Aramid and Imidazole Based Polyelectrolytes: Physical Properties and Ternary Phase Behavior with Poly(benzobisthiazole) in Methanesulfonic Acid

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ABSTRACT: Four polyelectrolytes, poly(*p*-phenyleneterephthalamido-*N*-propanesulfonate) (PPTA-PS), poly(*p*-phenyleneterephthalamido-*N*-methylbenzenesulfonate) (PPTA-BzS), poly[2,2′-*m*-phenylene-5,5′-bibenzimidazolyl-*N*-propanesulfonate] (PBI-PS), and poly[2,2′-*m*-phenylene-5,5′-bibenzimidazolyl-*N*-methylbenzenesulfonate] (PBI-BzS), based on the all-aromatic parent polymers poly(*p*-phenylene terephthalamide) (PPTA; Kevlar, Du Pont) and poly[2,2′-*m*-phenylene-5,5′-bibenzimidazole] (PBI; Celazole, Hoechst-Celanese), have been synthesized via a general derivatization procedure for attachment of alkanesulfonate or arenesulfonate side chains onto polymers containing reactive N–H sites. All of the polyelectrolytes are soluble in polar aprotic solvents and in some instances are water soluble at high levels of derivatization. NMR, elemental analysis, GPC, and viscosity results show no evidence for main-chain degradation during the derivatization procedures. Thermogravimetric analyses indicate the pendant ionic groups to be the initial sites for thermal degradation. The PBI derivatives exhibit essentially the same thermal stability as the parent polymer in an ambient atmosphere. Solution viscosity results show all of the polymers to exhibit the polyelectrolyte effect at low concentrations (<0.25 g/dL). The ternary solution phase behavior of PPTA-PS and PBI-PS with the rodlike polymer poly(*p*-phenylenebenzobisthiazole) (PBT) and methanesulfonic acid indicates significant deviation from Flory behavior. The deviation is attributed to the formation of symplexes between protonated PBT and the polyelectrolyte.

Introduction

The introduction of pendant ionic substituents onto the backbone of organic polymers leads to polyelectrolytes and ionomers whose properties are controlled by the nature, composition, and content of these ions.[1] For example, these pendant ions can induce water solubility into polymers whose backbone chemistry is incompatible with aqueous systems. In the case of aromatic polymers, such as polybenzimidazoles and aramids whose structures lead to high thermomechanical stabilities but which are often difficult to process, pendant ion incorporation can improve solubility and potential for further use. Here we report on the preparation and physical properties of two new families of polyelectrolytes based on the all-aromatic parent polymers poly(*p*-phenylene terephthalamide) (PPTA; Kevlar, Du Pont) and poly[2,2′-*m*-phenylene-5,5′-bibenzimidazole] (PBI; Celazole, Hoechst-Celanese).

In general, ion-containing aromatic polymers are prepared by two different methods. The polymerization of monomers substituted with ionic groups leads directly to ion-containing polymers. This method was used in early work for the polymerization of 2-sulfoterephthalic acid and disulfoisophthalic acid with aromatic tetraamines to prepare polybenzimidazoles with sulfonates directly attached to the aromatic chain.[2] Ion-containing poly(*p*-phenylene terephthalamide) derivatives have also been prepared by direct polymerization of ion-containing monomers.[3]

A second method for preparation of ion-containing polymers involves the introduction of ionic groups onto existing polymers by derivatization reactions. An advantage of this method is that ionic interferences during polymerization can be avoided while, in some cases, high ion contents can still be obtained. Direct sulfonation and alkyl carboxylation of poly(2,2′-octamethylene-5,5′-bibenzimidazole) to prepare ion transport membranes were early uses of this method.[4] Takayanagi developed a method for derivatization by reaction at the protonated nitrogen atom of the amide linkage of PPTA,[5] and this method has been used by others for grafting of polymeric and ionic side chains onto the polymer backbone.[6] A similar route has been used for the derivatization of polybenzimidazoles by reaction at the protonated nitrogen of the benzimidazole ring.[7] Recently, a combination of the two approaches for polyelectrolyte formation has been used in the preparation of propanesulfonated poly(2-sulfo-*p*-phenylenebenzobisimidazole), a polymer made from sulfonated monomers.[8]

We have utilized the derivatization method of polyelectrolyte formation to prepare both alkyl- and arylsulfonate soluble derivatives of Kevlar[9] and Celazole[9a,10] to form PPTA and PBI derivatizes, respectively. The derivatization process, illustrated schematically in Scheme I, takes advantage of the reactivity of the protonated nitrogen atoms inherent in the backbones of both types of parent polymer. After deprotonation for formation of the polymeric anion of the parent, an appropriate reagent for introduction of the sulfoalkyl or sulfoaryl group is added, and the polyelectrolyte is formed.

Four polyelectrolytes, poly(*p*-phenyleneterephthalamido-*N*-propanesulfonate) (PPTA-PS; **1**), poly(*p*-phenyleneterephthalamido-*N*-methylbenzenesulfonate) (PPTA-BzS; **2**), poly[2,2′-*m*-phenylene-5,5′-bibenzimidazolyl-*N*-propanesulfonate] (PBI-PS; **3**), and poly[2,2′-*m*-phenylene-5,5′-bibenzimidazolyl-*N*-methylbenzenesulfonate] (PBI-BzS; **4**), have been synthesized with a range of sulfonation levels and the pendant sulfonates randomly distributed

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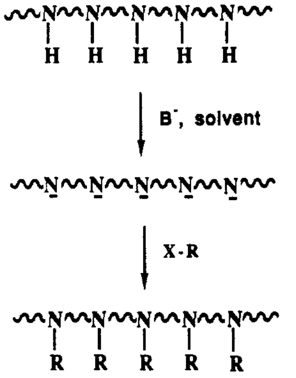
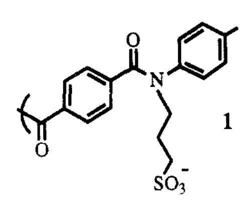
Scheme I



along the polymer backbones. In this paper, the fractional extent of substitution of a particular sample is indicated in parentheses after the acronym for the polyelectrolyte, e.g., PPTA-PS(0.66) indicates that 66% of the amide nitrogens are propanesulfonated along the PPTA backbone. Structures 1–4 are intended to show the presence of both substituted and protonated nitrogen atoms in the polymers, not strict alternation of substitution.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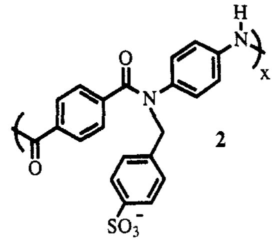
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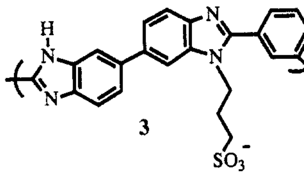
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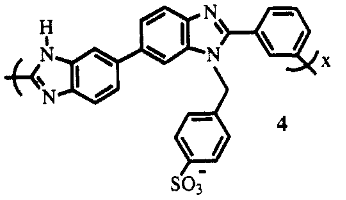
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The aromatic backbones of PPTA and PBI are responsible for their high thermal stabilities, mechanical strengths, and chemical resistances. These all-aromatic backbones are also responsible for the poor solubility of the materials in virtually everything except strong acid. PBI is soluble in DMAc but can only be dissolved under high pressure at well above the boiling point of the solvent. Polyelectrolytes are highly soluble in polar solvents, including water. Most common polyelectrolytes have aliphatic backbones, having been prepared by addition polymerization of vinyl monomers, which contributes to their high solubility but also limits their thermal and mechanical stabilities.

