Polyphosphazene Membranes. III. Solid-State Characterization and Properties of Sulfonated Poly[bis(3-methylphenoxy)phosphazene]

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ABSTRACT: Poly[bis(3-methylphenoxy)phosphazene] was sulfonated in a solution with SO_3 and solution-cast into 100-200- μ m-thick membranes from N,N-dimethylacetamide. The degree of polymer sulfonation was easily controlled and water-insoluble membranes were fabricated with an ion-exchange capacity (IEC) as high as 2.1 mmol/g. For water-insoluble polymers, there was no evidence of polyphosphazene degradation during sulfonation. The glass transition temperature varied from -28 °C for the base polymer to -10° C for a sulfonated polymer with an IEC of 2.1 mmol/g. The equilibrium water swelling of membranes at 25°C increased from near zero for a 0.04-mmol/g IEC membrane to 900 % when the IEC was 2.1 mmol/g. When the IEC was < 1.0 mmol/g, SO_3 attacked the methylphenoxy side chains at the *para* position, whereas sulfonation occurred at all available aromatic carbons for higher ion-exchange capacities. Differential scanning calorimetry, wide-angle X-ray diffraction, and polarized microscopy showed that the base polymer, poly[bis(3-methylphenoxy)phosphazene], was semicrystalline. For sulfonated polymers with a measurable IEC, the 3-dimensional crystal structure vanished but a 2-dimensional ordered phase was retained. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 387-399, 1999

Key words: polyphosphazene; sulfonation; ion-exchange membrane; crystal structure; thermal stability

INTRODUCTION

Charged, water-soluble polymers are potentially useful materials as ligands for transitionmetal molecules in homogeneous catalysis,¹ as carriers for biomolecules and drugs,² and as

Contract grant sponsor: National Science Foundation; contract grant numbers: ARI-9512258 and CTS-9632079. polyfunctional resins.³ Water-insoluble polymers that contain positively or negatively charged ionexchange groups can be fabricated into ion-exchange membranes for a variety of processes/devices including electrodialysis separations, electrochemical reactors, sensors, batteries, and fuel cells.⁴⁻⁶ To qualify as a membrane material, the polymer must combine a number of properties including chemical, thermal, and dimensional stability and a high concentration of fixed-charge groups.

Polyphosphazenes are a broad class of hybrid inorganic/organic polymers whose basic repeating unit is shown below:

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With appropriate functionalization of the -N=P- backbone with R_1 and R_2 side groups, a number of specialty polymers can be synthesized with properties tailored for a specific application. As a consequence of the stability and flexibility of the phosphorus-nitrogen backbone, polyphosphazenes have a low glass transition temperature and are reported to be resistant to thermal, chemical, and radiological degradation.⁷⁻⁹

There are several reports in the literature on the sulfonation of phosphazene polymers although none of these studies was directed at fabricating an ion-exchange membrane nor was the structure of the sulfonated polyphosphazenes examined in detail. The sulfonation of aryloxy- and (arylamino)phosphazenes via reaction with sulfuric acid was studied by Allcock and Fitzpatrick¹⁰ while the reaction of (aryloxy)polyphosphazenes with sulfur trioxide was studied by Montoneri and coworkers.^{11,12} During the initial stages of SO₃ addition, Montoneri et al. found no C-sulfonation, but, rather, the formation of a $\equiv N \rightarrow SO_3$ complex. When the SO₃/mer molar ratio was ≥ 1 , C-sulfonation was observed. A comprehensive review of the literature on sulfonated phosphazene polymers can be found in ref. 4.

