# Influence of Anion Exchange in Self-Assembling of Polymeric Ionic Liquid Block Copolymers

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ABSTRACT: A new technique for the modification of lamellar domain sizes in polymeric ionic liquid block copolymers has been proposed. Anion exchange in polymeric ionic liquids opens new ways to modify the sizes of lamella domains without modifying the ratio between the two different blocks of the neat copolymer. This study focuses on the influence of quaternization of poly(2-vinylpyridine) in poly(styrene-b-2-vinylpyridine) (PS-b-P2VP) and the effect of anion exchange in the nanostructured phases for thin films. The resulting materials obtained from the quaternization modification technique of the block copolymers and the anion exchange of the polymeric ionic liquid were characterized with Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and nuclear magnetic resonance (NMR). Furthermore, morphological characterization of the initial block polymer and several polymeric ionic liquid block copolymers has been carried out by atomic force microscopy (AFM) in order to analyze the influence of the anion in the nanostructures of these block copolymers.
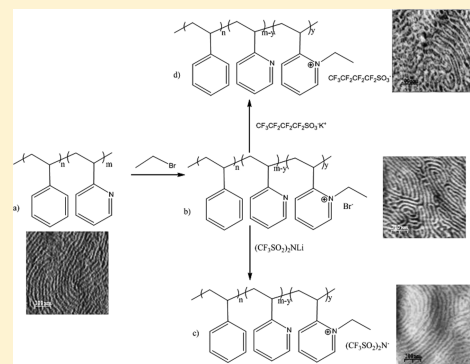
INTRODUCTION

Block copolymers have been a subject of extensive research as a consequence of their ability to self-organize at the nanometer scale. Microphase separation at the mesoscopic scale is generated by the repulsion between the different covalently linked blocks. A wide variety of nanostructures can be generated depending on the nature of the blocks, molecular weight, composition, and the processing characteristics. This has opened a wide application field range for block copolymers, where a regular and tunable periodicity is required.[1−10]

On the other hand, ionic liquids (IL) are organic salts exhibiting low melting point. They have currently received an increasing attention due to their unique physicochemical properties. ILs are chemically composed of an organic asymmetric cation (e.g., imidazolium, pyridinium, or tetraalkylammonium) and an inorganic anion such as halide, tetrafluoroborate, hexafluorophosphate, triflate, amidotriflate, etc.[11−19] Polymeric ionic liquids (PILs) made out of ionic liquids are described as a new class of polymers, combining the characteristics mentioned above. PILs can be used in emerging areas such as biosensors, supports for catalysts, polymeric surfactants for the construction of porous polymers, high CO_2 absorbing resins, polymer electrolytes for electrochemical devices, and microwave absorbing materials.[20−26] The solvents and sensitivity of PILs and IL-based random copolymers have already been widely demonstrated,[27,28] while in contrast, only a few reports have been described for block copolymers consisting of PIL block, referred to as IL-based block copolymers.[29−32]

This study focuses on the investigation of the influence of quaternization of poly(2-vinylpyridine) in poly(styrene-b-2-vinylpyridine) (PS-b-P2VP) and the effect of anion exchange in the nanostructured phases in thin films based on a block copolymer and their corresponding polymeric ionic liquids. Scheme 1 shows a schematic representation for the quaternization of PS-b-P2VP and several anion exchanges that were carried out in order to obtain different types of polymeric ionic liquids based on a block copolymer. The resulting materials obtained from the quaternization modification technique of the block copolymers and the anion exchange of the polymeric ionic liquid were characterized with Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and nuclear magnetic resonance (NMR). Furthermore, morphological characterization of the neat block polymer and several PILs has been carried out by atomic force microscopy (AFM) in order to analyze the influence of anion in the nanostructures of these block copolymers

EXPERIMENTAL PART

Materials. Bis(trifluoromethylsulfonyl)imine lithium salt, potassium hexafluorophosphate, nonafluoro-1-butanesulfonic acid potassium salt, bromoethane, deuterated chloroform, deuterated dimethyl

