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Synthesis and characterization of poly(arylene ether sulfone)s with pendant amines on the main chain

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Summary

Synthesis of poly(arylene ether sulfone)s with random incorporation of pendant aryl amines was achieved by copolymerization of dichlorodiphenylsulfone (DCDPS) and bisphenol-A with bis(4-fluorophenyl)-3-aminophenylphosphine oxide (amino DFTPPO) with N-methylpyrrolidone (NMP) as the solvent, toluene as the azeotrope and potassium carbonate (K_2CO_3) as the weak base. A unique feature of this polymerization is that one of the comonomer (amino DFTPPO) contains both an amine functionality as well as activated dihalides which can undergo aromatic nucleophilic displacement by the phenolate, the degree of amination on the main chain can be controlled very precisely by regulating the amount of the amino DFTPPO monomer relative to the other activated dihalide monomer (DCDPS) and bisphenol-A. The synthesis and characterization of poly(arylene ether sulfone)s with various concentration of amine groups on the backbone will be discussed in this paper.

Introduction

In the area of poly(arylene ether)s, amine terminated poly(arylene ether sulfone)s have been demonstrated to toughen brittle epoxy networks and the amine terminated poly(arylene ether sulfone)s have also been chemically modified to maleimides which under proper conditions can either be thermally or microwave induced to undergo chain extension or crosslinking reactions to afford crosslinked networks.(1-4). The synthesis of amine terminated poly(arylene ether sulfone)s involves the addition of a monofunctional encapper such as m-aminophenol.(5) Various molecular weights of amine terminated poly(arylene ether sulfone)s can be synthesized by using the Carothers equation which determines the amount of monofunctional encapper that is needed to obtain the desired molecular weight. As the concentration of the monofunctional encapper increases, the molecular weight decreases, if the concentration of the monofunctional encapper decreases, the molecular weight increases. With this approach, due to the amine groups being only on the polymer chain ends, there is an inverse relationship between the concentration of amines and the molecular weight. Therefore, the synthesis of high molecular weight poly(arylene ether sulfone)s with high concentration of amine groups is not possible

Recently, Naik et al. (6) reported on the synthesis and the characterization of amination on the main chain of a copolymer of poly(ether sulfone) (PES) and poly(ether ether sulfone) (PEES) which was aminated by nitrating the hydroquinone unit of the repeat unit. The nitro groups were reduced to amines to afford amination on the main chain. The synthesis of pendant amines on poly(ether ether ketone)s has also been investigated in our laboratories by reacting a small mole percentage of 4,4'-difluoro(N-benzohydryl-p-amino aniline) with difluorobenzophenone (DFB) and

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hydroquinone(7). The pendant amines reacted with the carbonyls on the polymer backbone and resulted in the generation of relatively stable ketimine crosslinks when the pendant amines on poly(ether ether ketone)s were thermally cured.

This paper describes recent investigations on the incorporation of pendant amines on the backbone of poly(arylene ether sulfone)s. Our efforts have been directed toward monomers that have the amine functionality, as well as activated dihalides which can undergo polymerization to afford a poly(arylene ether sulfone) backbone, with the incorporation of the pendant amines. Polymerization incorporating various mole percentage of the pendant amine monomer resulted in polymers with a predictable amination along the polymer backbone. In contrast to amine terminated polysulfones, the pendant amines are no longer restricted to be only on polymer chain ends. Therefore, the concentration of amines can be controlled independently of the molecular weight by varying the amount of the amine containing monomer relative to the other comonomers. The synthesis and characterization of poly(arylene ether sulfone)s with various concentration of amine groups on the polymer backbone were investigated by this novel approach.

Experimental

Materials: Monomer grade 4,4'-dichlorodiphenylsulfone (DCDPS) was provided by Amoco and was used without further purification. Bisphenol-A was provided by Dow Chemical in a monomer grade and was also used as received. However, both the DCDPS and bisphenol-A were dried in a vacuum oven at 80°C for 24 hours prior to being used. Bis (4-fluorophenyl) phenylphosphine oxide (DFTPPO) was synthesized according to the procedure reported in the literature (8) and was purified by distillation. N-methyl pyrrolidone (NMP) (Fisher) was vacuum distilled from calcium hydride. Anhydrous potassium carbonate (Fisher), toluene (J.T. Baker), tin chloride dihydrate (Aldrich), and deuterated chloroform (Isotech Inc.) were all used as received.