The motivation behind the work reported here was the property benefits to be gained by combining the desirable properties of aromatic backbone polymers with those of polyelectrolytes to produce new types of aromatic polyelectrolytes. These new materials are highly soluble due to the presence of the ionic functional groups in their structures. The higher solubility of the new polyelectrolytes should expand their applications beyond those of the parent materials, perhaps even into the realm of applications presently available to aliphatic polyelectrolytes.

Here we describe the molecular structure of the four polyelectrolytes (1-4) and present the results of physical property studies which verify the success of the derivitization procedure and illustrate the polyelectrolytic behavior of the polymers. In addition, the phase behavior of the polyelectrolytes in ternary systems with a rigid-rod polymer poly(*p*-phenylenebenzobisthiazole) is described.

Results and Discussion

Polyelectrolyte Structure. The first step of the derivatization procedure for preparation of the polyelectrolytes is the formation of a soluble polyanion of the parent polymer. The method is similar for both parent polymers, differing in that the polyanion of PPTA is formed in a heterogeneous reaction between Kevlar pulp and NaH, while a solution of Celazole in DMAc is treated with LiH for the PBI anion formation. The parent polyanion solution is then treated with the appropriate reagent for introduction of the side chain. For the propanesulfonate derivatives 1,3-propane sultone was reacted with the polyanion, and for the benzylsulfonate derivatives sodium 4-(bromomethyl)benzenesulfonate was employed.

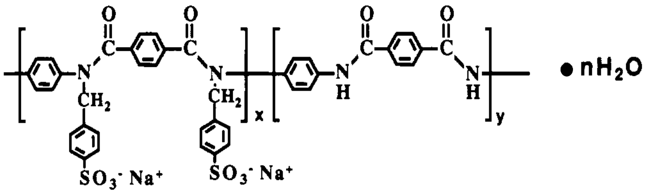
Control of the extent of substitution of the nitrogens along the parent polymer backbone is easily achieved by varying the number of equivalents of base and/or side-chain reagent used in the preparation. To obtain very high levels of substitution (>85%), sequential reactions can be utilized. Variation in the substitution level is exemplified by the elemental analysis results shown in Tables I–III for PPTA-BzS, PBI-PS, and PBI-BzS. Analytical results for PPTA-PS have been published previously in work where we used the PPTA-PS as the charge-balancing counterion and electrolyte in the electrochemical polymerization of pyrrole.[9b] Again, the structures shown in the tables are not meant to suggest any regiospecificity of the derivatization reaction; the sulfonate side chains are randomly distributed along the parent polymer backbone.

The solubility of the polyelectrolytes depends on the nature of the side chain and the extent of substitution. In general, the propanesulfonated derivatives are more soluble than the methylbenzenesulfonates, and the PPTA derivatives are more soluble than those of PBI. All the polyelectrolytes are easily soluble in polar aprotic solvents, even at sulfonation levels as low as 20%. PPTA-PS becomes water soluble at ca. 50% substitution, PPTA-BzS at 66% substitution, and PBI-PS at 60% substitution. Free-standing films of the polyelectrolytes can be cast from water, and in the case of PBI-PS the films are very pliable and tough.

Spectroscopic techniques were used to confirm the structures of the polyelectrolytes. FTIR spectra were useful for detection of the sulfonate stretching vibrations at *ca.* 1200 and 1050 cm^{-1} in the spectra of all of the polyelectrolytes. In addition, a diminishment or complete disappearance of the parent polymer's N–H stretching vibration at *ca.* 3300 cm^{-1} was observed.

^{13}C NMR spectroscopy confirmed the success of the derivatization process. For example, Figure 1 shows a ^{13}C NMR spectrum of PPTA-BzS(0.66) and is representative of all of the PPTA derivatives. It displays the expected series of aromatic carbon resonances and a single alkyl peak due to the methylene carbon of the benzyl side chain. The presence of two carbonyl resonances is expected due to the proximity of a substituted or protonated nitrogen atom. Integration of the two carbonyls provides a quick estimate of the extent of substitution of the PPTA backbone, but the accuracy of such an estimate is limited

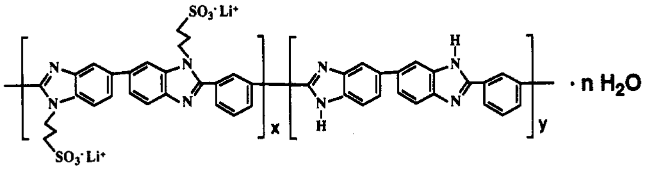
Table I. Elemental Analysis of PPTA-BzS at Various Sulfonation Levels



sample	PPTA-Bz(0.53)	PPTA-BzS(0.66)	PPTA-BzS(0.39)	PPTA-BzS(0.66)
equiv of Br-Tos	1	>1	<1	1.5
x	0.53	0.66	0.39	0.66
y	0.47	0.34	0.61	0.34
n	3	2	1	1

	PPTA-Bz(0.53)		PPTA-BzS(0.66)		PPTA-BzS(0.39)		PPTA-BzS(0.66)	
elem anal.	theory	actual	theory	actual	theory	actual	theory	actual
C	51.90	54.69	52.85	53.17	57.49	57.88	55.22	53.68
H	4.31	4.31	3.90	3.98	3.91	3.84	3.68	3.91
N	5.67	5.60	5.29	5.53	6.87	6.99	5.55	5.67
S	6.81	6.72	8.04	8.37	6.20	6.29	8.34	8.52
EA % sub	53		66		39		66	
NMR % sub	35		41		35		40	

Table II. Elemental Analysis of PBI-PS at Various Sulfonation Levels



sample	PBI-PS(0.55)	PBI-PS(0.99)	PBI-PS(0.53)	PBI-PS(1+)
Equiv of LiH	1	2	2	4
Equiv of sultone	1	2	1	2
x	0.55	0.99[a]	0.53	1+[a]
y	0.45	0.01	0.47	
n	4	2	4	1.5

	PBI-PS(0.55)		PBI-PS(0.99)		PBI-PS(0.53)		PBI-PS(1+)	
elem anal.	theory	actual	theory	actual	theory	actual	theory	actual
C	54.35	56.07	52.47	51.04	54.32	52.48	53.12	50.46
H	4.96	4.93	4.50	4.50	5.09	4.75	4.83	4.41
N	10.89	10.90	9.43	9.12	10.90	10.28	9.39	8.57
S	6.84	6.85	10.72	10.37	6.70	6.31	11.45	11.11
Li	0.27	0.27	1.42	1.37	0.46	0.43	0.0	0.0[b]
O (by difference)	22.70	20.98	21.47	23.60	22.52	25.75	21.20	25.45

[a] S/N ratio and ^{13}C NMR spectrum indicate some imidazole rings are substituted on both nitrogens. [b] Polymer dialyzed in HCl prior to deionized H_2O dialysis.