Scheme 1. Schematic Representation of the Synthesis of the Polymeric Ionic Liquid Block Copolymers: (a) PS-*b*-P2VP, (b) PS-*b*-[P2VP-*r*-poly(ViEtPy$^+$Br$^-$)] (poly(1)), (c) PS-*b*-[P2VP-*r*-poly(ViEtPy$^+$(CF$_3$SO$_2$)$_2$N$^-$)] (poly(2)), and (d) PS-*b*-[P2VP-*r*-poly(ViEtPy$^+$(CF$_3$(CF$_2$)$_3$SO$_3$$^-$)] (poly(3))
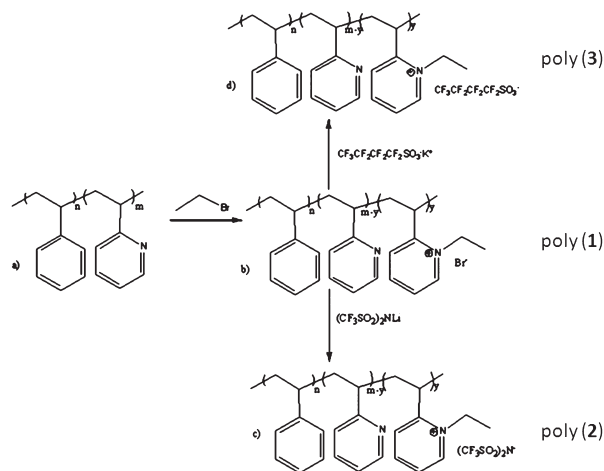

sulfoxide, calcium hydride (CaH$_2$, purity 95%), *sec*-butyllithium (*sec*-BuLi, 1.4 M in cyclohexane solution), dibutylmagnesium (1 M solution in heptanes), 2-vinylpyridine (2-VP, 97%), and triethylaluminum (TEA, 25% in toluene) were purchased from Sigma-Aldrich. Tetrahydrofuran (THF, purity 99.99%) and *n*-hexane (95%) was purchased from Fisher Scientific, styrene (St, 99%) from Acros Organics, methanol (MeOH) (99.9%, analytical grade) from Fluka, and chloroform from Scharlab.

Synthesis of the Block Copolymers. The synthesized copolymers were diblock copolymers of the PS-*b*-P2VP type [PS: polystyrene and P2VP: poly(2-vinylpyridine)] via anionic polymerization using high vacuum techniques by sequential addition of the monomers.[33−37] All the reactants used were purified according to the standard methods required for anionic polymerization which have already been reported in the literature.[33,34]

Tetrahydrofuran, the solvent for the polymerization, was purified via freezing−degassing cycles in the presence of calcium hydride and distillation in a sodium/potassium alloy (Na/K: 1/3). The initiator *sec*-butyllithium (*sec*-BuLi) was diluted in purified hexane, in a specific glass apparatus. The first monomer, styrene (St), was purified according to the literature via calcium hydride and dibutylmagnesium and last distilled in precalibrated ampules. 2-Vinylpyridine (2-VP) was purified via calcium hydride (twice), distilled in at least two consecutive sodium mirrors, then in triethylaluminum (TEA), and finally collected through distillation in several precalibrated ampules. During the anionic polymerization procedure the purified 2-VP was stored at −196 °C through liquid nitrogen in order to avoid any side reactions. For termination, methanol was used, which was purified after freeze−degassing cycles and distilled in precalibrated ampules as well.

