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# Specific Counterion Repercussions on the Thermal, pH-Response, and Electrochemical Properties of Side-Chain Leucine Based Chiral Polyelectrolytes

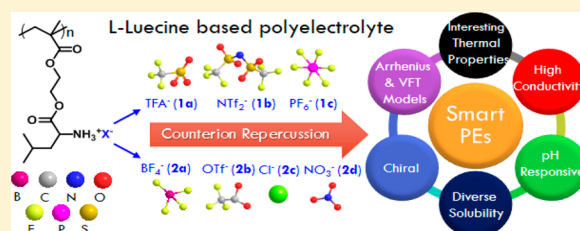
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## S Supporting Information

**ABSTRACT:** Effects of counterions of side chain amino acid based polyelectrolytes (PEs) on the solubility in aqueous medium, pH responsiveness, thermal properties, and ionic conductivities have been appraised. Deprotection of the *tert*-butyl carbamate (Boc) group from poly(Boc-L-leucine methacryloyloxyethyl ester) [P(Boc-L-Leu-HEMA)] was carried out to produce PE with trifluoroacetate as an associative counteranion (**1a**). PEs with bis-(trifluoromethylsulfonyl)imide and hexafluorophosphate counteranion were prepared through anion exchange reactions of **1a**.

Protonation of the neutralized polymer (**2**) obtained from **1a**, followed by anion exchange, leads to the production of miscellaneous PEs bearing different counteranions, such as tetrafluoroborate, trifluoromethanesulfonate, chloride, and nitrate. Differential scanning calorimetry traces of the PEs reveal that the comparatively larger and weakly coordinated counteranions require less thermal energy to dissociate, and thus, the glass transition temperature ( $T_g$ ) of the PEs fall off with an increase in the size of the counteranion. A remarkable conductivity of 2.1 mS/cm was obtained in deionized water when  $\text{Cl}^-$  acted as the counteranion. Steric and electronic factors of the counteranion induce a change of transition pH in different PEs, although the chiroptical nature was retained, as confirmed by circular dichroism spectroscopy.



## 1. INTRODUCTION

Polyelectrolytes (PEs) are polymers with ionizable repeating units along the polymer chain. In polar solvents such as water, these pendant groups can dissociate, leaving charges on the polymer chains and releasing counterions in solution.<sup>1</sup> The important features of PEs include high chemical and thermal stability, negligible volatility, and high ionic conductivity. A PE differs from a neutral polymer in its response toward light scattering, osmotic pressure, solution rheology, and molecular entanglement.<sup>2,3</sup> In this regard, a substantial amount of effort has been put by theoreticians on the basis of Manning's condensation theory and its scaling approach to understand the ionic conductivity in various concentration regimes.<sup>4</sup> Water-soluble PE-surfactant complexes have been used for diverse applications, including designing conductive membranes,<sup>5</sup> electroactive devices,<sup>6</sup> and gas separation<sup>7</sup> and microwave-absorbing materials.<sup>8</sup> Liu reported the effect of counteranions on the viscosity behavior of protonated polyethylenimine (PEI) in aqueous media, as well as in mixed water-ethanol solutions. They concluded that the effect is due to the induced intramolecular associations of the PE.<sup>9</sup> The ionic conductivity of a PE can be tuned by modulating the parameters like anion-cation separations, noncovalent interactions such as hydrogen bonding, molecular symmetry, ion pair dissociation energy, and charge density.<sup>10</sup>