In our previous study,⁴ two semicrystalline phosphazene polymers, poly[(3-methylphenoxy)-(phenoxy)phosphazene] and poly[(4-methylphenoxy)(phenoxy)phosphazene], with an alkylphenoxy/phenoxy molar ratio of 1.0, were sulfonated to varying degrees with SO₃. Water-insoluble cation-exchange membranes with good mechanical properties were fabricated with an ion-exchange capacity (IEC) as high as 2.0 mmol/g. Polyphosphazenes with an IEC in the range of 2-3 mmol/g were also synthesized, but these polymers were found to be water-soluble. Preliminary ¹³C-NMR and ¹H-NMR analyses indicated that the methylphenoxy side groups were sulfonated preferentially. When poly[(4-ethylphenoxy)(phenoxy)phosphazene] was sulfonated with SO_3 , the sulfonation rate was very slow (due to both steric interference by the ethyl substituents on the ethylphenoxy side groups and the poor reactivity of the phenoxy groups) and significant polymer degradation was observed.

It is obvious from the data in ref. 4 that methyl substituents on the phenoxy side chains of the phosphazene polymer were activating the ring for electrophilic attack by SO_3 . In the present article, we report on the sulfonation of poly[bis(3-methyl-phenoxy)phosphazene], a semicrystalline polymer with only methylphenoxy side groups. The reaction mechanism for polymer sulfonation, the crystalline structure (before and after sulfonation), and the physical and chemical properties of the sulfonated polymers were studied using polarized microscopy, DSC, WAXD, solid-state NMR, and IR techniques.

EXPERIMENTAL

Materials and Procedures for Polymer Sulfonation

Poly[bis(3-methylphenoxy)phosphazene], purchased from "technically" Inc. (Andover, MA), was used as the base polymer without further purification. The molecular weight of this polyphosphazene, as determined by gel permeation chromatography (Waters Styragel HT 6E column in THF), was 2.0×10^6 daltons.

To sulfonate the polyphosphazene, a known weight of polymer (1.0 g) was first dissolved in 40 mL of 1,2-dichloroethane (DCE) and stirred for 24 h at 50°C. A given amount of SO_3 in 10 mL of DCE was then added dropwise to the polymer solution in a dry nitrogen atmosphere. The resulting precipitate was stirred for 3 h at 0°C followed by the addition of 50 mL of a NaOH solution (water/methanol solvent) to terminate the reaction. After evaporation of the solvent at 70°C for 24 h, the polymer was preconditioned by soaking sequentially in distilled water, 0.1M NaOH, distilled water, 0.1M HCl, and distilled water (each soaking was for 48 h). The polymer product was then dried thoroughly and dissolved in N,N-dimethylacetamide (DMAc). Membranes were cast from this solution on a polypropylene plate and then dried at 70°C for 3 days. The thickness of the dry membranes was $\approx 200 \ \mu m$.

IEC and Equilibrium Swelling Measurements

The IEC (with unit of mmol/g of dry polymer) of sulfonated polyphosphazene membranes was determined by measuring the concentration of H^+

that was exchanged with Na⁺ when the membrane samples were equilibrated with a NaCl solution. A known weight of dry polymer (0.2-0.4 g)in acid form (after preconditioning) was placed into 100 mL of a 2.0*M* NaCl solution and shaken occasionally for 48 h. Three 25-mL samples were then removed and the amount of H⁺ released by the polymer was determined by titration with 0.01M NaOH.

Equilibrium water swelling of the sulfonated membrane samples at room temperature was quantified in terms of the percent increase in dry membrane weight, according to the following formula:

% swelling =
$$\frac{m_{\rm wet} - m_{\rm dry}}{m_{\rm dry}} \times 100$$
 (1)

where m_{wet} and m_{dry} are the weights of the water swollen and dry membrane (in its H⁺ form), respectively.

Polymer Characterization Procedures

IR measurements were made on films (approximately 200 nm in thickness) that were cast from either a DCE solution (base polymer) or a DMAc solution (sulfonated polymer). All films were preconditioned for 10 days, as described above, and were vacuum-dried for 48 h prior to performing an IR scan. The maximum absorption of the films was less than 1 absorbance unit and the spectra were within the linearity limit of the detector. A minimum of 100 scans at 4 cm⁻¹ resolution were obtained for each sample using a Mattson Instruments, Galaxy Series FTIR apparatus.

DSC measurements were carried out using a TA instruments DSC 2970 apparatus at a heating rate of 10°C/min, under a dry nitrogen atmosphere. Calibration was performed using indium.