Synthesis of bis(4-fluorophenyl)-3-nitrophenylphosphine oxide (Nitro DFTPPO) To a 500ml four neck round bottom flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, and an addition funnel was added 22.79g (0.0725 moles) of DFTPPO and 200ml H_2SO_4. The contents in the flask were stirred at room temperature until a homogeneous solution was obtained. Then the flask was immersed in a ice water bath until the temperature inside the flask reached approximately 5°C. At this point, a solution of 7.51g (0.0834 moles) of HNO_3 and 28 ml H_2SO_4 in an addition funnel was introduced dropwise. When the addition was completed, the ice water bath was removed and the contents inside the flask was stirred for another two hours. After 2 hours, the reaction mixture was slowly poured into 3000ml of water and ice. The precipitate was filtered and washed with a copious amount of water. It was then dissolved in chloroform and washed with water two times, once with a solution of sodium bicarbonate, and then finally with a saturated sodium chloride solution. The chloroform layer was separated and dried with magnesium sulfate and removal of the chloroform resulted in approximately 90% yield of the crude product which was a yellow material with a melting point of 146-148°C. This material was used for the next synthesis shown below without further purification.

Synthesis of bis(4-fluorophenyl)-3-aminophenylphosphine oxide (Amino DFTPPO) Reduction of the nitro DFTPPO was carried out in 95% ethanol with tin chloride dihydrate and hydrochloric acid. To a 1000 ml four neck round bottom flask equipped with a nitrogen inlet, mechanical stirrer, condenser, and a thermometer was added 21.42g (0.0596 moles) of nitro DFTPPO and 306ml of ethanol. A heating mantle was used to induce a gentle reflux of the ethanol. Then, tin chloride dihydrate and the HCl were added in three portions 18g (0.0798 moles) of tin chloride dihydrate and 33ml (0.3690 moles) of HCl in each addition. After the third addition, the solution was refluxed for another two hours. The heating mantle was then removed and the solution was cooled to room temperature. The solution was transferred to a round bottom flask and the ethanol was removed under reduced pressure. The resulting solution was made alkaline using a solution of sodium hydroxide. The alkaline solution was poured into 3000ml of water and ice. The resulting solid was filtered and washed with a copious amount of water and dried in a vacuum oven at 60°C overnight. After drying, 15.37g (0.0467 moles) of the product was obtained, a yield of 78%. The product was purified by vacuum distillation and the melting point of the resulting material was 157-159°C. ^{1}H-NMR (chloroform-d, ppm) 7.61(m, 4H, ortho to P=O), 7.08(m, 5H, four ortho to fluorine and one para to amine), 7.05(d, 1H, meta to amine and P=O), 6.90(m, 2H, ortho to amine), 4.00(s, 2H, amine). IR (KBr pellet, cm-1) NH_2 (3319, 3219), Ar-H (3056), aromatic C=C (1594, 1500), P-Aromatic carbon (1434), P=O (1187), Aromatic carbon-F (1162). Titration of the amine group yielded an average value of 327g/mole (theoretical 329g/mole) after three titrations.

Synthesis of pendant amino polysulfones To a four neck round bottom flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, and a dean stark trap with a condenser was added the monomers that were carefully weighed on a teflon coated weighing pans. For the synthesis of a high molecular weight polysulfone with a 10% incorporation of amino DFTPPO monomer, 10g (0.0438 moles) of bisphenol-A, 11.3218g (0.0394 moles) dichlorodiphenyl sulfone, 1.4424g (0.0044 moles) amino DFTPPO were transferred to the reaction flask along with 6.9627g (0.0504 moles) of K_2CO_3 under a constant purge of nitrogen. A total of 114 ml of NMP and 57 ml of toluene was added. Initially, the polymerization was conducted at 145°C for approximately four hours to azeotrope off the water. Then the temperature was raised to 165°C for an additional sixteen hours. The viscous brown solution was then filtered and coagulated into a large excess (5-10 times) of methanol and water (80:20). The polymer was filtered and washed with more methanol and dried in a vacuum oven at 80°C for 24 hours. The dried polymer was redissolved in chloroform and coagulated into excess methanol and dried in a vacuum oven at 80°C.

Nuclear Magnetic Resonance (NMR) The proton NMR spectra was obtained using a Varian Unity 400 MHz instrument. The samples were dissolved in chloroform that contained 0.05% tetramethylsilane (TMS) and all of the peaks were referenced relative to TMS peak at 0 ppm.