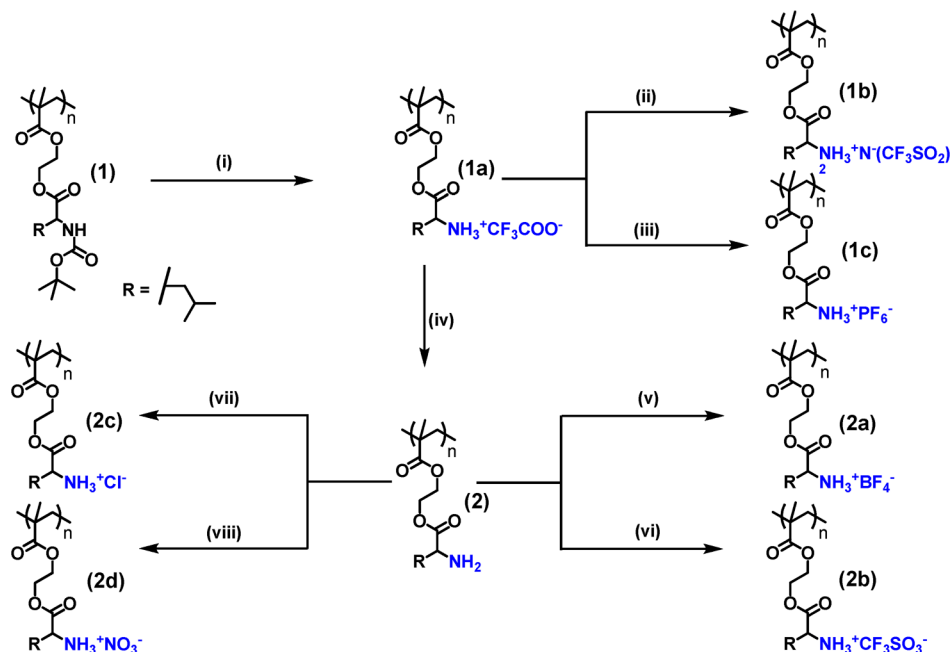
The higher thermal stability, diverse solubility, and high ionic conductivity make PE-based layer-by-layer systems dominant

enough to replace inorganic metal conductors in various electronic devices.<sup>11,12</sup> Ohno's group explored the impact of the ionic conductivity on glass transition temperature ( $T_g$ ) of polymerized ionic liquids (PILs) obtained *via* hydroboration polymerization between 1,3-diallylimidazolium bromide and monobromoborane dimethyl sulfide complex.<sup>13</sup> Long and co-workers have examined the effect of different counterions on the thermal and solution behavior of poly(2-(dimethylamino)-ethyl methacrylate) (PDMAEMA). It was found that the bulkier counteranions, such as bis(trifluoromethylsulfonyl)imide ( $\text{NTf}_2^-$ ) and trifluoromethanesulfonate ( $\text{OTf}^-$ ), significantly reduce the  $T_g$ , and the thermal and solution behavior of various PDMAEMA-based PEs are significantly dependent on the counteranions.<sup>14</sup> The homogeneity on the molecular level is an essential feature in order to have regular packing and increased ionic conductivity. There are reports of fabrication of electroactive devices composed of polycation- and polyanion-based PEs using polymers such as PEI<sup>15</sup> and polystyrenesulfonate (PSS).<sup>16</sup> Although there are a lot of reports on the effect of counterion on the solution, thermal, and electrochemical properties of PEs,<sup>4,14,17</sup> relatively little attention has been paid to elucidate the nature of the interaction between polycation and monovalent counteranions of PE salts.

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Scheme 1. Schematic Representation of the Synthesis of Different Polymeric Salts<sup>a</sup>

<sup>a</sup>(i) TFA, 1 h. (ii) LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>, pH 4–5, 1 h. (iii) KPF<sub>6</sub>, pH 4–6, 3 h. (iv) pH 9–10. (v) Dil. HBF<sub>4</sub>, pH 2–3, 4 h. (vi) Dil. CF<sub>3</sub>SO<sub>3</sub>H, pH 2–3, 6 h. (vii) Dil. HCl, pH 2–3, 24 h. (viii) Dil. HNO<sub>3</sub>, pH 2–3, 24 h.