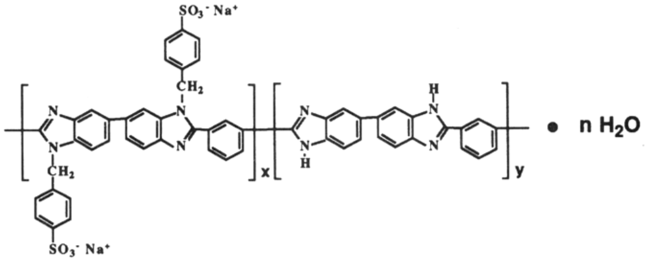
due to differences in delay times for the different carbon nuclei (see EA % sub vs NMR % sub data in Table I).

Gel Permeation Chromatography (GPC). Having performed derivatization reactions on exisiting high polymers, a primary concern was verification that derivatization had proceeded without polymer chain degradation. Approximate molecular weight determinations were carried out using GPC with an aqueous base (0.3 N NaOH) mobile phase. The high ionic strength eluent was necessary to effectively suppress intrachain ionic interactions and also served as the solvent for the polymer samples. To determine the stability of the polymers to these conditions, the ^{13}C NMR spectrum of a basic solution of PPTA-PS was analyzed just after its preparation and at 1-, 2-, and 7-day intervals. No change in the spectrum was observed, indicating that side-chain degradation does not occur under these conditions.

The results of the GPC study for PPTA-PS, PPTA-BzS, and PBI-PS are summarized in Table IV. The molecular weights are reported relative to poly(styrenesulfonate) (PSS) standards, and, due to the fundamental differences in the structures of the polyelectrolytes compared to PSS, complete quantitative comparison are not valid. Qualitative comparisons, on the other hand, are possible and informative. PBI-BzS was not included in the study because the samples available were not substituted to a high enough level to allow them to dissolve in aqueous base.

It is evident from inspection of the GPC results that all the polyelectrolytes are high polymers, and the strong base used in the derivatization reaction does not cause degradation of the backbone of the parent polymers. These results are supported by ^{13}C NMR results, which also give no indication of chain degradation, as manifested by the presence of chain terminus functional groups. In addition, initial static light scattering results[11] have been obtained on PPTA-PS(0.75) and indicate a weight-average molecular weight between 35 000 and 50 000. These results validate the use of the polymer anion derivatization process as a general method for modification of these aromatic polymers.

Table III. Elemental Analysis of PBI-BzS



sample	PBI-BzS(0.39)	PBI-BzS(0.22)
Equiv of LiH	1 + 1[a]	4
Equiv of sultone	1 + 1[a]	2
x	0.39	0.22
y	0.61	0.78
% Na^+ salt	90	93
n	4	3

elem anal.	PBI-BzS(0.39)		PBI-BzS(0.22)	
	theory	actual	theory	actual
C	57.89	55.15	63.96	59.72
H	4.54	4.14	3.35	4.30
N	10.64	9.56	12.95	11.88
S	4.68	4.22	3.20	2.95
Na	3.06	2.75	0.60	0.56
Li		<0.1		<0.1

[a] Made in a two-step reaction with 1 equiv used each step.

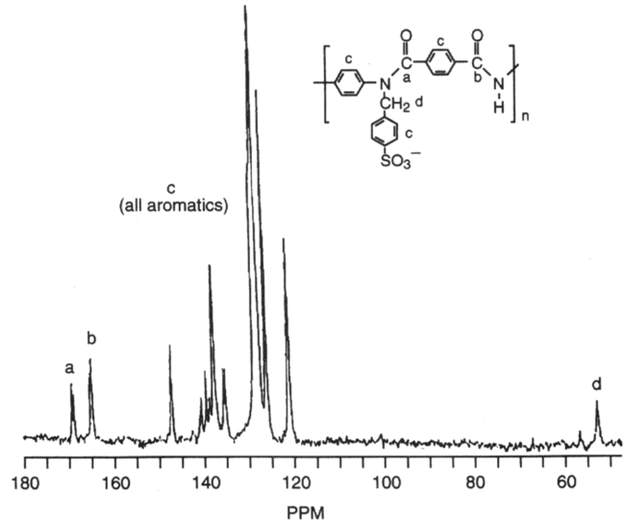


Figure 1. ^{13}C NMR spectrum of PPTA-BzS(0.66), 10% in DMSO-d_6, using an inverse-gated decoupling pulse program and a 30-s delay.

Table IV. Aqueous GPC Results for PPTA-PS, PPTA-BzS, and PBI-PS at Varied Sulfonation Levels

sample	M_w	M_n	M_w/M_n
PPTA-PS(0.66)	16 800	16 300	*a*
PPTA-PS(0.66)	16 100	15 700	*a*
PPTA-PS(0.75)	15 900	15 500	*a*
PPTA-PS(0.47)	21 100	18 100	*a*
PPTA-BzS(0.53)	25 700	20 700	*a*
PPTA-BzS(0.66)	31 300	23 600	*a*
PPTA-BzS(0.66)	34 700	25 800	*a*
PBI-PS(0.99)[b]	178 500	57 700	3.1
PBI-PS(0.54)	120 500	45 700	2.6
PBI-PS(1.13)	120 700	55 700	2.2

[a] Value not reliable due to tailing in chromatogram. [b] S/N ratio and ^{13}C NMR indicate that some imidazole rings are substituted on both nitrogen atoms.

A closer look at the GPC results for PPTA-PS indicates that the least substituted sample exhibits the highest hydrodynamic volume, suggesting the highest molecular weight relative to PSS. Recalling that the parent PPTA can attain a rigid-rod conformation in solution affords an explanation of this trend. Segments of a chain that are not substituted are more extended than the substituted segments of the chain, resulting in polymers with low overall substitution levels exhibiting larger hydrodynamic volumes. In this instance we expect the hydrodynamic volume to continue to increase with decreasing substitution level, and this is the focus of further studies.[11]

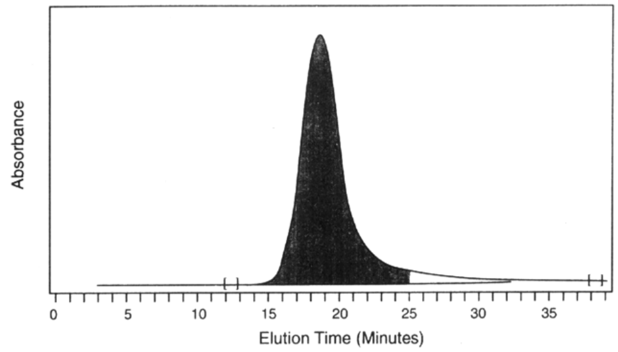


Figure 2. Gel permeation chromatogram for PBI-PS(0.54). Eluent is 0.3 M aqueous NaOH.