Polymer specimens were examined by polarized microscopy (Carl Zeiss D-7082 microscope). Thin films were prepared by casting from either a DCE solution (base polymer) or a DMAc solution (sulfonated polymer) onto a glass plate. All films were dried at 70°C for 3 days.

¹³C solid-state NMR spectra were recorded on a Bruker ASX 400 MHz spectrometer. A sample spinning rate of 10 kHz and proton decoupling at a level of 45 kHz were employed under magic angle spinning (MAS) conditions using dipolar decoupling with cross-polarization. Tetramethylsilane was used as a reference for ¹³C.



Figure 1 IEC of sulfonated poly[bis(3-methylphenoxy)phosphazene] membranes as a function of the SO₃/POP molar ratio.

Wide-angle X-ray diffraction patterns were obtained using a Rigaku Model RU200B diffractometer operated at 55 kV and 190 mA with a nickelfiltered CuK_{α} X-ray beam. Diffraction data were collected from the cast films at a scan rate of 2.0°/min. The temperature was controlled to within ± 1.0 °C by a custom-made electrical heating device. For oriented polyphosphazene films, a flat photographic film camera was used to record Laue diffraction patterns at room temperature, where the exposure time varied from 30 to 60 min. The oriented films were mounted with the draw axis parallel to the camera axis and perpendicular to the X-ray beam.

RESULTS AND DISCUSSION

Polymer Sulfonation Studies

Membrane IEC and Water Swelling

The measured IEC of sulfonated poly[bis(3-methylphenoxy)phosphazene] polymer samples is plotted versus the SO₃/polyphosphazene (henceforth denoted as POP) mer molar ratio in Figure 1. When the SO₃/POP ratio was \leq 0.64, the IEC of the membranes was detectable, but very low (0.01–0.06 mmol/g). A gradual increase in the IEC was observed as the SO₃/POP ratio was increased from 0.64 to 1.92. The detection of a high IEC (0.95 mmol/g) at a SO₃/POP ratio of 0.96 for the bis(3-methylphenoxy) polymer confirmed our supposition that the methyl constituent on the methylphenoxy side groups was promoting aromatic ring sulfonation.



Figure 2 The reaction scheme for poly[bis(3-methylphenoxy)phosphazene] sulfonation with SO₃.

The overall reaction of SO_3 with poly[bis(3methylphenoxy)phosphazene] is shown in Figure 2, including the formation of a $\equiv N \rightarrow SO_3$ complex. During polymer preconditioning with NaOH and water, some or all of this complex is hydrolyzed and the resulting $\equiv N^+H \cdots HSO_4^-$ product is flushed from the sample. To determine the

amounts of \equiv N \rightarrow SO₃ and \equiv N⁺H \cdots HSO₄⁻ in the polymer for a given SO₃/POP ratio, NCHS elemental analysis of the sulfonated poly[bis(3methylphenoxy)phosphazene] membrane samples was performed (after preconditioning and before a NaCl soak for the IEC determination). From the hydrogen analysis, the polymer's IEC, and the calculation of hydrogens associated with aromatic and alkyl carbons, the concentration of the $\equiv N^+H \cdots HSO_4^-$ species was determined. The difference between the total sulfur content and the amounts of SO_3^- (equal to the measured IEC) and $\equiv N^+H \cdots HSO_4^-$ gave the concentration of the \equiv N \rightarrow SO₃ complex. The results of this analysis are presented in Table I. As the SO₃/POP molar ratio was increased during the polymer sulfonation, there was more aromatic ring C-sulfonation and a higher concentration of both $\equiv N \rightarrow SO_3$ and $\equiv N^+H \cdots HSO_4^-$. A 10-day polymer preconditioning in base, water, and acid was insufficient to hydrolyze all of the backbone $\equiv N \rightarrow SO_3$ complex, nor was it sufficient to flush all of the H_2SO_4 from the membrane (especially at high SO₃/POP molar ratios). The presence of the $\equiv N \rightarrow SO_3$ and $\equiv N^+H \cdots HSO_4^-$ species make the polymer more hydrophilic, which affects the polymer swelling in water, but they had essentially no bearing on the measurement of the polymer's IEC (the concentration of $\equiv N^+H \cdots$ HSO_4^- was so low that its decomposition and the elution of H_2SO_4 would affect the IEC by no more than 7%).

