Water-Soluble Polybenzimidazole-Based Polyelectrolytes

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Polymers with fully aromatic backbones generally exhibit high thermal stabilities, mechanical strengths, and chemical resistance. While these properties make these polymers valuable for industrial applications, they tend to be coupled with processing problems due to poor solubility and infusibility. Modification of the structure of the polymer to impart solubility without sacrificing the desirable properties of aromatic polymers has been a focus of our research, exemplified by our previously reported[2] derivatization of the aramid poly(p-phenyleneterephthalamide) (PPTA; Kevlar, Du Pont) to form the highly soluble polyelectrolyte poly[(p-phenyleneterephthalamido)propanesulfonate] (PPTA-PS). The derivatization method involves the initial formation of a polyanion of the parent polymer, followed by reaction with an appropriate sidechain reagent to produce an alkylsulfonate derivative. PPTA-PS is highly soluble in polar aprotic solvents and water.

Substitution of the nitrogen atom on the backbone of PPTA destroys its rigid-rod nature,[3] resulting in a randomcoil conformation of the polymer backbone. The rigidrod character of PPTA is largely responsible for its desirable physical properties; thus, loss of the highly chainextended conformation with derivatization causes a significant loss of mechanical integrity and thermal stability. It is desirable to impart solubility to a material without destroying the conformational dynamics of the parent polymer backbone. To accomplish this, a polymer with the appropriate physical properties, and a potentially reactive site that would not disrupt chain conformation when substituted, is necessary.

Polybenzimidazoles are ideal candidates for this type of derivatization reaction. They possess two potentially reactive N-H bonds per repeat unit, and substitution of these nitrogens does not alter the conformation of the polymer backbone. The "all para-linked" and rigid-rod form of PBI, poly(p-phenylenebenzobisimidazole) first synthesized by Marvel and co-workers,[4] is likely the best choice as the parent polymer for polyelectrolyte formation, yet it is not easily available. During the review of this paper, the propanesulfonate derivative of this polymer has been reported.[5] In this study, we have used commercially available poly(2,2'-m-phenylene-5,5'-bibenzimidazole) (PBI; Celazole, Celanese) (1) as the parent material, which should exhibit similar chemical reactivity to poly(p-phenylenebenzobisimidazole), to prepare a new family of polyelectrolytes containing both aliphatic and aromatic sulfonate pendant groups as illustrated in Scheme I.

As in the preparation of PPTA derivatives, the first step in the derivatization of PBI is the formation of a solution of its anion, using the method described by Sansone.[6] A solution of PBI in DMAc is treated with LiH, which deprotonates the nitrogens of the benzimidazole rings in the polymer backbone creating the PBI polyanion (2). With deprotonation, the previously dark-brown PBI solution changes to a very deep red with a noticeably higher viscosity. Subsequent treatment of this polyanion with
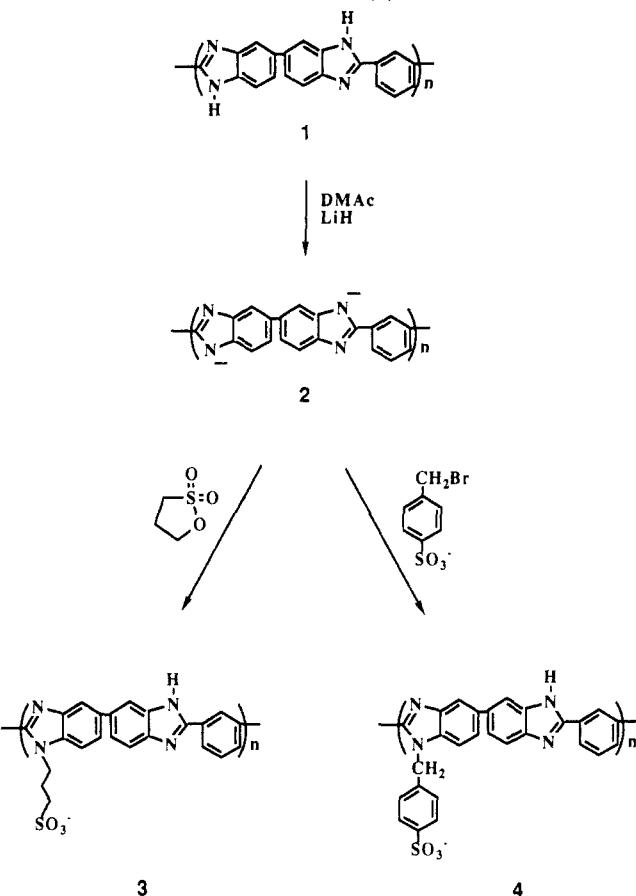
an appropriate side-chain reagent results in the facile formation of the alkylsulfonated or arylsulfonated derivative polyelectrolyte as shown.