The GPC results for the methylbenzenesulfonate derivative of PPTA indicate that the hydrodynamic volume of this polyelectrolyte is higher overall than that of PPTA–PS, despite the use of the same parent polymer. This indicates that the more sterically bulky methylbenzenesulfonate group causes the conformation of the chains to be more extended than when substituted with an alkanesulfonate side chain.

Figure 2 shows a GPC chromatogram for PBI-PS(0.54). Again, the hydrodynamic volumes, represented by the molecular weight values (Table IV), and the narrowness of the distribution indicate that modification of the PBI backbone by the derivatization procedure proceeds with no chain degradation.

It should be noted that there are no sites that are particularly vulnerable to chain cleavage on the PBI backbone; all linkages are between aromatic rings. PBI is a semiladder polymer, such that any degradative reaction at the majority of the carbon atoms in the backbone might result in ring opening but not chain degradation. In contrast, PPTA has amide linkages with carbonyl groups that are susceptible to nucleophilic attack by the base. Since the PPTA backbone is stable to the derivatization process, it is not surprising that the PBI backbone is also.

Thermal Stability. The polymers on which the polyelectrolytes are based possess all-aromatic backbones, leading to high thermal stability in the parent materials. The aim of derivatization of the parent polymers was to improve their solubilities but retain a significant fraction of their high thermal stabilities.

Thermogravimetric analysis (TGA) of the polymers was carried out in both inert and oxidative atmospheres as shown in Figure 3 for the PBI's and Table V for both sets of polymers. All samples were vacuum oven dried at 80–100 °C for at least 24 h prior to analysis. Many of the samples studied, especially those based on PBI, are hygroscopic and quickly reabsorb water after oven drying or retain water so well that it is not removed under these drying conditions. These types of polymers can have such a tenacious hold on water that it is not lost until temperatures well above 150 °C.[12] Due to the difficulty encountered in drying and/or keeping the samples dry, a method for *in situ* drying followed by immediate thermal analysis was developed. Samples were loaded into the

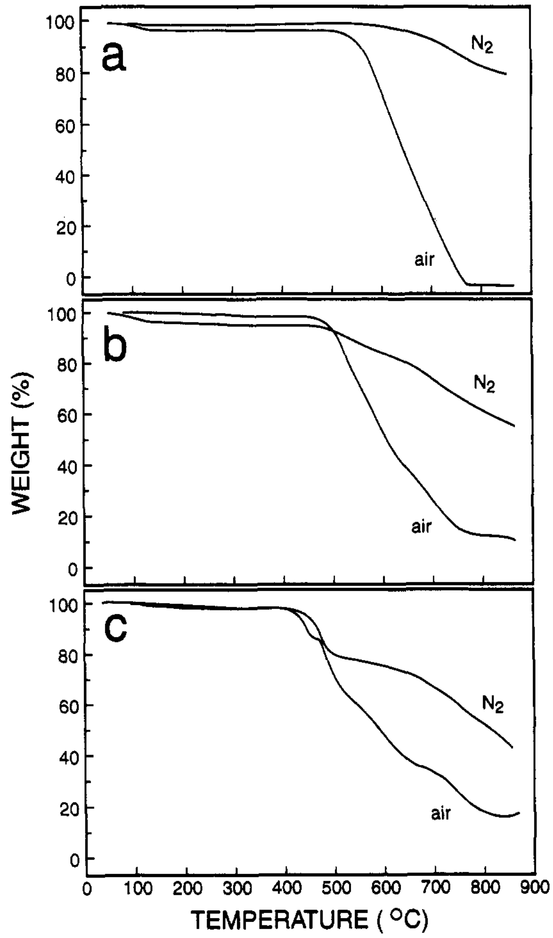


Figure 3. Thermogravimetric analysis traces in air and N_2 of (a) PBI, (b) PBI-BzS(0.22), and (c) PBI-PS(0.54). Heating rate: 20 °C/min.

Table V. Thermogravimetric Analysis Results for Polyelectrolytes and Parent Polymers

	nitrogen		air	
sample	5% wt loss (°C)	mass 800 °C (wt %)	5% Wt loss (°C)	mass 800 °C (wt %)
PPTA	570	45	513	0
PPTA-PS(0.66)	407	38	350	23
PPTA-BzS(0.66)	487	51	459	17
PBI	700	86	561	0
PBI-PS(0.54)	454	51	430	15
PBI-BzS(0.22)	517	63	500	15

TGA instrument, heated to 200 °C, and held for 3–5 min. After cooling, the sample was analyzed without removing it from the instrument. This technique allows successful acquisiton of thermal analyses of samples with essentially all of the water of hydration removed. The temperatures recorded in Table V are those at which a total mass loss of 5% has been realized. This was done to eliminate subjective bias in the determination of the onset of degradation temperatures, which can be rather indistinct as is evident in the thermograms.

Celazole is extremely thermally stable, as expected for an all-aromatic polymer. In an inert atmosphere, it exhibits an onset of degradation around 650 °C (5% mass loss at 700 °C) and retains more than 80% of its mass at 800 °C. The onset of degradation temperatures for the polyelectrolytes in an inert atmosphere is significantly lower than for Celazole, as expected with the addition of pendant groups which are not conjugated with the backbone.[13] The degradation of PBI–BzS(0.22) begins at about 480 °C, and PBI-PS(0.54) shows mass loss beginning at 420 °C. After removal of the side chains degradation is gradual with high residual masses (50–60%) at 800 °C.

The onset of degradation of Celazole in an atmosphere of dry air, shown in Figure 3a, begins at a significantly lower temperature relative to the parent polymer. Here the polymer begins to degrade at approximately 520 °C, a full 100 °C below the degradation temperature in an inert atmosphere. The PBI based polyelectrolytes show little difference in their onset of degradation temperatures in changing from an inert to an oxygen-containing atmosphere as shown in parts b and c of Figure 3. The major difference in the behavior in air compared to nitrogen is that the magnitudes of the mass losses are much higher and percentages of residual char at high temperature are much lower in the oxidative atmosphere. This is apparently the result of the lower stability of the parent polymer, rather than a consequence of the addition of the pendant side chain.

The parent polymer Kevlar is also highly thermally stable. Onset of degradation does not occur until above 550 °C, after which a sharp decrease in mass begins so that at 600 °C a residue with 50% of the original mass remains. After derivatization with a propanesulfonate side chain, PPTA-PS(0.66) shows retention of thermal integrity until approximately 400 °C, followed by a steady degradation to 40 wt % at 800 °C. The methylbenzenesulfonated derivative is more thermally stable; degradation initiates at about 470 °C. Again after an initial loss, a gradual decrease in mass to a residue of 50% at 800 °C occurs.

Thermal analyses of Kevlar and its derivatives in an atmosphere of dry air were also carried out. As was the case with PBI, Kevlar itself is much less stable in air, with degradation beginning about 70 °C lower than in nitrogen. Once degradation begins, the entire mass of the polymer is volatilized. The TGA traces of the PPTA-BzS(0.66) run in air and in N_2 indicate a relatively small decrease ($\sim$20 °C) in the onset of degradation temperature of the polyelectrolyte in air compared to N_2. Again the major difference in behavior is that the mass decrease is steeper after the initial loss, and the amount of the residue at high temperature is much lower due to oxidative degradation of the polymer backbone. PPTA-PS shows the same trend.