Only a fraction of the total added SO_3 produced sulfonate fixed-charge sites on the polymer. From a comparison of the SO_3 /POP mer molar ratios and the mol % C-sulfonation in Table I, the reaction yield for the SO_3^- site creation was deter-

Table I Elemental Analysis of Sulfonated Poly[bis(3-methylphenoxy)phosphazenes]

SO ₃ /POP Molar Ratio	Elemental Analysis (% w/w)					Mol %		
	IEC (mmol/g)	N	С	Н	S	Mol % C-sulfonation ^a	$\stackrel{=}{=} N \rightarrow SO_3$ Complex ^b	${ m Mol}\ \%$ $\equiv { m N}^+{ m H}^{ m b}$
0.64	0.04	5.361	64.334	5.361	0.327	0.52	1.63	_
0.96	0.95	4.748	56.973	4.787	4.726	14.0	9.86	5.75
0.96 ^c	0.95	4.870	58.445	4.893	3.880	13.6	4.43	3.18
1.28	1.69	4.357	52.289	4.407	7.576	27.1	13.9	7.97
1.60	2.10	4.172	50.067	4.224	8.941	35.2	14.7	8.63

^a Mol % of sulfo groups attached to methylphenoxy side groups, related to the total moles of methylphenoxy rings. ^b Related to total nitrogen functions. ^c Elemental analysis and IEC determination after additional membrane soaking for 6 days in NaCl, HCl, and water (48 h for each soaking).

SO ₃ /POP Molar Ratio	Membrane IEC (mmol/g)	Membrane Swelling (% Dry Membrane Weight)
0.64	0.04	5.0
0.80	0.80	25.0
0.96	0.95	42.0
1.28	1.69	230
1.6	2.1	900

Table IIEquilibrium Water Swelling of Sulfonated Poly[bis(3-methylphenoxy)phosphazene]Membranes at 25°C

mined (noting that there are two methylphenoxy groups per mer) and varied from a low of 1.6% at $SO_3/POP = 0.64$ to 44% at a SO_3/POP ratio of 1.6. These results are in agreement with the work of Montoneri et al.^{11,12} who found that backbone nitrogens in polyphosphazenes were attacked first by SO_3 and are also consistent with our previous sulfonation studies with poly[(3-methylphenoxy)(phenoxy)phosphazene],⁴ where no IEC was detected for a SO_3/POP ratio ≤ 0.8 .

The equilibrium swelling of sulfonated polyphosphazene membranes in water was found to be dependent on the SO₃/POP molar ratio (i.e., membrane IEC), as illustrated by the data in Table II. The base polymer prior to exposure to SO_3 was highly hydrophobic and did not sorb any water. Once the polyphosphazene contacted SO_3 (even at a low SO₃/POP molar ratio), water uptake was observed, due to the presence of the $\equiv N \rightarrow SO_3$ and $\equiv N^+H \cdots HSO_4^-$ species and a small number of sulfonic acid sites. As expected, the extent of polymer swelling increased with increasing IEC. Membranes prepared from the sulfonated polymers with a SO_3/POP ratio ≥ 1.92 (an IEC \geq 2.1 mmol/g) were found to be water-soluble. For comparison purposes, a sulfonated poly-[bis(3-methylphenoxy)phosphazene] membrane with an IEC of 0.95 mmol/g swelled 42% at room temperature, whereas a Nafion[®] perfluorosulfonic acid membrane (with an IEC of 0.909 mmol/g) swelled 34%.¹³

IR Spectroscopy

IR spectra of the base bis(3-methylphenoxy)phosphazene polymer and three sulfonated polyphosphazene samples (synthesized with different SO_3/POP molar ratios) are shown in Figure 3 for wavenumbers in the 600–1650 cm⁻¹ range. There was no obvious change in the P—O— methylphenoxy stretching band (at 1140 cm⁻¹) and the P—N

band (at 1243 cm⁻¹) for polymers sulfonated with a SO₃/POP ratio \leq 1.28. As expected, a new peak corresponding to S=O (at 1085 cm⁻¹) appears and grows with increasing SO₃/POP. At a SO₃/POP ratio of 1.92, the P=N band decreased slightly, which was attributed to some degradation of the polyphosphazene main chain.