Differential Scanning Calorimetry Measurements were made using a Perkin Elmer DSC-7 with a heating rate of 10°C/min. The sample sizes were in the range of 10-20 mg.

Thermogravimetric Analysis Measurements were made using a Perkin Elmer Thermogravimetric Analyzer TGA-7 with a heating rate of 10°C/min in air.

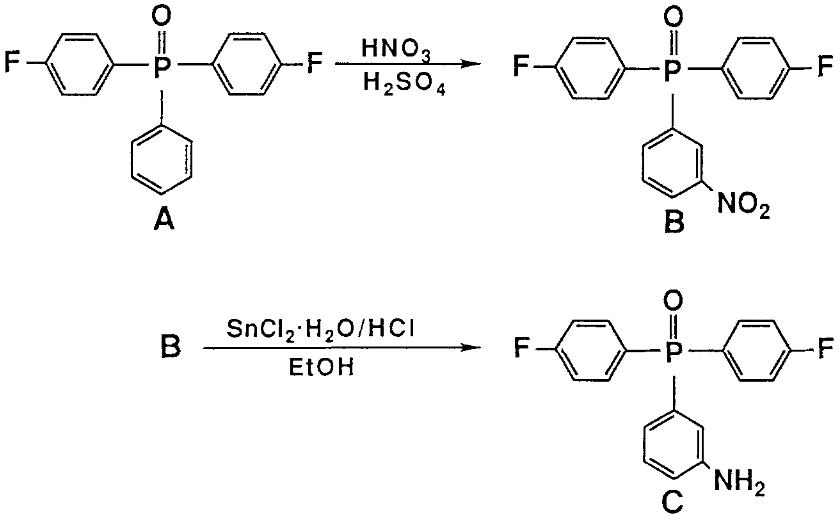
Gel Permeation Chromatography (GPC) GPC's were performed using Waters 150-C ALC/GPC with a differential refractive index and viscosity detectors. The concentration was 3 mg/ml in NMP. The Permagel columns in the range of 100Å to 10^6 Å were used as the separation system with a flow rate of 1 ml/min. at 60°C.

Intrinsic Viscosities Intrinsic viscosities were measured at 25°C in Ubbelohde viscometers with chloroform as the solvent.

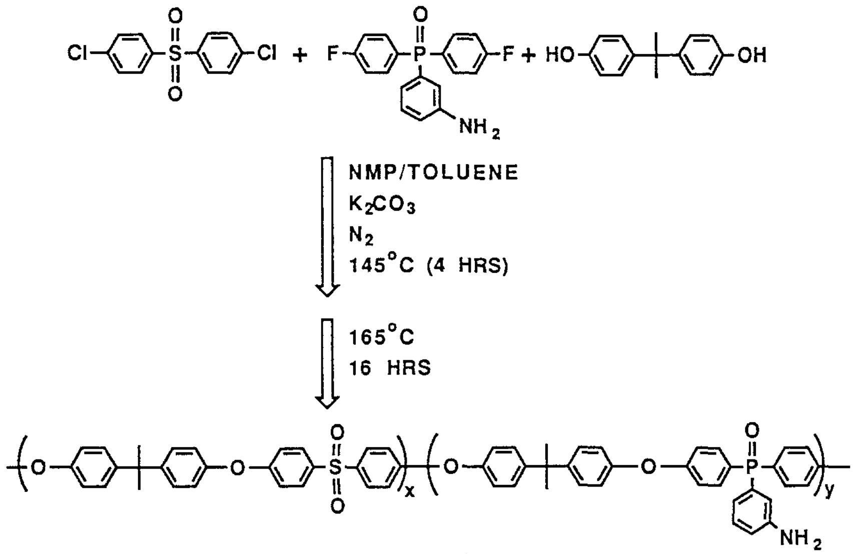
Titration Potentiometric titrations for aromatic amines on both the monomer and polymers were performed using an MCI GT-05 automatic titrator. Samples were dissolved in 60 ml chloroform and 10 ml acetic acid and then titrated with HBr (0.025N) in acetic acid as the titrant.

