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Influence of Bound Ion on the Morphology and Conductivity of Anion-Conducting Block Copolymers

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Abstract

Polystyrene-\textit{block}-polychloromethylstyrene (PS-\textit{b}-PCMS) copolymers, with molecular weights ranging from 4 to 60 kg/mol, were synthesized by nitroxide-mediated controlled radical polymerization. Separate aliquots of the PS-\textit{b}-PCMS samples were quaternized to transform the PCMS block. This resulted in block copolymers with ionizable blocks containing either trimethylammonium chloride or n-butylimidazolium chloride. We refer to ion-containing block copolymers synthesized from the same precursor as matched pairs: SAM (containing trimethylammonium chloride) and SIM (containing n-butylimidazolium chloride). The volume fraction of the ion-containing block, $\phi$, ranges from 0.26 to 0.50 for the case of SAM and from 0.35 to 0.60 for the case of SIM. Self-assembly in these copolymers resulted in the formation of lamellar phases regardless of $\phi$, chemical formula of the bound ion, and chain length. Chloride ion conductivity and water uptake measurements on one of the matched pairs led to similar results. In this matched pair, the changes in conductivity are reported as the chloride ions are replaced by hydroxide ions.

Keywords

Block copolymer, anion-conducting membranes, morphology, conductivity, water uptake
1. Introduction

Anion-conducting membranes are being extensively studied due to their potential application in fuel cells and artificial photosynthesis.\textsuperscript{1-3} While most of the work on fuel cells and artificial photosynthesis is focused on proton-based reactions, there are many advantages to consider devices that take advantage of the hydroxide anion.\textsuperscript{4} For example, catalysts for proton-based fuel cells are usually precious metals like platinum while catalysts for hydroxide-based fuel cells are non-precious metals like nickel.\textsuperscript{1, 5, 6} Both fuel cells and artificial photosynthesis devices require a membrane between the electrodes to physically separate the electrodes and transport the ion of interest from one electrode to the other. A common example of such a membrane is Nafion which is used in hydrogen fuel cells (proton-based).\textsuperscript{7, 8} These membranes are composed of polymer chains wherein a fraction of the monomers are charged. One of the charged species is covalently bound to the polymer chain while the other can dissociate and is thus mobile. In most cases, mobile counterions (either protons or hydroxide ions) are only obtained when the membrane is hydrated. It is difficult to work with polymers containing mobile hydroxide ions because most polymers degrade in their presence. In this paper, we focus on polymers with mobile chloride anions. The bound cations on our polymers are either trimethylammonium or n-butylimidazolium. Our choice of cations is motivated by previous studies suggesting that these cations lend stability to polymers with mobile hydroxide ions.\textsuperscript{6, 9, 10}

Virtually all polymer electrolyte membranes comprise co-continuous hydrophilic and hydrophobic domains. The hydrophilic domains provide channels for ion transport while the hydrophobic domains impart other properties to the membranes such as
structural integrity, chemical stability, ability to block the transport of certain gases, etc.

Block copolymers with a hydrophilic and a hydrophobic block may be considered as model polymer electrolyte membranes. The properties of the hydrophilic block can be tuned independently to enhance ion transport while those of the hydrophobic block can be tuned to optimize mechanical properties. While several papers have been written on the subject of proton transport in block copolymers,\textsuperscript{11-13} we are only aware of a few papers on the subject of anion transport in these systems.\textsuperscript{14,15}

Our study begins with the synthesis of a series of polystyrene-\textit{block}-polychloromethylstyrene copolymers (PS-\textit{b}-PCMS). The overall molecular weights of the block copolymers was varied from 4 to 60 kg/mol and mol fraction of the PCMS block was varied from 18 to 43 mol\%. We use simple chemical reactions to convert the PCMS block into either a poly(4-vinylbenzyltrimethylammonium chloride) (PVBTAmC) or poly(4-vinylbenzyl-n-butylimidazolium chloride) (PVBBImC) block. In most cases, separate aliquots of the PS-\textit{b}-PCMS precursor were converted into the PS-\textit{b}-PVBTAmC and PS-\textit{b}-PVBBImC. For simplicity, we refer to PS-\textit{b}-PVBTAmC as SAM and to PS-\textit{b}-PVBBImC as SIM. SAM and SIM copolymers originating from the same PS-\textit{b}-PCMS precursor are referred to as matched pairs. Matched pairs are identical to each other except for the nature of the bound ion. This enables a systematic study of the effect of the bound ion on the morphology and ion transport. Preliminary ion transport data obtained upon replacing the chloride ions by hydroxide ions is also presented.
2. Experimental