IR spectra of a sulfonated POP membrane (synthesized with a SO_3/POP molar ratio of 0.96) that was preconditioned in the usual manner (48 h soakings each in water, base, water, acid, and water) prior to film casting and later soaked for another 6 days in NaCl, HCl, and water (48 h for each soaking) is shown in Figure 4. With additional soaking, the S=O peak (at 1085 cm⁻¹) decreased, but the measured IEC of the membrane was unchanged. A small stretching band at $3500\ \text{cm}^{-1}\text{,}$ which was associated with $\breve{N^{+}H}$ (from the $\equiv N^+H \cdots HSO_4^-$ complex) also decreased after prolonged soaking. Although we did not determine if all the complexed nitrogen species had been removed from the membrane after prolonged soaking, the IR results in Figure 4, in conjunction with the data in Table I, do indicate that both \equiv N \rightarrow SO₃ and \equiv N⁺H·····HSO₄⁻ are long-lived and surprisingly stable to hydrolysis conditions. We also found that the equilibrium swelling of a sulfonated membrane (with an IEC of 0.95 mmol/g) in pure water decreased from 42 to 36% after prolonged soaking, which provided additional evidence that the hydrophilic backbone nitrogen complexes had been neutralized.

NMR Spectroscopy

To determine the location of the SO_3 attack on the polyphosphazene's methylphenoxy side groups, ¹³C solid-state NMR spectra of the base and sulfonated polymers were collected, as shown in Figure 5. Six resonance peaks in the 100–180 ppm range were assigned to the six aromatic carbon

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P=N

-<u>0</u>-Ø

in the resonance signal of a sulfonated poly[bis(3methylphenoxy)phosphazene] for a SO₃/POP ratio \leq 1.92. For a poly[bis(3-methylphenoxy)phosphazene] sample sulfonated at a SO₃/POP ratio of 0.76, the C4 (*para* position) signal at $\delta = 125.9$ decreased significantly and shifted downfield by 14-15 ppm, producing an increase in the intensity of the C3 peak at 139.5 ppm (relative to the peak at 152.6 ppm). This observation, along with subsequent calculations, is consistent with paraposition sulfonation of the polyphosphazene's methylphenoxy side groups. Our finding here is in agreement with the prior work of Allcock and Fitzpatrick,¹⁰ who also found SO₃ attack at the para position of aromatic side groups of poly-[bis(3-ethylphenoxy)phosphazene]. When poly-[bis(3-methylphenoxy)phosphazene] was sulfonated at SO_3/POP molar ratios >1.0, the intensities of the four resonance signals for aromatic carbons at the C5, C4, C2, and C6 positions decreased significantly, indicating that all phenoxy carbons except C1 and C3 were undergoing SO₃ attack.

C6, $\delta = 119.9$ ppm. As compared to the nonsulfonated, base polymer, no new peaks were found

Physical Properties and Crystal Structure of the Polymers

IR Spectroscopy

IR spectra of nonsulfonated and sulfonated (0.95 mmol/g IEC) poly[bis(3-methylphenoxy)phosphazene] samples, after heating to various temperatures for 30 min in air, are compared to those of the unheated polymer in Figure 6 (all spectra were collected with the samples at room temperature). No changes were observed in the nonsulfonated polymer spectra for heat treatments up to 400°C. When the polymer was heated to 450°C, the P—O—Ø stretching peak (at 1145 cm⁻¹) retained its intensity but the P=N band at 1243 cm^{-1} decreased significantly and the aromatic C-C stretching bands between 1400 and 1600 cm^{-1} vanished. These results suggested that thermal decomposition of both the polymer main chain and aromatic rings occurred in the polyphosphazene at 450°C. In the case of the sulfonated polymer, the IR spectra remain unchanged for samples heat-treated up to 350°C. At 400°C, however, the intensities of the P=N, aromatic C-C vibrations, and S=O stretching bands decreased, with the eventual disappearance of these bands at 450°C. The IR data were found to be in