The addition of pendant groups to both aromatic polymers results in loss of thermal stability due to the lower temperature at which the side chain cleaves, regardless of the nature of the atmosphere. This is the expected behavior because the side chain is not stabilized by resonance to the backbone. The methylbenzenesulfonate side chain is more stable than the propanesulfonate side chain, regardless of which parent polymer is derivatized. This suggests that the point of cleavage of the side chain is not exclusively at the N–C bond. Homolytic cleavage of this bond in a methylbenzenesulfonate would generate a benzylic radical, which is more stable than the primary alkyl radical generated by cleavage of the same bond in a propanesulfonate. The degradation process is likely more complex.

The practical implications of these results are that the polyelectrolyte derivatives of PPTA and PBI, especially the methylbenzenesulfonates, are nearly equal in thermal stability to the parent polymers in an ambient oxidative atmosphere. In this sense, the desirable thermal properties of the parent polymers have been retained to a large extent in the polyelectrolyte derivatives.

Solution Viscosity. The solution viscosites of the polyelectrolytes have been analyzed in either water, DMSO, or a mixture of both solvents in which the ionizable

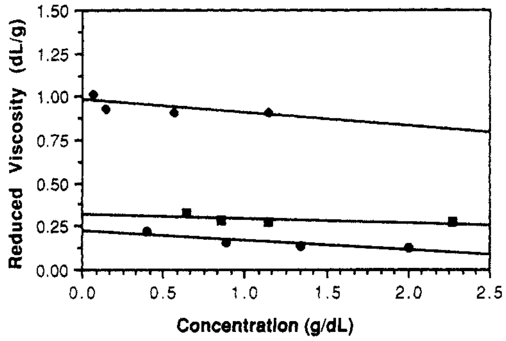


Figure 4. Intrinsic viscosity results for PPTA-BzS(0.67) (), PBI-PS(0.54) (◆), and PPTA-PS(0.66) (). Solvent is 9/1 DMSO/H_2O containing 1% by weight LiCl.

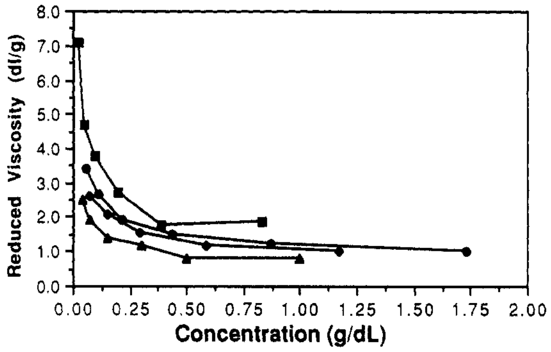


Figure 5. Reduced viscosity as a function of polyelectrolyte concentration demonstrating the polyelectrolyte effect for PBI-BzS(0.39) (◆), PPTA-BzS(0.67) (), PBI-PS(0.54) (), PPTA-PS(0.66) ×10 (). Solvent is water for PPTA derivatives and DMSO for PBI derivatives.

polymers are expected to be highly dissociated when dissolved. Experiments intended to exhibit the polyelectrolyte effect were carried out without added salt, while intrinsic viscosities were determined in 1% LiCl solutions.

The intrinsic viscosity of the parent polymer Kevlar was determined in 97% H_2SO_4, and the molecular weight of the material was determined to be 33 500 when calculated from the [η] value (6.85 dL/g).[14] The inherent viscosity of the parent Celazole is 0.561 dL/g at a concentration of 0.400 g/dL in H_2SO_4, indicating a weight-average molecular weight of 24 000.[15] The intrinsic viscosity of the Celazole was determined in DMAc solution, and its value is 0.72 dL/g. Comparison of the magnitude of the viscosities of the two parent polymers is as expected since Kevlar behaves as a rigid-rod and Celazole as a random coil in solution. The reduced viscosity of Celazole at 0.400 g/dL (0.56 dL/g) is more than an order of magnitude less than the extrapolated η_{red} of Kevlar at that concentration.

Intrinsic viscosity has been used to lend insight into the conformations of the polyelectrolytes in solution as shown in Figure 4 using 9/1 DMSO/H_2O containing 1% w/w (0.24 M) LiCl. This concentration of salt is 10 times higher than that of the polymer repeat units in the solutions, which suppresses the polyelectrolyte effect. An intrinsic viscosity determination of the PBI-BzS(0.39) was attempted, but the results were unreliable due to insolubility at this level of substitution. Consequently, a single value of the reduced viscosity of PBI-BzS(0.39) of 1.23 dL/g at 1.00 g/dL was determined.

The viscosities of the PBI derivatives are very similar in magnitude to one another and to Celazole due to conformational similarity to the parent polymer. The magnitudes of the viscosities of the polyelectrolyte derivatives give further assurance that the polymer backbone has not been degraded by the derivatization reaction. This has allowed us to estimate approximate molecular weights of the polyelectrolytes based on their degrees of substitution in cases where aqueous GPC has not been possible due to lack of water solubility.

Unlike the PBI derivatives, the PPTA derivative polyelectrolytes show a tremendous decrease in their intrinsic viscosities when compared to Kevlar because substitution of the nitrogen atoms of the Kevlar backbone results in destruction of the rigid-rod nature of the macromolecules.[16] Comparison of the viscosities of the PPTA derivatives with the parent material as an indication of molecular weight is not valid.

In both the PPTA and PBI derivatives, the methylbenzenesulfonate derivative exhibits a higher viscosity than the propanesulfonate derivatives. This suggests that the conformations of the polymer chains of the methylbenzenesulfonate substituted polymers are more extended than those substituted with propanesulfonate side chains, most likely due to increased steric repulsion between the backbone and the side chain. Additional evidence of this was seen in the GPC studies, which indicate a higher hydrodynamic volume for PPTA-BzS than for PPTA-PS.

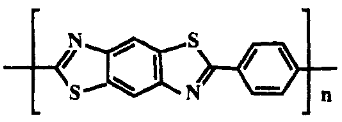
The increase of the reduced viscosity of polyelectrolytes with decreasing polymer concentration in solutions of low ionic strength, the polyelectrolyte effect, is a well-known phenomenon,[17] and study of the dilute solution viscosity of the materials was useful in confirming their polyelectrolyte natures. Although the mechanism of this behavior is the subject of debate, specifically as to whether the phenomenon is the result of intramolecular or intermolecular ionic interactions,[18] the characteristic viscosity behavior is often used to detect the presence of ionizable groups on a macromolecule.

The results of a study verifying the polyelectrolytic nature of the derivatized polymers are shown in Figure 5. The derivatization reactions successfully introduce propanesulfonate or methylbenzenesulfonate side chains onto the backbone of both polymers, and these ionic side chains cause the derivative polymers to exhibit properties typical of ionic polymers.

A study of the change in the relative viscosity of PPTA-PS at high polymer concentration was carried out, and it provides further proof that the rigid nature of the PPTA backbone is destroyed with substitution of the nitrogen atoms. As expected for a random-coil polymer, a continual increase in the relative viscosity with concentration is seen with no evidence of lyotropic liquid crystalline ordering.