Sulfonates were chosen as the ionic moiety for our polyelectrolytes because of their stability and high solubility in aqueous systems. 1,3-Propane sultone was reacted with 2 for the preparation of the N-propanesulfonate PBI-PS (3). Upon addition of the solid sultone to the anion solution, an immediate decrease in the viscosity and a lightening to orange/brown occurs. The PBI-PS was precipitated into a large excess of THF, collected by vacuum filtration, and then dialyzed in water for several days to remove ~20% DMAc present in the as-synthesized polymer. The yield in a typical experiment is 95% of a polyelectrolyte soluble in polar aprotic solvents and also *soluble in water*.

Sodium 4-(bromomethyl)benzenesulfonate[7] was reacted with 2 to form the N-benzylsulfonate PBI-BzS (4). Again an immediate color change to light orange/brown and a viscosity decrease occurred when the side-chain reagent was added. Isolation and purification of this polyelectrolyte was carried out using the same techniques as described above for PBI-PS. In this case, the bromide salts produced as side products were removed along with trapped solvent during dialysis. High yields were obtained, and the benzylsulfonated polyelectrolyte is soluble in polar aprotic solvents, such as DMSO, up to 10 wt %.

In order to verify the PBI-PS and PBI-BzS syntheses, the N-propanesulfonate and N-benzylsulfonate derivatives of phenylbenzimidazole were prepared. Using reaction conditions similar to those used for the polymers, the model compounds were synthesized and isolated by evaporation

Table I
^{13}C NMR[a] (ppm) and FTIR (cm^{-1}) Results for PBI Polyelectrolytes and Model Compounds

R	C_a	C_b	C_c	$\nu(SO_2)$	C_a	C_b	C_c	$\nu(SO_2)$
a, b, c, SO$_3^-$	43.5	25.9	48.3	1060, 1218	43.7	26.0	48.2	1050, 1194
a CH$_2$, SO$_3^-$	47.3			1047, 1197	47.6			1040, 1221

[a] Spectra obtained in a ~10% DMSO-d_6 solution; referenced to solvent at 39.5 ppm.

of the solvent. Purification by multiple precipitations from alcohol with ether resulted in the isolation of the compounds as hygroscopic, white powders. The model compounds were analyzed spectroscopically, with the results providing points of reference for spectroscopic characterization of the polyelectrolytes. Table I shows the pertinent ^{13}C NMR and FTIR results for the characterization of the model compounds and the polyelectrolytes. There is close correlation of the chemical shifts of the methylene carbons in the sulfonate side chains between the small-molecule models and the polyelectrolytes. As expected, there are three methylene resonances in the spectra of the propanesulfonates and a single methylene resonance in the spectra for the benzylsulfonates. In addition, the FTIR spectra of the sulfonated model compounds and polyelectrolytes correspond closely to those of the respective starting materials, except for the addition of two strong bands near 1050 and 1200 cm^{-1} resulting from the symmetric and asymmetric stretching vibrations of the sulfonate sulfur to oxygen double bonds. The frequencies of these bands are shown in the table for each of the sulfonated compounds.