Materials

Styrene (S, 99.9%), 4-vinylbenzyl chloride (chloromethylstyrene, CMS, ≥90%), (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO, 99%), 2,2'-azobis(2-methylpropionitrile) (AIBN, 98%), n-butylimidazole (BuImid, 98%), anisole (99%), dimethylformamide (DMF, 99.8%), tetrahydrofuran (THF, 99.8%), methanol (99.8%) and deuterated solvents were purchased from Sigma-Aldrich. Trimethylamine (Me₃N, 7.3 M, 50 wt% aqueous solution) was purchased from Acros. All chemicals were used as received.

Synthesis of diblock copolymer, PS-b-PCMS

Polystyrene homopolymers were synthesized from the deoxygenated mixture of styrene, AIBN and TEMPO (molar ratio TEMPO:AIBN 2:1) at 125 °C under argon. TEMPO-terminated polystyrene (PS-TEMPO) powder was obtained after two precipitations into methanol and drying. PS-TEMPO as macronitiator, chloromethylstyrene as monomer and anisole as solvent were used to obtain block copolymers and they were purged with argon in a reactor, which was then placed in an oil bath thermostated at 125 °C (see Scheme 1). The polymerization of both PS and PCMS blocks was stopped at about 50% conversion of the monomers. We used this procedure to synthesize a variety of PS-b-PCMS block copolymers with molecular weights between 4 to 60 kg/mol and CMS mol fractions, $x_{CMS}$, ranging from 18 to 43%.¹⁶
After synthesis, the reaction solutions containing the PS-b-PCMS copolymers were diluted with THF, and polymers were isolated by two precipitations in methanol. The products were dried under vacuum at 60 °C resulting in white powders.

Scheme 1: Synthesis of PS-b-PCMS

Quaternization of block copolymers
The PS-b-PCMS diblock copolymers were then modified to obtain neutral-cationic diblock copolymers. The chloride group of the PCMS block was modified by reacting with either trimethylamine or n-butylimidazole as shown in Scheme 2. The procedure used here was reported by Stancik et al.\textsuperscript{17} PS-b-PCMS and n-butylimidazole (CMS:BuImid 1:2.5) were dissolved in DMF and refluxed at 80 °C for 3 days. DMF was then evaporated under reduced pressure. The obtained solid was immersed in water, filtered, and washed extensively with water. They were finally dried in a vacuum oven at 60 °C overnight.

A second type of cationic segment was obtained by stirring the block copolymer in a 50 wt% trimethylamine aqueous solution for 3 days. The polymer was then reprecipitated in isopropanol, filtered, and washed with water. The obtained ion-containing polymers were finally freeze-dried (>90% yield). Dry polymer samples of polystyrene-b-poly(4-vinylbenzyltrimethylammonium chloride) (SAM) and of
polystyrene-\(b\)-poly(4-vinylbenzyl-\(n\)-butylimidazolium chloride) (SIM) were then kept refrigerated in the dark until they were used.

SAM and SIM polymers synthesized from the same PS-\(b\)-PCMS block copolymer are referred to as matched pairs. Table 1 summarizes the characteristics of the polymers used this study.