Table 1. Solubility of Various Polymeric Ionic Salts in Aqueous and Organic Solvents<sup>a</sup>

PEs	DI H <sub>2</sub> O	CHCl <sub>3</sub>	MeOH	acetone	DMSO	THF	H <sub>2</sub> O/MeOH		
							80/20 <sup>b</sup>	65/35 <sup>b</sup>	50/50 <sup>b</sup>
1a	+	–	+	+	+	–	+	+	+
1b	–	–	+	+	+	+	–	+	+
1c	–	–	+	–	+	–	–	–	+
2a	–	+	+	+	+	–	+	+	+
2b	+	–	+	–	+	–	+	+	+
2c	+	–	+	–	+	–	+	+	+
2d	+	–	+	–	+	–	+	+	+

<sup>a</sup>Solubility indicated by “+” for soluble and “–” for insoluble or only sparingly soluble. <sup>b</sup>Volume/volume.

With DNA being the major representative of PEs, bioinspired polymeric materials indeed have been the center of attraction in the present decade due to their homogeneity in topology, physiochemical properties, enhanced processability, and stability.<sup>18–20</sup> Therefore, investigations on the ionic conductivity of polymers with biological motifs are warranted. Thus, in the present study we first synthesized side chain amino acid based poly(*tert*-butyl carbamate-*L*-leucine methacryloylox-yethyl ester) [P(Boc-*L*-Leu-HEMA)] homopolymer by reversible addition–fragmentation chain transfer (RAFT) polymerization, one of the controlled radical polymerization techniques. Subsequently, we deprotected the Boc group using trifluoroacetic acid (TFA) to produce a polymeric salt P(TFA<sup>–</sup>NH<sub>3</sub><sup>+</sup>-Leu-HEMA), and it was further neutralized with 0.1 N NaOH to obtain the neutral amine group containing polymer. We then adopted two prime methods, such as direct anion exchange and protonation of the neutralized polymer, followed by anion exchange to produce miscellaneous PEs bearing different counteranions (Scheme 1). We explored the pH responsiveness, thermal properties, electrochemical conductivity, and the chiroptical properties of the synthesized PEs. Interestingly, we found that the PEs have a novel, advantageous property of high

ionic conductivity, which makes this set of compounds a novel library of “smart” PEs.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** Lithium bis(trifluoromethane)sulfonimide (LiNTf<sub>2</sub>, Sigma), TFA (99.5%, Sisco Research Laboratories Pvt. Ltd., India), trifluoromethanesulfonic acid (CF<sub>3</sub>SO<sub>3</sub>H, Sigma, 98%), tetrafluoroboric acid (HBF<sub>4</sub>, Sigma, 48 wt % in H<sub>2</sub>O), potassium hexafluorophosphate (KPF<sub>6</sub>, Sigma, 98%), hydrochloric acid (HCl, Merck, 35%), nitric acid (HNO<sub>3</sub>, Merck), and anhydrous *N,N'*-dimethylformamide (DMF, 99.9%, Sigma) were used as received. 2,2'-Azobisisobutyronitrile (AIBN, Sigma, 98%) initiator was purified by recrystallization from methanol. Boc-*L*-Leu-HEMA<sup>21</sup> and 4-cyanopentanoic acid dithiobenzoate (CTP)<sup>22</sup> were synthesized as per previous reports. Methanol-*d*<sub>4</sub> (CD<sub>3</sub>OD, 99.8% D) was purchased from Cambridge Isotope Laboratories, Inc. The solvents such as hexanes (mixture of isomers), acetone, ethyl acetate, methanol (MeOH), and dichloromethane (DCM) were purified by standard procedures and used.<sup>23</sup>