This experiment illustrated the high solubility of PPTA-PS, with isotropic solution forming at concentrations up to 65% by weight PPTA-PS, where they become gel-like and will not flow. It is expected that the polyelectrolyte is soluble up to 100% solids in water.

Ternary Phase Behavior. A potential application for these polyelectrolytes is in the preparation of molecular composites.[19] Analogous to glass-reinforced epoxy composites, molecular composites are made by dispersion of a rigid-rod polymer reinforcing agent into an amorphous polymer matrix. A common reinforcing polymer component for molecular composites is rod-like poly(*p*-phenylenebenzobisthiazole) (PBT, **5**), and the materials are



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generally processed from ternary solutions in methanesulfonic acid (MSA). It has been found that these ternary composite processing solutions consisting of PBT and a noninteracting amorphous polymer matrix are isotropic at low (*ca.* 2–3%) total polymer concentration. At higher concentrations aggregation and phase separation occurs, resulting in an anisotropic solution unsuitable for processing to molecularly homogeneous materials. Recently it has been shown that ternary solutions of much higher total polymer concentrations are possible when a strong rod–coil interaction is present.[20]

A statistical thermodynamic theory concerning the phase relationships of ternary systems has been put forth by Flory.[21] Critical to the theory is that the system is athermal; therefore, it is assumed that no interaction occurs between the rod and coil components. The theory allows prediction of the concentration at which phase separation will occur (C_{cr}) of a mixture of the two types of polymers and solvent at any composition.

The phase separation that occurs in ternary solutions consisting of PBT (or another rod-like polymer) and a noninteracting random-coil polymer in a common solvent can be attributed to the discrepancy in geometric form between the rodlike and coil polymer chains. The coil polymer chains assume the expected random configuration in such a solution, and the rod-like chains can also exist in a random arrangement below C_{cr}. The saturation point for this type of solution is low and, beyond the saturation point, the rod-like solute forms regions in which polymer chains approach a parallel arrangement, resulting in phase-separated domains containing almost exclusively rodlike solute and solvent. These ordered regions are nematic liquid crystalline domains and are optically anisotropic. When ternary solutions of this sort are intended for processing of molecular composites, it is imperative to know the concentration at which the phase transition occurs for any polymer composition.

In ternary systems involving a negatively charged sulfonated polyelectrolyte as the coil component, a strong possibility exists that an electrostatic interaction will occur between protonated PBT and the polyelectrolyte, forming a polyelectrolyte complex (or symplex).[20,22] If a symplex does form, the system will not be athermal, and deviation from the behavior predicted by Flory is likely. The ionic interaction between the negatively charged sulfonates and the positively charged protonated PBT rods may be strong enough to overcome the thermodynamic driving force toward phase separation. Such a deviation has been found for the ternary system of PBT/poly(sodium 2-acrylamido-2-methylpropanesulfonate) (PAMPS)/MSA,[20] and homogeneous solutions of much higher total polymer concentrations than previously seen can be prepared from this system.

The phase behavior of PPTA-PS(0.66) and PBI-PS(0.54) in ternary systems with PBT and the common solvent MSA has been studied. To the best of our knowledge, this represents the first detailed study (outside of the initial studies on our PPTA-PS[20d]) of the phase behavior of these types of solutions with polyelectrolytes having all-aromatic backbones. The bright colors of the birefringence of the nematic regions in the two-phased ternary mixtures were used to locate an anisotropic to isotropic phase transition for the solutions. Observation of a solution with decreasing total polymer concentration showed decreasing areas of birefringence that eventually disappeared completely. The point at which the birefringence was no longer seen was taken to be the transition point (C_{cr}).

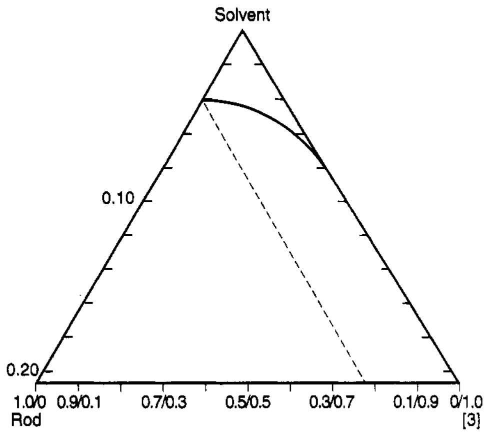


Figure 6. Flory theory determined phase boundaries for ternary systems consisting of solvent, rodlike polymer with a large axis ratio (≥200), and coil polymers [3] of different contour lengths. Solid line: contour length ≥ 1000 (high polymer). Dashed line: contour length = 1 (small molecule).

In Flory's theory for athermal systems, the major influences on the phase behavior are the contour length of the coil polymer and the axis ratio of the rod-like component. The two binodial curves of the phase diagram shown in Figure 6 illustrate the extremes of the effect of the contour length of the coil component on ternary phase behavior. It can be seen that when the contour length is large, the phase transition occurs at low polymer concentrations, whereas in the case where the coil component has a contour length of 1, in effect the system consists of the rod polymer and two solvents.

The binodial curve denoting the anisotropic to isotropic phase transitions for a ternary system was constructed by determination of C_{cr} for six solutions of each polyelectrolyte with PBT/polyelectrolyte compositions varying from 100/0 to 10/90. After complete equilibration of anisotropic starting solutions (total mass = 2–6 g), solvent was added at a rate of ≤0.4 g/day, with constant stirring after each addition. Small volumes and long stirring times between additions were necessary to ensure that the equilibrium morphology was reached. The change in weight fraction was monitored as the solvent was added. Visual inspection of the solutions was used to prompt further solvent addition until the concentration was within $\sim 1\%$ of C_{cr}. As the phase transition concentration was approached, an optical microscope with crossed polarizers was used to examine the morphology of the solution.

The anisotropic solutions were yellow/green and opaque. As solvent was added, the color gradually darkened and, near the transition, turned dark brown and transparent. When the color change occurred, the first sample was inspected with the microscope. Samples were not viewed under the microscope until visual inspection indicated that the transition was eminent, to prevent altering the concentration of the solution. The small size ($\sim$1 mg) and limited number (2–3) of samples removed from a single solution resulted in a negligible volume change.

When viewed under crossed polarizers, an anisotropic solution which was visually light green and opaque was brightly colored (yellow, green, orange, red, black) and showed a featherlike pattern which could be sheared by moving the coverslip, typical of a nematic liquid crystalline solution.[23] This type of solution did not show dark areas of isotropic solution.

When the solution was anisotropic, but near C_{cr}, it showed a dark field (isotropic matrix) with bright multicolored patches (nematic domains) dispersed throughout. When the solution was past the phase transition and

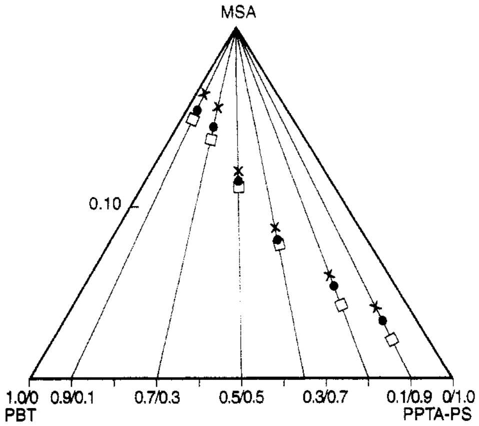


Figure 7. Experimentally determined phase diagram for a ternary system consisting of MSA, PBT, and PPTA-PS(0.66): phase transition points (); anisotropic bracket solutions (); isotropic bracket solutions (×).

