophenone (**4d**) and difluorophenyl sulfone (**4e**), yielding polymers **5d** and **5e**, respectively.

The glass transition temperatures of the polymers ranged from 151 to 227 °C, with the T_g of **5c** being the highest (Table 1). The high T_g of **5c** is consistent with the high T_g's observed with other poly(aryl ethers) which incorporate the fluorene-based monomer, Bisphenol F (**4c**). All of the polymers were thermally stable to about 300 °C, at which point it is known that the azino functionality undergoes thermal decomposition.[19] The polymer molecular weights were measured by GPC and ranged from 14 000 to 32 000. Polymer **5c**, derived from **1** and the fluorene Bisphenol F (**4c**), had the highest measured molecular weight and a measured intrinsic viscosity of 0.62 dL/g. The poly(aryl ether–azines) were soluble in a variety of organic solvents (e.g., chloroform, NMP, etc.) and could be solvent processed into thin films.

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