![Scheme 2: Quaternization of PS-\(b\)-PCMS block copolymers. Protons borne by the various carbons of the polymer chains are labeled for NMR analysis purposes (\(a, b, a', b', c', d_{AM}, d_{IM}\)).](image)

*Gel permeation chromatography*

Polymer samples of PS-TEMPO and PS-\(b\)-PCMS were characterized to quantify their molecular weight distributions on a Gel Permeation Chromatography (GPC): Viscotek TDA 320 system with four Viscotec columns (300 mm \(\times\) 7.8 mm, T-6000,
5000, 4000, and 3000) at a flow rate of 1 mL/min with DMF as solvent at 30 °C. The GPC was calibrated using PS standards and the molecular weight of the PS block was determined from measurements on the PS-TEMPO samples. The polydispersity index (PDI) of these macroinitiators was always found to be below 1.15. GPC measurements on the PS-\textit{b}-PCMS samples were used to determine the PDI of the block copolymers. The PDIs of the block copolymers ranged from 1.12 to 1.44, in agreement with previous results reported in the literature.\textsuperscript{16}

![Figure 1: GPC traces of TEMPO-terminated PS homopolymer (11.4 kg/mol) and PS-\textit{b}-PCMS block copolymer (17.6 kg/mol)](image)

**Thermogravimetric analysis (TGA)**

Thermogravimetric analyses (TGA) were performed on a “tga Q20” instrument from TA Instruments under nitrogen flow rate of 100 mL/min. In the first step, the samples were heated from 30 °C to 110 °C at 10 °C/min and the temperature was
maintained at 110 °C for 1 hour. In the second step, the samples were cooled down to 30 °C at 10 °C/min and heated again at 10 °C/min until the temperature reached 600 °C.

\textit{1H Nuclear Magnetic Resonance (NMR)}

All of the NMR experiments were conducted on a 400 MHz Bruker AVB400 spectrometer. Typical NMR spectra (in chloroform-\textit{d}) obtained from PS-\textit{b}-PCMS are shown in Figure 2a. Styrene units exhibit peaks at 6.4-6.8 ppm (\textit{a}) and 6.9-7.3 ppm (\textit{b}); see Scheme 2 for labeling of protons. Chloromethylstyrene units exhibit peaks (\textit{a}’) and (\textit{b}’) at the same chemical displacement as (\textit{a}) and (\textit{b}), and an additional peak at 4.3-4.7 ppm (\textit{c}’). The mol fraction of CMS (\(x_{CMS}\)) in PS-\textit{b}-PCMS copolymers was calculated by the equation:

\[
x_{CMS} = \frac{\text{moles of CMS}}{\text{moles of CMS} + \text{moles of S}} = 2.5 \frac{\text{integrals of peak c'}}{\text{integrals of (peak a + a') + peak (b + b') + peak c'}/2}
\]

In Figures 2b and 2c, we show NMR spectra obtained from the matched pair based on the PS-\textit{b}-PCMS shown in Figure 2a.

\[\text{Figure 2: NMR spectrum of (a) PS-\textit{b}-PCMS, (b) SAM, and (c) SIM}\]
The NMR spectra also confirmed the quantitative modifications of the PCMS block. After modification with Me$_3$N, a new peak is obtained at 2.9-3.4 ppm ($d_{AM}$). After modification with BuImid, new peaks are obtained – in particular the one at 1.7-2 ppm ($d_{IM}$). Quantitative modifications were confirmed by comparing the integrals of $d_{AM}$ and of $d_{IM}$ with the integrals due to the aromatic protons at 6.3-7.4 ppm ($a$, $a'$, $b$ and $b'$).

Table 1 lists the diblock copolymer samples used in this study. Different samples are named as SAM or SIM followed by the nominal molecular weight of the PS block ($M_n$, kg/mol) and the nominal molecular weight of the unmodified PCMS block ($M_n$, kg/mol); $M_n$ is the number averaged molecular weight of the chains.