Styrene was distilled in the purified polymerization reactor before adding the initiator into the mixture to obtain an orange-colored solution due to the PS$^{(-)}$Li$^{(+)}$ living ends. Afterward, the system was stirred for ∼1 h at −78 °C using a bath of 2-propanol and liquid nitrogen. 2-Vinylpyridine was again added via distillation into the mixture, and as the polymerization of the second monomer initiated, a red color appeared due to successful polymerization of the 2-VP. The mixture was allowed under stirring for ∼1 h at −78 °C. Finally, a small quantity of methanol was added for termination of the living ends, and the red color disappeared. The polymer solution was then precipitated into hexane, dried, and stored under vacuum in sealed ampules.
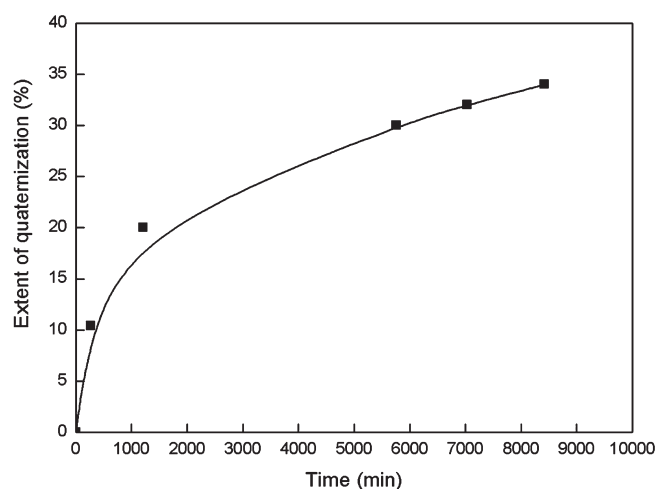
Synthesis of the Polymeric Ionic Liquid. Polystyrene-*b*-[P2VP-*r*-poly(1-ethyl-2-vinylpyridinium bromide)] (poly(1)) was
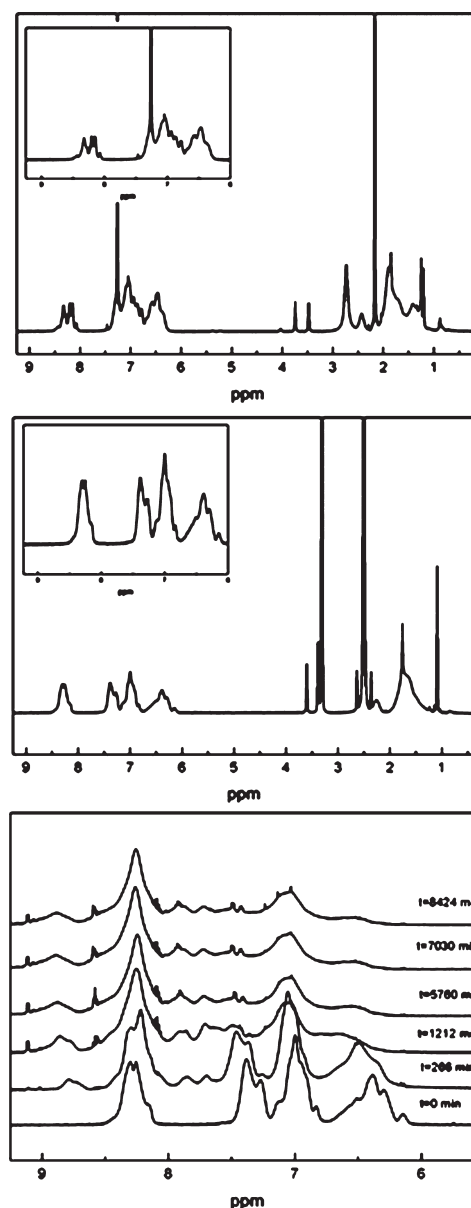
Figure 1. ^{1}H NMR spectra of neat PS-*b*-P2VP in CDCl$_3$ (top), PS-*b*-P2VP in DMSO-d_6 (center), and poly(1) in DMSO-d_6 spectra for quaternization kinetics (bottom).

prepared following the procedure described in the literature.[38,39] Under vigorous stirring, 1.2 mL of bromoethane was added to 0.5 g of PS-*b*-P2VP in a round-bottom flask. The mixture was refluxed for 16 h. Samples were withdrawn, at timed intervals, from the flask using syringes for kinetic assays. The resulting yellowish solid was allowed to cool down to room temperature and then washed several times with ethyl acetate. The product was isolated and dried at 50 °C under vacuum.