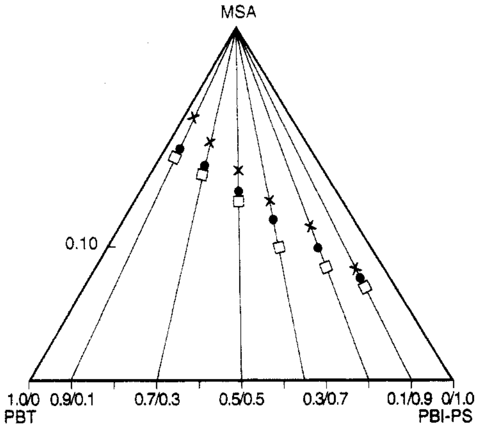


Figure 8. Experimentally determined phase diagram for a ternary system consisting of MSA, PBT, and PBI-PS(0.54): phase transition points (); anisotropic bracket solutions (); isotropic bracket solutions (×).

completely isotropic, the field was totally black. The phase transition was taken to be midway between the last concentration that was determined to be anisotropic and the first concentration that was determined to be isotropic. The series of six of these C_{cr} points define the shape of the binodial for a particular system.

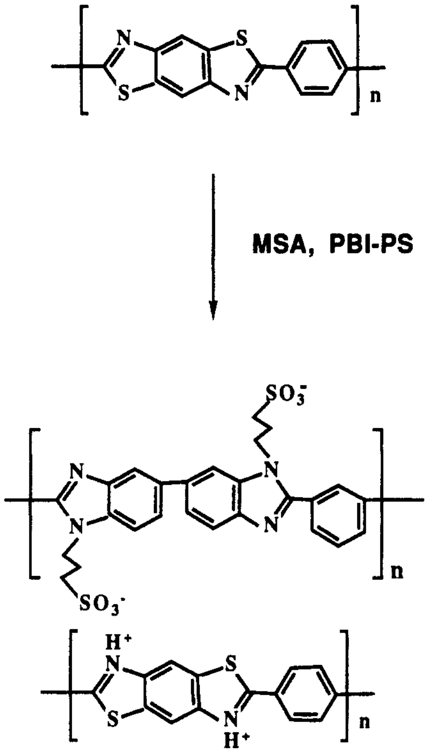
Verification of the location of the phase transition points obtained in these titration experiments, to validate the position of the binodal curves, was accomplished by bracketing experiments. For each titration point, two solutions of the same polymer composition were prepared, one at a concentration 0.5–1.0% higher than C_{cr} and the other at a concentration 0.5–1.0% lower than C_{cr}. If, when viewed under the microscope, the solution at a concentration less than C_{cr} was isotropic and the solution at a concentration greater than C_{cr} was anisotropic, the position of the transition point was guaranteed to be within the bracket concentrations.

Commercially available PAMPS was analyzed in a ternary system with PBT and MSA, as has been done in several other studies.[20] Similar results were obtained and, as has been seen previously, significant deviation from Flory predicted behavior was observed.

Figures 7 and 8 are the ternary phase diagrams prepared for PPTA-PS(0.66) and PBI-PS(0.54). The behavior for both of these polyelectrolytes deviates significantly from the theory predicted by Flory for a ternary system including a coil component with a large contour length.

The shape of the binodials for all three polyelectrolytes studied is similar to that of an athermal system in which the coil component has a very short contour length; that is, the polyelectrolyte component behaves like a small molecule. This suggests that there is a "per repeat unit", interaction between the PBT and the ionic polymer. In other words, the rodlike PBT segments "see" the repeat units of the polyelectrolyte as individual entities. The logical extension of this observation is that the negatively charged sulfonate moieties of the polyelectrolyte interact with the positively charged nitrogen atoms of protonated PBT. This interaction results in the formation of a soluble polyelectrolyte complex, or symplex, such as shown in Scheme II for PBT and PBI-PS.

Scheme II



It is known that the primary driving force for the formation of symplexes is the electrostatic interaction between the oppositely charged ions of the two polymeric components of the solution.[22] Such an interaction between the two polymers in a ternary system violates Flory's criterion of an athermal system, thus resulting in the failure of the binodials found for the MSA/PBT/polyelectrolyte systems to match those predicted by the theory. In order to accurately predict the binodials' shapes, the theory must be modified to include this per repeat unit interaction between the polymeric components. Flory states in his derivation of the partition function of the solvent/rod/coil ternary system that he is purposefully omitting noncombinatory contributions.[21b] He further states that they could be acknowledged by adding the usual term in χ, the Flory–Huggins interaction parameter, which represents exchange interactions. The incorporation of χ into the theory for a rod/coil/solvent ternary system would not be an easily accomplished task, however, because there most probably is a change in entropy associated with the electrostatic interaction between first neighbors. If one visualizes the placement of a symplex into the lattice, it seems impossible to insert the rod polymer independently of the coil polymer, which is the method used by Flory for construction of the partition function for the athermal system. Therefore, χ would need to be expressed in two parts, one expressing the enthalpy change and one expressing the entropy change. The partition function would also have to be modified to allow simultaneous placement of the two types of polymers into the lattice.

The results of the phase boundary determination experiments provide information beyond proof of the failure of Flory theory for solvent/rod/ionic coil ternary systems. The difference in the shape of the binodial is significant because it shows that isotropic ternary solutions of much higher total polymer concentration are possible before the onset of phase separation of the PBT into nematic domains occurs. This fact is important when processing of these solutions into films or fibers of molecular composites is considered; the opening of the isotropic window may alleviate some of the limitations currently encountered in molecular composite processing.[19]

Symplex formation is possible between any sulfonated polyelectrolyte and protonated PBT, so it is believed that the same type of behavior would be observed for systems in which the methylbenzenesulfonated polyelectrolytes PPTA-BzS and PBI-BzS served as the coil polymer. The shape of the binodial is expected to vary with the extent of sulfonation of the polyelectrolyte, approaching contour length = 1 behavior at high levels of substitution and contour length $\gg$ 1 behavior at low sulfonation.

The new aromatic backbone polyelectrolytes present an advantage over traditional polyelectrolytes for use as components in molecular composites as their stability, and potentially their strength, is greater than that of the aliphatic polyelectrolytes. This advantage should translate itself into superior properties for the molecular composites.