The structures shown for the polyelectrolytes (3 and 4) are general representations of the actual structures of the polymers. They are not intended to express the extent of substitution or the microstructure of the polymers. In fact, the level of substitution of the polymers, as determined from the sulfur to nitrogen ratio obtained from elemental analysis, can be controlled by variation of the number of equivalents of LiH and/or side-chain reagent in the polyelectrolyte synthesis.

The introduction of the sulfonate side chains onto the PBI backbone successfully imparts improved solubility to the derivative polymer. Both PBI–PS and PBI–BzS are much more easily soluble than the parent PBI in polar aprotic solvents such as DMAc and DMSO. In addition, aqueous solutions of greater than 8% can be made from 80% sulfonated PBI–PS, although at concentrations much higher than 2% the solution viscosity becomes too high for casting into films. Orange films of PBI–PS, cast from an aqueous solution, are transparent and tough. These films are stronger than DMAc-cast films of PBI.

The thermogravimetric analysis traces in N$_2$ of the PBI–PS (at 62% sulfonation) along with PBI–BzS (22% sulfonated) are shown in Figure 1. The polymers are all hygroscopic, and even after vacuum oven drying at 100 °C for 48 h, and holding at 200 °C in the TGA for several minutes before testing, an initial weight loss of 5% or less
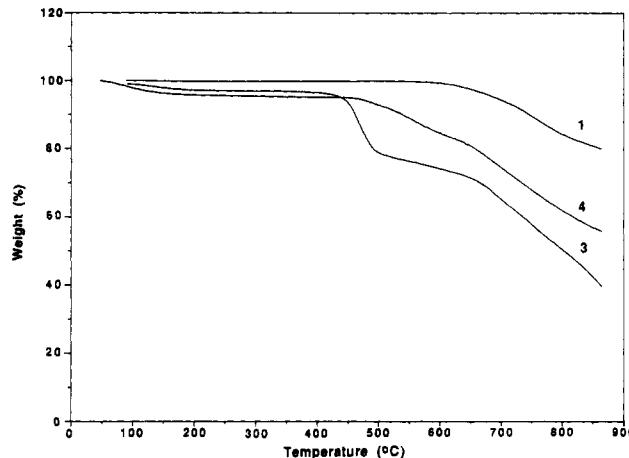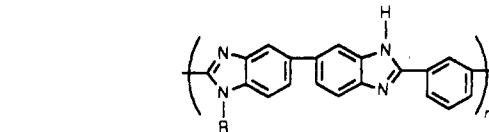

Figure 1. TGA thermograms for PBI (1), PBI–PS (3), and PBI–BzS (4) carried out under a N$_2$ atmosphere at a heating rate of 20 °C/min.

is seen due to loss of water. PBI is extremely stable, with no degradation until greater than 600 °C in an inert atmosphere. The polyelectrolytes also exhibit high thermal stability, with the propanesulfonate derivative not degrading until well above 400 °C and the benzylsulfonate derivative showing even greater stability to 450 °C. The degradation of the polyelectrolytes apparently begins with the side chain, and the higher stability of the aryl side chain is not unexpected. The larger weight loss for the propanesulfonate derivative despite the lower weight of the side chain results from the higher extent of sulfonation of the PBI–PS in these particular samples. These results indicate that much of the desirable thermal stability of the parent polymer is retained in the soluble polyelectrolyte derivatives. Interestingly, the PBI–BzS exhibits an onset temperature for decomposition identical with that of the parent PBI in an ambient atmosphere, indicating that there is essentially no loss in thermooxidative stability.

In this work we have synthesized two new polyelectrolytes based on an all aromatic backbone parent polymer. The new polymers exhibit a significantly higher solubility than the parent material but retain much of its thermal stability. The technique of polyanion formation followed by reaction with an appropriate ion-containing side-chain reagent has proven itself useful as a general method for the preparation of new, water-soluble polyelectrolytes.

References and Notes

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