1200

1000

Wavenumbers (cm⁻¹)

800

nuclei on the methylphenoxy side groups: C1, δ = 152.6 ppm; C3, δ = 139.5 ppm; C5, δ = 129.8 ppm; C4, $\delta = 125.9$ ppm; C2, $\delta = 123.7$ ppm, and

(a)

(b)

(c)

(d)

1600

1400

Absorbance



Figure 4 IR spectra (750–1200 and 2400–3800 cm⁻¹ wavenumber ranges) for (a) preconditioned sulfonated polymer with an IEC 0.95 mmol/g and (b) the same polymer after additional soaking for 6 days in NaCl, HCl, and water (48 h for each soak).

good agreement with the thermogravimetric analysis (TGA) results of the sulfonated and nonsulfonated poly[bis(3-methylphenoxy)phosphazene] samples, which showed that the base polymer began to lose weight at 420°C while the sulfonated polymer exhibited a weight loss at 390°C.

DSC Analysis

The glass transition temperature (T_g) of the base polymer and the sulfonated poly[bis(3-methylphenoxy)phosphazene] samples, as determined from the DSC curves, is shown in Figure 7. The observed T_{σ} variation with the SO₃/POP molar ratio mimics the IEC plot in Figure 1. No change in the $T_{\rm g}$ was observed when the polymer was exposed to a low concentration of SO_3 (i.e., for SO_3 /POP \leq 0.64, where there is essentially no aromatic Csulfonation). The polymer's T_g increased monotonically with increasing IEC when the SO₃/POP molar ratio was > 0.64. The observed increase in the T_g is associated with electrostatic interactions among fixed-charge groups in the ionomeric portions of the polymer and the general incompatibility of charged domains and nonpolar polymer backbone (which can restrict polymer chain mobility and produce an increase in the T_g).^{14,15}

The first DSC heating scans of sulfonated samples of poly[bis(3-methylphenoxy)phosphazene] and the base polymer prior to SO_3 exposure are shown in Figure 8. For the nonsulfonated polymer and for polyphosphazene exposed to SO_3 but exhibiting essentially no IEC (i.e., for SO_3 /POP mo-



Figure 5 ¹³C solid-state NMR spectra of nonsulfonated and sulfonated poly[bis(3-methylphenoxy)phosphazene] membrane samples.



Wavenumbers (cm⁻¹)

Figure 6 IR spectra (500–1800 cm⁻¹ wavenumber range) of heated samples of nonsulfonated and sulfonated poly[bis(3-methylphenoxy)phosphazene] with an IEC of 0.95 mmol/g. The samples were held at the indicated temperature for 30 min and then cooled to 25°C to record the spectra.

lar ratios ≤ 0.64), two endothermic peaks are clearly visible in the heating curves. The two transitions for the base polymer are centered at 48.7°C (with an endothermic heat flow, ΔH , of 1.1 J/g) and 98.1°C ($\Delta H = 18.4$ J/g), whereas the

polymer exposed to small amounts of SO₃ exhibited endotherms at 49.8°C ($\Delta H = 5.5 \text{ J/g}$) and 96.8°C (ΔH =10.3 J/g). The high heat flow for the two endothermic peaks of the base polyphosphazene ($\Delta H = 19.5 \text{ J/g}$) is characteristic of a polymer



Figure 7 Glass transition temperature of sulfonated poly[bis(3-methylphenoxy)phosphazene] membranes as a function of the SO₃/polyphosphazene mer molar ratio.

with a 3-dimensional ordered phase, which was attributed to the symmetric nature of the polymer, where only 3-methylphenoxy side groups are substituted onto the P=N backbone. Although there was a decrease in both the ΔH for the upper transition endotherm and the total endothermic heat flow (15.8 J/g) of the polymer samples exposed to a low concentration of SO₃, most of the 3-dimensional crystal structure was retained.