Procedure for the Anion Exchange Method. To prepare both polystyrene-*b*-[P2VP-*r*-poly(1-ethyl-2-vinylpyridinium bistrifluoromethane-sulfonimide)] (poly(2)) and polystyrene-*b*-[P2VP-*r*-poly(1-ethyl-2-vinylpyridinium nonafluoro-1-butanesulfonic acid)] (poly(3)), a solution of 0.30 g of respectively bis(trifluoromethylsulfonyl)imide lithium salt and nonafluoro-1-butanesulfonic acid potassium salt was dissolved in 5 mL of distilled water in a round-bottom flask. A solution of 0.15 g of poly(1) with a 20% quaternization extent, corresponding to 960 min, in 5 mL of distilled water was added to the previous salt solution. After

Figure 2. Extent of quaternization versus time of reaction of neat PS-*b*-P2VP.

Figure 3. FTIR spectra (top) of (a) PS-*b*-P2VP, (b) poly(**1**), (c) poly(**2**), and (d) poly(**3**).

30 min of stirring at room temperature, the resulting yellowish solid was isolated, and then the formed PILs were washed several times with water and dried at 50 °C under vacuum.

Techniques. ^{1}H NMR experiments were performed on a Bruker AVANCE III spectrometer at 500 MHz. Samples were measured at room temperature in CDCl₃ and DMSO-*d₆*.

For the size exclusion chromatography (SEC) measurements the instrument used involved a PL-120 SEC system equipped with three PL gel columns and an RI (refractive index) detector. Dimethylformamide (DMF) was used as the eluent at 60 °C. The temperature was raised in the SEC instrument in order to enhance the solubility of the P2VP segments in the specific eluent and to avoid any segregation phenomena in the columns during the measurements. The detailed setup of the instrumentation is described elsewhere.[40]

TGA was performed with a TA Instruments TGA Q500 under nitrogen atmosphere at a heating rate of 10 °C/min from room temperature to 800 °C.

FTIR spectra were recorded at room temperature on a Nicolet Avatar 360 spectrophotometer. All samples were cast directly onto KBr pellets. A 4 cm^{-1} resolution in a wavenumber range from 4000 to 400 cm^{-1} was used.

AFM images of the samples were obtained in a tapping mode at room temperature using a scanning probe microscope (Molecular Imaginǵs PicoScan) equipped with a Nanosensors tips/cantilever, a resonance frequency of ∼330 kHz, and a spring constant of about 42 N/m with a tip nominal radius lower than 7 nm.

■ RESULTS

To carry out this study, the copolymer used was PS-*b*-P2VP with M_n = 68 600 g/mol and a polydispersity index of 1.09, which were calculated from HT-SEC using DMF as eluent and also from ^{1}H NMR with deuterated chloroform (CDCl₃) as solvent. According to the measurements, the final copolymers exhibited low compositional and molecular heterogeneity.