<table>
<thead>
<tr>
<th>$M_n$, PS (kg/mol)</th>
<th>$M_n$, PCMS (kg/mol)</th>
<th>PDI</th>
<th>$x_{CMS}$ (mol%)</th>
<th>Quaternizing reagent: Me$_3$N</th>
<th>Quaternizing reagent: BuIm</th>
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<tr>
<td>2.7</td>
<td>1.5</td>
<td>1.15</td>
<td>25</td>
<td>SAM(3-2)</td>
<td>SIM(3-2)</td>
</tr>
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<td>1.0</td>
<td>1.09</td>
<td>18</td>
<td>SAM(3-1)</td>
<td>SIM(3-1)</td>
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<tr>
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<td>1.17</td>
<td>24</td>
<td></td>
<td>SIM(3-1)</td>
</tr>
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<td>3.5</td>
<td>1.38</td>
<td>34</td>
<td>SIM(5-3)</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>3.7</td>
<td>1.18</td>
<td>36</td>
<td>SAM(5-4)</td>
<td></td>
</tr>
<tr>
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<td>3.5</td>
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<td>28</td>
<td>SIM(6-4)</td>
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</tr>
<tr>
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<td>SIM(27-21)</td>
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<td>1.45</td>
<td>43</td>
<td>SAM(27-30)</td>
<td>SIM(27-30)</td>
</tr>
</tbody>
</table>

Molecular weights of the PS blocks and polydispersity indices were obtained from GPC; molecular weights of the PCMS blocks, and mol fractions of CMS ($x_{CMS}$) by NMR. The last two columns are the names used in the following sections for each sample.
Small Angle X-ray Scattering

1 mm thick SAM and SIM samples were prepared by hot-pressing at 145 °C. Synchrotron Small-Angle X-ray Scattering (SAXS) measurements were performed using either the 7.3.3 beam line at the Advanced Light Source (ALS, Lawrence Berkeley National Laboratory), or the 1-4 beam line at the Stanford Synchrotron Radiation Lightsource (SSRL, SLAC National Accelerator Laboratory). At the ALS, the wavelength $\lambda$ of the incident X-ray beam was 0.124 nm ($\Delta\lambda/\lambda = 10^{-4}$) and sample-to-detector distance of 2 m was used. At SSRL, $\lambda = 0.1488$ nm ($\Delta\lambda/\lambda = 10^{-3}$) and sample-to-detector distance of 1 m was used. The resulting two-dimensional scattering data were averaged azimuthally to obtain intensity versus magnitude of the scattering wave vector $q$ ($q = 4\pi \sin(\theta/2)/\lambda$, where $\theta$ is the scattering angle). The scattering data were corrected for the detector dark current and the scattering from air and Kapton windows.

Electrochemical impedance spectroscopy

In-plane chloride conductivity of hydrated membranes with dimensions 2 cm × 1 cm × 450 µm was measured by AC impedance spectroscopy using platinum electrodes in the standard four probe configuration using a BekkTech sample clamp. The samples were immersed in a temperature controlled water bath. Data were collected using a 10 mV amplitude over a frequency range of 1 Hz–10 MHz. Separate experiments were conducted to ensure that the response of the sample was linear in this window. Samples were annealed at the temperature of interest for 24 to 48 hours until the measured impedance did not change. Conductivity, $\sigma$, is given by

$$\sigma = \frac{w}{rS}$$
where $S$ is the cross-sectional area of sample film, $r$ is the intercept of the Nyquist semi-circle on the real axis ($\Omega$), and $w$ is the distance between the inner platinum electrodes.

Water uptake

450 μm thick polymer films were prepared by hot-pressing. The films were dried in a vacuum oven at room temperature until the weight of the film was constant. The dry sample weights were measured immediately after they were removed from the vacuum oven. The films were then immersed in water in a sealed vial and the vial was placed in an oven at the temperature of interest. A minimum of 48 hours was used to ensure equilibration at each temperature. The first measurements of water uptake were conducted at 66 °C. The mass of the film was measured after removing the excess water from the sample and the film was returned to the vial containing water. The vial was then placed in the oven and the water uptake measurements were repeated as a function of decreasing temperature. The degree of hydration, $\lambda_W$, defined as the moles of water per mole of cationic groups in the membrane, is calculated using:

$$\lambda_W = \frac{[H_2O]}{[AM] \text{ or } [IM]} = \frac{\text{hydrated film weight}-\text{dry film weight}}{\text{dry film weight}} \times \frac{M_{\text{FB}} + (x_{c_{\text{CMS}}}^{-1} - 1)M_S}{M_W}$$

where the molar mass of water and of the styrene (S), vinylbenzyltrimethylammonium chloride (AM) and vinylbenzyl-n-butylimidazolium chloride (IM) monomers are $M_W = 18.02$ g/mol, $M_S = 104.15$ g/mol, $M_{\text{AM}} = 211.73$ g/mol and $M_{\text{IM}} = 276.80$ g/mol. The subscript FB in the definition of $N$ stands for functional block (either AM or IM).