The data in Figure 8 also show that the two sharp endothermic peaks vanish, with the appearance of a broad peak at 95°C, when the polymer sulfonation degree was high, indicating a substantial, but not complete, loss in the polymer crystal structure (this interpretation of the 95°C peak was confirmed by X-ray data, as described below). Preliminary SAXS experiments on the sulfonated poly-[bis(3-methylphenoxy)phosphazene] films showed ionic cluster formation; hence, the broad 95°C DSC peak was also due to an ionic aggregate order– disorder transition (a detailed presentation of the SAXS work will appear in a future publication).

X-ray Diffraction and Polarized Microscopy

X-ray diffractograms of the base polymer prior to sulfonation are shown in Figure 9(a,b) for different temperatures. The polymer was found to be semicrystalline at 25°C, with reflections centered at 12.72, 11.34, 8.08, 4.47, 4.22, 3.84, and 3.58 Å. At the low-temperature transition, between 25 and 65°C, all reflection intensities decreased significantly, except the two at 12.72 and 11.34 Å, which merged into a single peak at 11.79 Å. At a temperature of 100°C, which was above the second transition shown in the DSC curve of Figure 8, the main peak increased in intensity and moved to a lower diffraction angle at 12.11 Å, while all the other peaks smeared out into an amorphous hole at 4.55 Å. The intensity of the main peak continued to increase when the sample was heated to 200°C, with a further shift in the peak to a lower Bragg angle at 12.28 Å. From Laue photographs of the oriented base polymer films at 25°C, it was determined that the two main peaks in Figure 9(a) (at 11.34 and 12.72 Å) were equatorial, even if the degrees of orientation achieved were small. To a first approximation, the equatorial band was associated with reflections from intermolecular planes.

X-ray diffractograms of the nonsulfonated and sulfonated poly[bis(3-methylphenoxy)phosp-



Figure 8 DSC curves of nonsulfonated and sulfonated poly[bis(3-methylphenoxy)phosphazene]. For each peak, the transition temperature and transition enthalpy (in J/g) are given.



Figure 9 X-ray diffractograms of poly[bis(3-methylphenoxy)phosphazene], recorded at different temperatures. (b) is a magnification of the intensity axis of the spectra in (a) for $10-40^{\circ}$.

hazene] samples, collected at room temperature, are shown in Figure 10. As expected, all the diffraction peaks were retained for a minimally sulfonated polymer (prepared with a SO₃/POP molar ratio of 0.64), although the intensity of the peaks between 8.08 and 3.58 Å was reduced, indicating that the main crystal structure of the base polymer was retained. At a higher SO₃ concentration (SO₃/POP = 0.96), all diffraction peaks between 8.08 and 3.58 Å smeared out into an amorphous hole centered at 4.77 Å. Also, the two main peaks at 12.72 and 11.34 Å merged into a single peak at 11.54 Å. A further increase in the SO₃/POP molar ratio to 1.92 produced a significant decrease in the intensity of the main peak and a shift in the peak position to 11.56 Å.

It was concluded from the X-ray results that the two endothermic peaks in the DSC scans of the base and minimally sulfonated polymer samples were due to mesophase transitions, as has been reported in the literature for polysilane¹⁶ and other phosphazene polymers.^{17,18} The loss or decrease in intensity of intramolecular reflections for the base polymer at 65 and 100°C [Fig. 9(a,b)] suggested that the polymer's 3-dimensional crystal structure vanished, but the presence of an



Figure 10 X-ray diffractograms of the base polymer and sulfonated poly[bis(3-methylphenoxy)phosphazene] samples at 25°C.

intermolecular reflection at 11.79 Å (at 65°C) or 12.11 Å (at 100°C) indicated the retention of a two-ordered phase. A similar 2-dimensional ordered structure was found for highly sulfonated poly[bis(3-methylphenoxy)phosphazene] samples, as evidenced by the intermolecular reflection at 11.54 Å (or 11.56 Å) in Figure 10.