Additionally, in order to exactly calculate the volume fraction of the polystyrene block (PS) in the PS-*b*-P2VP block copolymer as well as the extent of quaternization of PS-*b*-P2VP, the initial diblock and the intermediate poly(**1**) were characterized by ^{1}H NMR. Figure 1 shows ^{1}H NMR spectra of PS-*b*-P2VP in CDCl₃ (top), PS-*b*-P2VP in DMSO-*d₆* (center), and poly(**1**) in DMSO-*d₆* spectra for quaternization kinetics (bottom). Protons of PS block and P2VP block protons could be clearly identified by
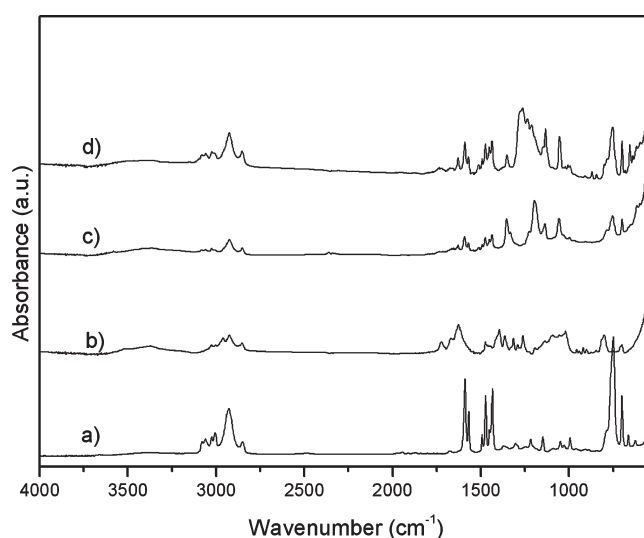
^{1}H NMR spectroscopy in CDCl₃ (Figure 1, top). The weight % of the PS was 31.3 and was determined taken into account the relative peak integration values at $\delta \approx 8.3$ ppm corresponding to the proton (N−CH−) of P2VP as well as the value $\delta \approx 7.24-6.57$ ppm was attributed to the pyridine component and the phenyl protons. After quaternization, poly(**1**) was dissolved in DMSO-*d₆* due to the higher solubility of pyridine block in DMSO-*d₆* compared to CDCl₃. A new peak at 8.82 ppm in the poly(**1**) ^{1}H NMR spectrum can be attributed to the proton (N−CH−) of P2VP after quaternization (Figure 1, center).

The bottom chart in Figure 1 shows ^{1}H NMR spectra for quaternization kinetics. There is an indication that allows corroborating the quaternization of P2VP: the decreasing of intensity of the phenyl proton peaks ($\delta \approx 7.24-6.57$ ppm) of pyridine when the intensity of phenyl proton peak ($\delta \approx 8.82$ ppm) of pyridine after quaternization increased. Furthermore, in the same group of spectra, a signal at $\delta = 8.3$ ppm corresponding to the proton (N−CH−) of P2VP that was a doublet at low reaction time became a singlet when time of reaction increased. Ruiz de Luzuriaga et al.[41] reported similar behavior in the quaternization of poly(4-vinylpyridine). This variation of the spectra was attributed to reduction of mobility of monomeric units during the quaternization reaction.

Figure 2 shows the kinetics of quaternization of PS-*b*-P2VP using ^{1}H NMR results, where a fast quaternization rate could be noticed during the 2000 min. Afterward, the rate of reaction decreased as a consequence of a higher steric hindrance related to modified 2-vinylpyridine units.