Results and Discussion

Functionalization of poly(arylene ether sulfone)s, particularly, amination on the main chain was accomplished by copolymerizing bis(4-fluorophenyl)-3-amino phenyl phosphine oxide (amino DFTPPO) with DCDPS and bisphenol-A. A unique feature of this polymerization stems from the fact that amine groups are no longer restricted to be only on polymer chain ends. Instead, a random statistical distribution of amine groups incorporated on the polymer chains, whereby, the average molecular weight between he amines can be obtained by the titration of those amines. The synthesis of amino DFTPPO is shown is Scheme 1.



Scheme 1 The Synthesis of Bis(4-fluorophenyl)-3-Aminophenylphosphine Oxide



Scheme 2 Synthesis of Pendant Amine Containing Poly(Arylene Ether Sulfone) Copolymers

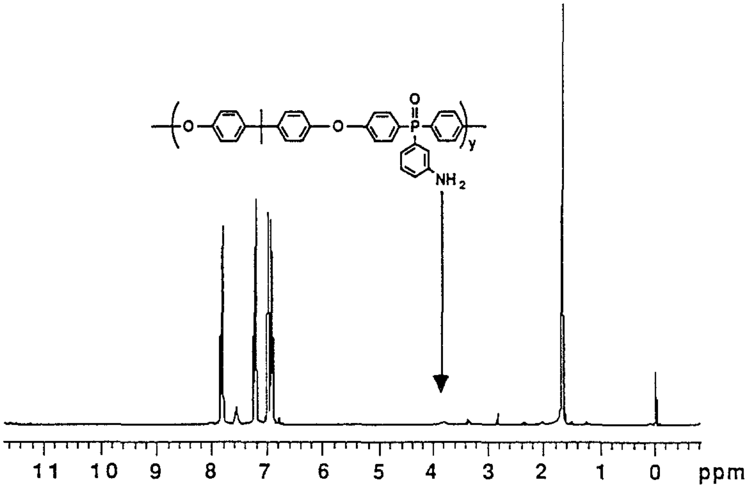


Figure 2 Proton NMR Spectra of 15 mole% Pendant Amino DFTPPO Incorporated Polysulfone

The starting material bis (4-fluorophenyl) phenylphosphine oxide (DFTPPO) was synthesized using grignard chemistry according to literature and was purified by distillation. Nitration of DFTPPO results predominately on the meta position to the phosphine oxide on the pendant phenyl ring. This is due to the presence of phosphine oxide and the resonance effect it has on the pendant phenyl ring. On the adjacent two phenyl rings, the presence of fluorine atoms on the para positions to the phosphine oxide deactivates electrophilic aromatic substitution on the unsubstituted positions on the aromatic rings and nitration on the adjacent phenyl rings is very unfavorable and unlikely. Conversion of the nitro groups to the corresponding amines were conducted according to the conditions shown in Scheme 1. The resulting monomer was purified by successive distillations. The proton NMR of amino DFTPPO is shown in Figure 1.

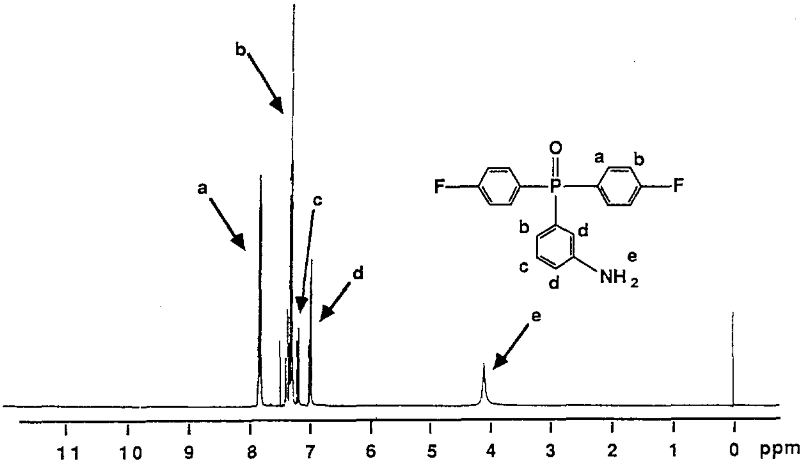


Figure 1 Proton NMR Spectra of Amino DFTPPO

The splitting of the aromatic protons with the phosphorus results in multiplets. The broad singlet at 3.9 ppm is from the amine and the ratio of the peak integrations of the amine peak to the aromatics was 6.7 as compared to the theoretical value of 6.0. Another method for the characterization of the monomer was titration. When the monomer was titrated for amines a molecular weight of 327 g/mol (average from three titrations) was obtained as compared to the theoretical vlaue of 329 g/mol.