Polarized micrographs of nonsulfonated poly-[bis(3-methylphenoxy)phosphazene] samples (in Fig. 11) show crystalline areas (birefringent spots, 5–10 μ m in size), indicating that the polymer is semicrystalline. When the polymer was exposed to low concentrations of SO_3 (with a SO_3 / POP ratio of 0.64), most of the birefringent spots were retained, which was in agreement with the X-ray and DSC results discussed above. For polymers exposed to higher SO₃/POP molar ratios, a substantial decrease in the crystal areas of the polarized micrographs was observed, with the disappearance of almost all crystalline regions in a sulfonated polymer prepared with a SO₃/POP ratio of 1.92. It should also be noted that unlike poly[bis(trifluoroethoxy)phosphazene],¹⁹ a birefringent spherulitic crystal structure was not found in films of nonsulfonated poly[bis(3-methylphenoxy)phosphazene], although a wide range of membrane-casting conditions were examined, including different solvent evaporation temperatures, different casting surfaces, and various casting solution concentrations.

CONCLUSIONS

Poly[bis(3-methylphenoxy)phosphazene] was sulfonated in solution to varying extents with SO_3 . Water-insoluble ion-exchange membranes were fabricated from the sulfonated polymers with an IEC as high as 2.1 mmol/g. The glass transition temperature varied from -28° C for the base polymer to -10° C when the IEC was 2.1 mmol/g.

From the IR spectroscopy and HNCO elemental analysis of the sulfonated polyphosphazene membranes, both aromatic C-sulfonation and the formation of a \equiv N \rightarrow SO₃ complex occurred when the SO₃/phosphazene mer molar ratio was greater than 0.64. Most of the \equiv N \rightarrow SO₃ species was hydrolyzed to \equiv N⁺H · · · · · HSO₄⁻ during polymer preconditioning (i.e., soaking in an aqueous NaOH solution and in water). Both backbone nitrogen complexes were surprisingly stable and were detected after many days of membrane emersion in water. Their presence increased the hydrophilicity of the polymer but did not contribute to the membrane's IEC.

The location of SO_3 attack on the methylphenoxy rings of sulfonated poly[bis(3-methylphenoxy)phosphazene], as determined by solid-



Figure 11 Polarized microscopy photographs of the base polymer and sulfonated poly[bis(3-methylphenoxy)phosphazene] samples at 25°C: (a) base polymer; (b) sulfonated polymer with $SO_3/POP = 0.64$ (IEC = 0.001-0.006 mmol/g); (c) sulfonated polymer with $SO_3/POP = 0.96$ (IEC = 0.95 mmol/g); (d) sulfonated polymer with $SO_3/POP = 1.92$ (IEC = 2.2 mmol/g).

state NMR, was found to be in the *para* position when the sulfonation degree was low and was multipositioned when the sulfonation degree was high. The sulfonated bis-methylphenoxy polymer was thermally stable up to 350°C; above this temperature, the polymer's main chains and aromatic rings decomposed. The nonsulfonated base polymer was thermally stable up to 420°C.

Two mesophase transitions, between 40 and 100°C, were observed in the DSC heating curve of the base phosphazene polymer. The DSC data, wide-angle X-ray diffraction measurements, and polarized microscopy results indicated that poly-[bis(3-methylphenoxy)phosphazene] was a semicrystalline polymer, with a 3-dimensional ordered phase. The main crystal structure was unchanged when the polymer was exposed to low concentrations of SO₃. For polymers with an appreciable IEC (sulfonic acid content), the 3-dimensional crystal structure vanished, as noted by the loss of birefringent spots in the polarized micrographs and by the disappearance of all X-ray reflection peaks between 8.08 and 3.58 Å. For sulfonated

polymers, the presence of an X-ray peak at 11.54-11.56 Å (depending on the IEC), which was identified as an intermolecular reflection peak, and a broad peak in the DSC heating curves (centered at 95°C) indicated the presence of a 2-dimensional ordered phase.

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