In order to investigate the PILs obtained, they were characterized by FTIR and TGA. Figure 3 shows FTIR spectra of PS-*b*-P2VP, poly(**1**), poly(**2**), and poly(**3**). The spectrum of PS-*b*-P2VP exhibited the characteristic signals related with aromatic rings from the styrene and pyridine units. After quaternization of poly(2-vinylpyridine), new absorption bands appeared in the region of the ethyl group. The IR spectrum of poly(**2**) showed the presence of the characteristics signals[32] (1348, 1187, 1130, and 1053 cm^{-1}) corresponding to the $(CF_3SO_2)_2N^-$. Similar behavior was observed in poly(**3**) where the bond signals in the region between 1400 and 1000 cm^{-1} can be attributed to $CF_3(CF_2)_3SO_3^-$ anions.
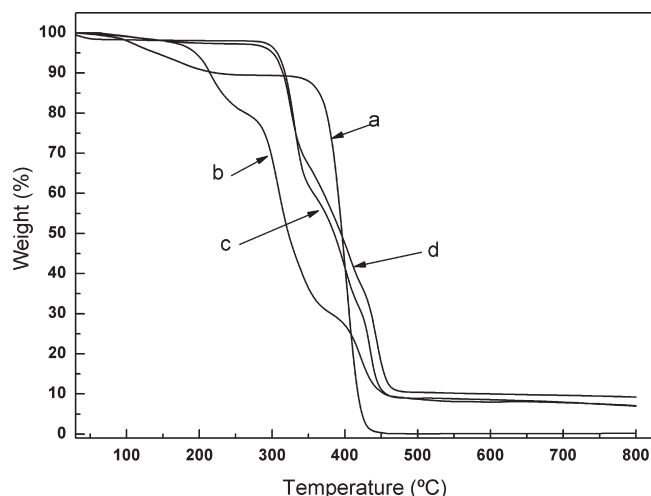
Figure 4. TGA curves of (a) PS-*b*-P2VP, (b) poly(**1**), (c) poly(**2**), and (d) poly(**3**).
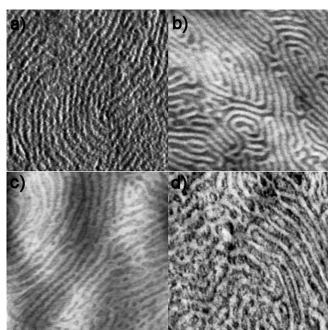
Figure 5. Phase AFM images for (a) PS-*b*-P2VP, (b) poly(**1**), (c) poly(**2**), and (d) poly(**3**). Scan size is 1 μm × 1 μm.

It is well-known that the nature of the anion influences the final properties of ionic liquids such as solubility, viscosity, and thermal stability. For this reason, thermal stability of the copolymers was studied. Figure 4 shows TGA curves of PS-*b*-P2VP, poly(**1**), poly(**2**), and poly(**3**). As it can be observed, thermal stability of quaternized copolymers depends on chemical structure of the anion employed. Besides, TGA curves showed that thermal stability followed the decrease order PS-*b*-P2VP > $(CF_3SO_2)_2N^-$ = $CF_3(CF_2)_3SO_3^-$ > Br^-, which seems to coincide with previously reported results.[38,42]

Self-assembly capability of block copolymers has been widely used due to the rich variety of nanostructures that can be generated depending on the nature of the blocks, molecular weight, composition, and processing characteristics. The composition of the PIL can be modified by anion exchange without altering the main structure of the block copolymer.

Morphological characterization was performed using AFM. AFM samples were prepared by casting onto glass wafers 0.5 wt % solutions of the neat PS-*b*-P2VP and the PIL in chloroform. Samples were dried at room temperature for 2 days. The AFM images taken in phase mode show the PS blocks pale in color, while the P2VP-*r*-PIL block is dark.

Figure 5a exhibits the AFM images for the neat PS-*b*-P2VP thin film, where a very soft microphase separation can be noticed. After quaternization of the 2-vinylpyridine with ethyl bromide,

Table 1. Domain Size of the Studied Materials

polymer	domain size (nm)
PS-*b*-P2VP	19
poly(**1**)	34
poly(**2**)	48
poly(**3**)	73

poly(**1**) was obtained, showing well-defined lamellar microphase separation (Figure 5b). This denoted that quaternization of 2-vinylpyridine with ethyl bromide increases the microphase separation between the two different blocks of poly(**1**). In order to study the anion influence on the self-assembling of PILs, the lamella size of each PILs was calculated. In the case of poly(**1**), the size of lamellar domains was estimated around 34 nm.