The copolymerizations of amino DFTPPO with DCDPS and bisphenol-A were conducted according to Scheme 2. The polymerizations were conducted to obtain high molecular weight polymers and 1:1 ratio of the activated dihalide monomers to bisphenol-A was used. However, the concentration of amino groups incorporated were varied. Shown in Figure 2 is a proton NMR of 15 mole% of amino DFTPPO monomer incorporated into poly(arylene ether sulfone), the peak from the pendant amines can be observed at 3.9 ppm as well as the peaks in the aromatic region from the amino DFTPPO monomer. The polymers were also titrated for the amines and titration results along with other characterizations are shown in Table 1.

Table 1 Characterizations of Pendant Amine Containing Poly(Arylene Ether Sulfone) Copolymers

Amino DFTPPO	Amine Titration	$[\eta]^{25^\circ C}_{CHCl_3}$	$<Mn>^{(1)}$	Tg
mole%	mole%	(dl/g)	(g/mole)	(°C)
0	----	0.89	56,000	192
5	5.0	0.59	36,000	194
10	9.8	0.51	31,000	195
15	14.4	0.49	29,000	198

(1) GPC, universal calibration

Titrations of the pendant amine poly(arylene ether sulfone)s indicate a quantitative or a near quantitative incorporation of the amine containing monomer. The intrinsic viscosity and GPC data indicate that indeed relative high molecular weight polymers were synthesized. The trend of intrinsic viscosity may lead to a premature conclusion that amino DFTPPO monomer may not be a monomer grade. As more of the amino DFTPPO monomer was incorporated, the intrinsic viscosity decreased from 0.59 dl/g for the 5 mole% amino DFTPPO incoporation to 0.49 dl/g for the 15 mole% incorporation of amino DFTPPO. The manner in which the polymers were synthesized may help to clarify and account for the intrinsic viscosity behavior. The polysulfone with the highest amine content (15 mole%) were synthesized first, followed by 10 mole% and 5 mole%. As shown in Scheme 2, the second stage of the polymerization is conducted at 165°C. For the 15 mole% incorporation, the polymerization was conducted at this temperature for approximately 8hrs, for the 10 mole% incorporation 12hrs and for the 5 mole% incorporation 15hrs. Another synthesis of 5 mole% incorporation of amino DFTPPO, whereby, the polymerization was conducted at 165°C for over 16hrs yielded an intrinsic viscosity of 1.00 dl/g which is higher than even the control (0.89 dl/g). So the reason why 5 mole% incorporated amino DFTPPO polysulfone has a higher intrinsic viscosity than the 15 mole% incorporation is due to a longer polymerization time at 165°C for the 5 mole% incorporation than the 15 mole% incorporation, and not from the notion that amino DFTPPO may not be a monomer grade. The pendant amines show a slight increase in Tg as more of the amino DFTPPO is incorporated, this is probably due to the hydrogen bonding of the pendant amines with both the sulfones and the phosphine oxides. The increase in Tg could also be due to a higher Tg for the homopolymer of bis (4-fluorophenyl) phenylphoshine oxide and Bisphenol-A relative to the homopolymer of DCDPS and Bisphenol-A.(9)

The pendant amino poly(arylene ether sulfone)s were also chemically modified to maleimides and crosslinked to afford insoluble networks as well as utilized as reactive thermoplastics to increase the fracture toughness of epoxy networks.(10) Current investigation involves reacting the pendant amines with phthalic anhydrides which would result in pendant pthalimides on the backbone of poly(arylene ether sulfone)s. Our rationale behind this work is that due to the relative bulkiness of pendant phthalimides, the Tg of the resulting modified pendant phthalimide poly(arylene ether sulfone)s will be higher. The degree of the increase in the Tg can be controlled by varying the amount of amino DFTPPO monomer relative to other comonomers.

Conclusion

Bis(4-fluorophenyl)-3-aminophenylphosphine oxide (amino DFTPPO) was synthesized and successfully copolymerized with DCDPS and bisphenol-A for the synthesis of random pendant amines on the backbone of polysulfones. A unique feature of pendant amines, particularly, with our approach is that molecular weight can be controlled independently of the concentration of the amines. Demonstration of this concept was experimentally supported by the synthesis of high molecular weight poly(arylene ether sulfone)s with various concentrations of amines on the backbone.

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