Galvanodynamic measurements

Through-plane anion conductivity was measured using galvanodynamic measurements using the H-cell setup, as presented by Slade et al.\textsuperscript{18} In this measurement
cell, the membrane is placed between two reservoirs and a small sinusoidal current is applied and the resulting voltage is measured. SAM and SIM membranes with chloride as counterion were obtained by hot-pressing. The membranes were equilibrated in Milli-Q water prior to being placed in the H-cell. 0.5 M sodium hydroxide solution was added in both reservoirs. The experiment, conducted at 22 °C, was started immediately. Current cycles were conducted between -5 and +5 mA at a rate of 0.1 mA/s using a Solartron Analytical 1287 Electrochemical Interface. This implies a cycle time of and 1000 s. The measured voltage was in phase with the applied current and the resistance of the membrane was determined by a linear fit of voltage versus current for each cycle. The measured cross sectional area and the thickness of the membranes were used to obtain the conductivity.

3. Results and Discussion

The volume fraction of the ion-containing block in SAM and SIM samples, $\phi_{AM}$ and $\phi_{IM}$, respectively, were calculated using pure component densities of PS, $\rho_{PS} = 1.080$ g/cm$^3$, poly(4-vinylbenzyltrimethylammonium chloride) (PAM), $\rho_{PAM} = 1.325$ g/cm$^3$, and poly(4-vinylbenzyl-n-butylimidazolium chloride) (PIM), $\rho_{PIM} = (1.110 \pm 0.003)$ g/cm$^3$, ignoring volume changes of mixing. The value of $\rho_{PIM}$ was measured in our laboratory.

Results of thermogravimetric analysis (TGA) of PS-b-PCMS(27-21), SAM(27-21) and SIM(27-21) are shown in Figure 3. The experiments are conducted in two steps. In the first step, samples were heated from 30 to 110 °C and the data thus obtained is shown in the inset of Figure 3. Weight loss recorded during this step is attributed to trapped water. The water content of SAM(27-21) was 4 wt% while that of SIM(27-21)
was 2 wt%. No weight loss was observed during the first step in any of the PS-\textit{b}\-PCMS samples. In the second step, samples were heated from 30 to 600 °C and the data thus obtained are shown in Figure 3. The SAM and SIM copolymers exhibit a two-step degradation process: degradation of the ionic species that begins at about 200 °C and degradation of the remainder of the polymer that occurs at about 350 °C. The PS-\textit{b}\-PCMS sample degrades in one step with an onset temperature of about 350 °C. TGA experiments were conducted on all of the samples listed in Table 1. The maximum water content observed in the SAM and SIM copolymers was 8 wt%. The mean water contents observed in the SAM and SIM copolymers were 5 and 3 wt%. The degradation characteristics of all of the samples were similar to that shown in Figure 3.