After two different anion exchanges two new PIL were obtained from poly(**1**). Poly(**2**) was the first PIL obtained after the exchange of Br anion by $(CF_3SO_2)_2N^-$ anion. As a result, a novel PIL with a new composition was obtained. Poly(**2**) showed a different morphology from the neat block copolymer, and even the intermediate poly(**1**) seemed different when analyzed by AFM (Figure 5c). The new PIL showed phase separation between lamellar and cylindrical morphology since some spots can be attributed to cylinders perpendicular to the surface. In this case, the size of lamella domain was ~48 nm. This value was larger than the size of the poly(**1**) domains and could be attributed to the larger group involved $[(CF_3SO_2)_2N^-$ compared to $Br^-]$.

The second PIL obtained after the exchange of the Br anion by $CF_3(CF_2)_3SO_3^-$ was poly(**3**) that showed a similar microphase separation to poly(**2**) (Figure 5d). The domain size for poly(**3**) was estimated to be 73 nm.

As a consequence of new anions incorporated in the structure, the domain sizes were consequently enlarged from 34 nm in poly(**1**) to 73 nm in poly(**3**).

Table 1 summarizes the size of the domains of the materials shown in Figure 5, denoting that the lamellar distance increased when different anions were used. Poly(**1**) showed the smallest lamellar domains, around 34 nm, due to bromide anion being the smallest one used. On the other hand, in the case of poly(**2**) and poly(**3**), the size of lamellae increased from 34 nm of poly(**1**) to 48 and 73 nm, respectively, because of the bigger size of bis(trifluoromethylsulfonyl)imide anion and nonafluoro-1-butanesulfonic acid anion. When domain sizes of poly(**2**) and poly(**3**) were compared, bigger values were observed for poly(**3**). This difference between domain sizes could not be attributed to sizes of anions because they are similar; the size increase of lamellar domains could be attributed to the decrease of the entropy inside the vinylpyridine block.[7] The equilibrium microphase structures of block copolymers result from a competition between entropic and enthalpic contributions to the free energy. The entropic contribution is related with stretching or compression of the polymer chains whereas enthalpic contribution is led by interfacial energy. While the interfacial energy favors larger lamellar spacing, the entropic stretching favors smaller ones where the chains stay in their most probable conformation.[7,43] Schmidt et al.[7] reported that lamellar distance decreases when chain conformation entropy increases, and conversely, lamellar spacing increases when conformational entropy decreases. Similarly, in our case, the increment of the size of lamellae could be attributed to a decrease of entropy as a consequence of the anion structure, static hindrance, and different conformations that polymeric

chains can take. Considering this fact, in our materials of study the entropy inside poly(**3**) should be smaller than poly(**2**) and, consequently, the lamellar domains bigger. The entropy in poly(**3**) could decrease (lamellar distance increase) due to three different reasons: (i) the anion charge is located at the end of the molecules, (ii) lower steric hindrance, and (iii) packed linear fluorinated chains are favored.[44] On the other hand, the entropy in poly(**2**) could increase (lamellar size decrease) by (i) a bigger steric hindrance, (ii) the charge is located in the middle of anion, and (iii) electrostatic repulsion between oxygen electron pairs of anion.

■ CONCLUSIONS

A new technique for the modification of lamellar domain sizes in polymeric ionic liquid block copolymers has been proposed. Anion exchange in polymeric ionic liquids opens new ways of modifing the sizes of lamellar domains without changing the composition ratio between the two different blocks of the initial copolymer.

In this study, thermal stability and phase behavior of a PS-*b*-P2VP thin film, its PIL obtained from quaternization of poly(2-vinylpyridine), and the subsequent anion exchange were investigated. TGA analysis led to the conclusion that thermal stability of PILs strongly depends on the nature of the counteranions.

AFM morphological studies showed that several sizes of lamellae can be generated simply by changing the type of anion incorporated into the block copolymer. Lamellar domain sizes became increased from 34 nm in the case of poly(**1**) to 74 nm of poly(**3**).

Work is in progress to understand the self-assembly of PIL block copolymers using anions with different sizes, compositions, and structures.

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