Experimental Section

Materials. All reagents and solvents used in the present work were received as donations or purchased from commercial suppliers as indicated. Unless specified otherwise, all reagents were used as received. Sodium 4-(bromomethyl)benzenesulfonate (Br-TOS) was prepared using a known procedure.[24]

PPTA Derivatives. In a typical preparation, the PPTA anion was prepared by charging 400 mL of anhydrous DMSO (Aldrich) and 1.20 g (0.04 mol) of an 80% NaH dispersion in mineral oil (Aldrich) into a dry, three-necked, round-bottom flask flushed with nitrogen and equipped with an overhead mechanical stirrer and thermometer. After the mixture was reacted at 75 °C for 1 h and cooled to 40 °C, 4.76 g (0.04 mol of reactive N-H) of vacuum-dried PPTA (Kevlar pulp) was added. The mixture was stirred vigorously for 24–48 h at ~30–35 °C. The resulting dark red anion solution contained no solid PPTA residue.

The side chains were introduced by addition of 0.04 mol of the appropriate reagent [e.g., 4.89 g of 1,3-propane sultone (Aldrich)] as a solid to the PPTA anion solution with stirring at 35 °C for 24 h. The PPTA derivative was precipitated into a large excess of distilled tetrahydrofuran (THF) and then dialyzed in water. After evaporation of the water, the polymer derivative was in the form of shiny yellow–brown flakes. If precipitated from water into THF after dialysis, the material was obtained as a light, fluffy powder ranging in color from pale yellow to orange, depending on the extent of substitution and the identity of side chain.

PBI Derivatives. The derivatization of PBI utilizes a solution of the parent polymer in anhydrous DMAc (Aldrich), which was prepared by heating a 20% by weight slurry of Celazole (Aldrich) in a Parr reaction bomb to 200 °C for 4–5 h. This viscous dark brown solution was then diluted to 5–10% by weight with anhydrous DMAc and used in the derivatization reactions.

In a typical preparation, the PBI anion was prepared by charging 100 mL of 8% PBI in DMAc solution (7.5 g PBI, 0.05 mol of reactive N-H) and 0.78 g (2 equiv, 0.10 mol) of LiH (Aldrich) into a dry, three-necked, round-bottom flask flushed with nitrogen and equipped with an overhead mechanical stirrer and thermometer. The mixture self-heated to 55 °C and was maintained at this temperature for 5 h. The PBI anion solution thus generated was more viscous and red/brown in color than the protonated form of the polymer in DMAc.

The side chains were introduced by addition of a variable number of equivalents of the appropriate reagent. For example, 6.02 g (1 equiv, 0.05 mol) of 1,3-propane sultone was added all at once as a solid to the PBI anion solution with stirring at 35 °C for 5 days. Some precipitation of the product occurred while stirring. The PBI derivative was precipitated into a large excess of a 50% mixture of distilled anhydrous ether and distilled THF and was dialyzed first in DMSO and then in water. After evaporation of the water, the polymer derivative was in the form of shiny yellow/brown flakes. If precipitated from water into THF after dialysis, the material was obtained as a light, fluffy powder ranging in color from beige to orange, depending on the extent of substitution and the identity of the side chain.

FTIR. Infrared spectra were obtained using a Digilab FTS-40 spectrophotometer. Samples were analyzed using either the diffuse reflectance technique on powdered dispersions of 1–3% in KBr or transmission through cast thin films.

NMR. All spectra were obtained on a Bruker MSL-300 (300 MHz) spectrometer at 5–10% by weight in deuterated DMSO. The methyl carbon resonance of DMSO served as the internal reference for the spectra. Long delay times (15–30 s) and gated decoupling were used in the acquisition of the spectra of the PPTA based polyelectrolytes to allow for integration.

Elemental Analysis. Combustion analysis of all materials was carried out in-house (C, H, N) on a Perkin-Elmer 2400 CHN analyzer. Samples were also sent to Robertson Microlit Laboratories, Inc. (Madison, NJ) for C, H, N analyses and for determination of S, Na, Li, Br, and Cl contents.

GPC. Molecular weight determinations were carried out on the water-soluble polyelectrolytes at Alcon Laboratories (Fort Worth, TX). Gel permeation chromatography was performed on a Waters GPC system with a Waters 860 data processing unit, using a UV detector operating at 254 nm. The column was a Jordi Associates "Jordigel" styrene/divinylbenzene substrate modified with glucose. The mobile phase was 0.3 M aqueous NaOH (pH 13), which was also the solvent used to dissolve the samples and the standards. Sodium poly(styrenesulfonate) standards (American Polymer Standard Corp., Mentor, OH) were used to generate the calibration curve using a quadratic fit.

TGA. Thermogravimetric analyses of the polymers were carried out on a Du Pont 951 TA system equipped with TGA, DSC, and DMA. The atmosphere was either dry nitrogen or dry air flowing at a rate of ~60 mL/min. The starting temperature varied from 25 to 60 °C, and the ending temperature was generally 900 °C. The heating rate was 20 °C/min. The sample size varied with the density of the sample and was in the range of 20–35 mg.

Viscometry. Stock solutions 1.00–5.00 g/dL in polyelectrolyte were prepared and diluted for use. All solvents were distilled before use, and solvents and solutions were filtered before placing in a Cannon-Fenske viscometer that was suspended in a water bath thermostated to 29.5 (±0.5) °C. Flow times were measured to 0.01 s, and the average value of four runs was used for data analysis.

Phase Behavior. The PBT used in this study was obtained from the Polymer Branch (Nonmetallic Materials Division) of Wright Research and Development Center, Wright Patterson Air Force Base, Dayton, OH. The intrinsic viscosity of the sample was 15.8 dL/g, which corresponds to a viscosity-average molecular weight of 27 000.[19a] The polymer was obtained as a dry flake and was dried in a vacuum oven at 100 °C for at least 24 h before use.

The solvent used was a mixture of 97% methanesulfonic acid (MSA) and 3% chlorosulfonic acid (CSA; $ClSO_3H$). The mixture was used to allow the CSA to scavenge any residual moisture in the MSA or that entered the system during the experiment. The MSA was distilled at reduced pressure before use, and the CSA was used as received. The density of the solvent mixture was calculated to be 1.489 g/mL based on the densities of MSA and CSA, which were assumed to be additive.

Poly(sodium 2-acrylamido-2-methylpropanesulfonate) (PAMPS) was purchased as a 10 wt % solution in water (Aldrich). The solution was further diluted with water (to ~2% by weight) and dialyzed for 3 days. After evaporation of the water, the polymer was obtained as white solid, which was vacuum oven dried for several days before use. The molecular weight of PAMPS is on the order of $(1-2) \times 10^6$.

The apparatus for determination of the phase transition concentrations consisted of a series of six three-necked conical flasks of 100-mL capacity. Each was equipped with an overhead mechanical stirrer, and the system was fitted with gas inlets so that all the flasks were subjected to a constant positive pressure of dried nitrogen. Polymer quantities were measured on an analytical balance to ±0.5 mg, and solvent volume was measured with a 1.00-mL syringe to ±0.005-mL accuracy.

The flasks were not insulated or thermostated in any way, and the temperature of the lab in the vicinity of the stirrers was monitored and found to be 23.5 ± 2.5 °C throughout the experiment. No significant effect on the results of the experiment is expected with a temperature variation of this magnitude. A sample of an anisotropic solution was heated with a hot stage on the transmission microscope, and no change in morphology was noted until the temperature had increased by a minimum of 20 °C.

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