Films of SAM and SIM block copolymers were prepared by hot-pressing at 145 °C and then annealed in a vacuum oven for 4 hours at 130 °C. The extent to which this procedure results in equilibrated morphologies is not clear as the glass transition temperatures of the ionic blocks are well above the degradation temperature. However,
130 °C is above the glass transition temperature of PS. SAXS experiments were conducted between 28 and 150 °C. In no case did we observe changes in the SAXS profile. We thus only report data obtained at 28 °C. Figure 5 shows SAXS profiles obtained from SAM copolymers. All of the profiles contain a primary peak at scattering vector \( q = q^* \). This enables the determination of the domain spacing \( d = 2\pi/q^* \), which changes from 8 to 40 nm in our samples. In addition to the primary peak, high order peaks or shoulders are seen in all cases. The primary peak and the higher order peaks are indicated by inverted solid triangles (\( \nabla \)). The higher order peaks occur at integral multiples of \( q^* \) (2\( q^* \), 3\( q^* \), 4\( q^* \), etc.). The locations of the higher order peaks indicate that all of the SAM samples are lamellar.
Figures 5: SAXS profiles of SAM samples as a function of polymer characteristics. The inverted triangles indicate the locations of the primary and higher order peaks at integral multiples of $q^*$. The scattering profiles are shifted vertically for clarity.
Figure 6 shows SAXS profiles obtained from SIM copolymers. The SAXS profiles of SIM copolymers are very similar to those of SAM copolymers (compare Figures 5 and 6). Higher order peaks corresponding to a lamellar phase are also seen in the SIM copolymers. In the case of SIM(6-4), higher order peaks at $2q^*$ and $4q^*$ are missing and their expected locations are indicated by grey inverted triangles in Figure 6. We attribute this due to the minima in the form factor of lamellae [$\phi = 0.5$ for SIM(6-4)]. The higher order peak at $5q^*$ is also missing for SIM(11-6). We have no explanation for this observation. A notable difference between SAM and SIM is that the peak widths obtained for SIM copolymers are significantly less than those of SAM copolymers (compare Figures 5 and 6).
Figures 6: SAXS profiles of SIM samples as a function of polymer characteristics.

The inverted black triangles indicate the locations of the detected primary and higher order peaks at integral multiples of $q^*$. The grey triangles indicate the location of the missing higher order peaks. The scattering profiles are shifted vertically for clarity.
The dependence of domain size, $d$, on chain length, $N$, of SAM and SIM is shown in Figure 7 and 8. $N$ was calculated using $N = \left( \frac{v_S}{v_0} \right) N_{PS} + \left( \frac{v_{FB}}{v_0} \right) N_{FB}$ based on a reference volume, $v_0$, of 0.1 nm$^3$ and where the volume of the styrene (S), vinylbenzyltrimethylammonium chloride (AM) and vinylbenzyl-n-butylimidazolium chloride (IM) monomers are $v_S = 0.179$ nm$^3$, $v_{IM} = 0.414$ nm$^3$ and $v_{AM} = 0.265$ nm$^3$.\textsuperscript{20} The subscript FB in the definition of $N$ stands for functional block (either AM or IM).

![Figure 7: Variation of the domain size $d$ of SAM block copolymer samples as a function of the number of monomers $N$.](image)
For matched pairs, the domain size of SIM is always slightly smaller than that of SAM. In the usual case of uncharged block copolymers of a fixed composition, the domain size is proportional to $N^{2/3}$. The power law fits to the data in Figures 7 and 8 give $d = 0.168 \times N^{0.88}$ for SAM and $d = 0.160 \times N^{0.86}$ for SIM. In principle, power laws are only applicable at fixed block copolymer compositions. Corrections for the fact that the compositions of the block copolymers discussed in Figures 7 and 8 are not fixed can be made using the theory of Leibler. These corrections have a negligible effect on the power laws given above. It is evident that SAM and SIM exhibit significantly larger extents of chain stretching than that expected from uncharged random coil block copolymers.
The observed phase behavior for SAM copolymers is summarized in Figure 9a. The abscissa of this figure is the volume fraction of the ionic block $\phi_{AM}$. The ordinate in Figure 9a is an estimate of segregation strength. In Leibler’s theory, $\chi N$ at the ODT is a constant that depends on $\phi$:

$$\chi_{i,j}N = c(\phi),$$

where $\chi_{i,j}$ is the Flory-Huggins interaction parameter between block $i$ ($i = S$) and $j$ ($j = AM$ or $IM$), and $c$ has different values depending on $\phi$, e.g., $10.5$ when $\phi = 0.5$. The SAM sample with the lowest segregation strength is SAM(3-1) and we know that this sample is ordered in our temperature window. We define $\chi_{S-AM,L}$ by the following equation:

$$\chi_{S-AM,L} = c(0.28)/N_{SAM(3-1)} = 17/86.5 = 0.197$$

where $N_{SAM(3-1)}$ is the value of $N$ for SAM(3-1). $\chi_{S-AM,L}$ represents the lower limit for $\chi$ between the S block and the AM block. The ordinate in Figure 9a is $\chi_{S-AM,L}N$ of the SAM copolymers. It is interesting to note in Figure 9a that for $\phi$ values between 0.26 and 0.5, and for $\chi_{S-AM,L}N$ values from 17 to 118, we obtain lamellar phases. This behavior is very different from uncharged block copolymers. It is also very different from polymers with mobile cations.

We also conducted the analysis described above for the SIM copolymers and the results are shown in Figure 9b where $\chi_{S-IM,L}N$ is plotted versus $\phi$, where $\chi_{S-IM,L}$ was found equal to 0.097. The SIM sample with the lowest segregation strength is SIM(3-2) and we know that this sample is ordered in our temperature window, and $c(\phi) = c(48.8) = 10.8$. For SIM samples, $\phi$ values lie between 0.35 and 0.60 and $\chi_{S-IM,L}N$ varies from...
10.8 to 70. As was the case with SAM, we observe lamellar morphologies for all of the SIM samples.

Figure 9: Phase behavior of (a) SAM and (b) SIM copolymers. Abscissa is volume fraction of ion-containing block, ordinate is the lower bound of the segregation strength between the ionic and non-ionic blocks. L signifies the lamellar phase that was found to exist in all samples.

The in-plane conductivity, \( \sigma \), of SIM(27-21), immersed in water, was measured as a function of increasing temperature. In Figure 10a, we show \( \sigma \) as a function of time after the sample temperature was changed from 25 to 40 °C. It is evident that \( \sigma \) increases in response to this temperature change and a stable value is obtained after 48 hours. To ensure equilibration, we waited for 48 hours before conducting our measurements at each temperature. The open circles in Figure 10b show the stable \( \sigma \) values of SIM(27-21) as a function of inverse temperature at temperatures between 22 and 72 °C. Note that this experiment required about 10 days for completion. After completion of this run, the sample temperature was decreased to 22 °C and SIM(27-21) was reexamined as a function of increasing temperature. The filled circles in Figure 10b show stable \( \sigma \) values obtained during this second run. It is clear that the measured
conductivity of SIM(27-21) in the second run is significantly higher than that obtained in the first run. The protocol described above was repeated for SAM(27-21). The conductivities obtained during the first run, shown by open diamonds, are in reasonable agreement with those obtained during the second run, shown by filled diamonds. In addition, the data obtained from the second run on SIM(27-21) are in agreement with those obtained from both runs on SAM(27-21). This suggests that the chloride ion conductivity of hydrated SAM and SIM matched pairs is independent of the chemical structure of the bound cation. The straight line in Figure 10b is the least squares fit through the equilibrated conductivity data [second run on SIM(27-21) and both runs on SAM(27-21)].
Figure 10: (a) Conductivity as a function of time after the sample temperature was changed from 25 °C to 40 °C for SIM(27-21). (b) Conductivity as a function of inverse temperature for the SAM(27-21) and SIM(27-21) matched pair.

The water uptake data for the matched pair SAM(27-21) and SIM(27-21) under equilibrated conditions is shown in Figure 11. In both cases the degree of hydration $\lambda_W$ is a weak function of temperature, increasing from a value about 28 at 25 °C to 32 at 66 °C. To a good approximation, $\lambda_W$ is about 30 in the temperature range of interest. In principle, the change in conductivity with temperature reported in Figure 10b can arise to changes in mobility in chloride ions or a change in ion concentration in the membrane. The fact that ion concentration in the membrane is constant indicates that the slope of the line in Figure 10b provides an estimate of the activation energy for transport of chloride ions through the membranes (Arrhenius law). The estimated activation energy is 22.7 kJ/mol, which is comparable to the value found by Ye et al.\textsuperscript{25},
17.1 kJ/mol, for the hydroxide conductivity at 90 % relative humidity of pure poly(1-
[(2-methacryloyloxy)ethyl]-3-butylimidazolium hydroxide).

Figure 11: Degree of hydration as a function of temperature for the matched pair

\[ A \] and \[ B \].

We conclude this section by describing preliminary results on the properties of the SAM and SIM membranes after the chloride ions are replaced by hydroxide ions. In these experiments, the through-plane conductivity of SAM(27-21) and SIM(27-21) membranes is measured as a function of time using an H-cell setup in the presence of 0.5 M NaOH. The time dependence of the conductivity measured during these experiments is shown in Figure 12. Based on elementary electrochemistry, we expect the chloride ions to be replaced by the hydroxide ions during this experiment. The through plane conductivities measured in these experiments at early times are substantially lower than the in-plane conductivities reported in Figure 10b. This is commonly observed in polymer electrolyte membranes and the difference between in-
plane and through plane conductivities is generally attributed to the non-random orientation of the domains in the membranes. On the time scale of about 3 hours, the conductivity of SAM(27-21) and SIM(27-21) membranes increases dramatically by a factor of about -10. It is well-known that hydroxide ions diffuse by the Grotthuss mechanism while chloride ions do not.\textsuperscript{26, 27} We thus expect an increase in conductivity as chloride ions in SAM and SIM are replaced by hydroxide ions. The data in Figure 12 indicate that upon completion of the ion-exchange process, the conductivity of both SAM and SIM increase by a factor of 10. The ratio of the diffusion coefficients of hydroxide and chloride ions in water is $D_{\text{OH}^-}/D_{\text{Cl}^-} \approx 3$.\textsuperscript{28} The fact that we observe larger changes in conductivity suggest changes in other factors such as counterion condensation, degree of hydration, etc. On the time scale of 100h, we see a small decrease in conductivity for SIM(27-21). This may be due to degradation of the membrane or the presence of carbonate ions due to contact with atmospheric CO$_2$. While much work remains to be done, these preliminary results indicate the promise that SAM and SIM membranes hold for applications that require the transport of hydroxide ions.
Figure 12: Conductivity of SAM(27-21) (○) and SIM(27-21) (●) as a function of time as the chloride ions are replaced by hydroxide ions.

Conclusion

Polystyrene-block-polychloromethylstyrene (PS-b-PCMS) copolymers, with molecular weights ranging from 4 to 60 kg/mol, were synthesized by nitroxide-mediated controlled radical polymerization, followed by quaternization to transform the PCMS block into an ionizable block. We studied two kinds of ionizable blocks with mobile chloride ions: trimethylammonium and n-butylimidazolium. Most of the block copolymers used in this study were quaternized in pairs starting from the same PS-b-PCMS precursor. We refer to these as matched pairs SAM (trimethylammonium) and SIM (n-butylimidazolium). The n-butylimidazolium ion is significantly larger and more hydrophobic than the trimethylammonium ion. We expect these factors to affect the self-assembly of the block copolymers. In particular, we find that the volume fraction of the ion-containing block, \( \phi \), ranges from 0.26 to 0.50 for the case of SAM and from
0.35 to 0.60 for the case of SIM. Regardless of $\phi$ and chain length, we obtained lamellar phases in these samples. The scaling of domain size with chain length is only weakly dependent on the nature of the bound cation. Conductivity and water uptake measurements were completed for one matched pair SAM(27-21) and SIM(27-21). The SIM copolymer equilibrates more slowly when exposed to liquid water than SAM copolymer. While 48 hours annealing times are adequate for equilibrating SAM in the temperature range of interest, this annealing protocol does not lead to equilibrated SIM samples at low temperature. In spite of the differences in $\phi$ and hydrophobicity of the bound cation, the conductivity and water uptake of equilibrated SAM(27-21) and SIM(27-21) are similar. Preliminary experiments indicate that replacing the chloride ions by the hydroxide ions increases the conductivity of the membranes by a factor of 10.

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References