**2.2. Instrumentation.** Molecular weights (*M*<sub>n</sub>) and molecular weight distributions (dispersity, *D*) were determined by a gel permeation chromatography (GPC) instrument consisting of a Waters 515 HPLC pump, a Waters 2414 refractive index detector, and two columns (Styragel HT4 and Styragel HT3) in THF at 30 °C, and the

flow rate was 1.0 mL min<sup>-1</sup>. The system was calibrated with polystyrene standard of narrow molecular weight distribution. <sup>1</sup>H NMR spectroscopy was conducted on a Bruker Avance<sup>III</sup> NMR spectrometer at a working frequency 500 MHz. FT-IR spectra were recorded on KBr pellets using a PerkinElmer Spectrum 100 FT-IR spectrometer. The UV–Vis spectroscopic study was carried out using a PerkinElmer Lambda 35 UV–Vis spectrophotometer. Solution conductivity measurements were done by Mettler Toledo Inlab738 electrode SevenGo conductimeter SG3 in both aqueous and aqueous with methanol as cosolvent medium, and an average of three conductivity values was taken. Circular dichroism (CD) spectroscopic measurements were carried out in a JASCO J-815 CD spectrometer in methanol (400  $\mu$ L quartz cuvette cell, 1.0 mm path length). The thermal behavior of the synthesized polymers was characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) at a heating rate of 10  $^{\circ}$ C/min in N<sub>2</sub> atmosphere by using Mettler Toledo DSC1 and TG/SDTA 851e instruments, respectively. The DSC temperature cycle was determined according to the TGA profile of the individual PEs.

**2.3. Synthesis of P(Boc-L-Leu-HEMA) (1).** Homopolymer of Boc-L-Leu-HEMA, P(Boc-L-Leu-HEMA) (1) ( $M_n$  = 21 600 g/mol,  $\bar{D}$  = 1.25) was synthesized by the RAFT polymerization technique using a procedure reported by our group.<sup>21</sup> Subsequent Boc group deprotection using TFA resulted in the formation of the polymeric salt P(TFA<sup>-</sup>NH<sub>3</sub><sup>+</sup>-Leu-HEMA) (1a), which is soluble in aqueous medium (Table 1). 1a was then neutralized with 0.1 N NaOH to obtain the neutralized polymer, P(NH<sub>2</sub>-Leu-HEMA) (2).

**2.4. Synthesis of Different Ionic Polymer Salts.** We adopted two prime methods to prepare miscellaneous PEs: direct anion exchange of 1a and protonation of the neutralized polymer 2, followed by anion exchange (Scheme 1). Among the library of polymeric ionic salts synthesized, P(NTf<sub>2</sub><sup>-</sup>NH<sub>3</sub><sup>+</sup>-Leu-HEMA) (1b) and P(PF<sub>6</sub><sup>-</sup>NH<sub>3</sub><sup>+</sup>-Leu-HEMA) (1c) were derived from 1a by direct anion exchange reactions. On the other hand, P(BF<sub>4</sub><sup>-</sup>NH<sub>3</sub><sup>+</sup>-Leu-HEMA) (2a), P(OTf<sup>-</sup>NH<sub>3</sub><sup>+</sup>-Leu-HEMA) (2b), P(Cl<sup>-</sup>NH<sub>3</sub><sup>+</sup>-Leu-HEMA) (2c), and P(NO<sub>3</sub><sup>-</sup>NH<sub>3</sub><sup>+</sup>-Leu-HEMA) (2d) were prepared from 2 by one-pot protonation prior to the anion exchange reactions. The polymer with the -NH<sub>2</sub> group at the pendant chain (2) was synthesized from 1a by the following procedure: 200 mg of 1a was placed in a 20 mL glass vial equipped with a magnetic spin bar and was dissolved in 3 mL of deionized (DI) water, and the solution was commingled for 10 min by constant stirring. pH 9–10 was attained by dropwise addition of 0.1 N NaOH under rigorous stirring, and the precipitation commenced. The precipitate was then washed four times with DI water to remove the salt produced as a result of neutralization and dissolved in DCM. The solution was dried by rotary evaporation followed by drying under vacuum at room temperature for 24 h, giving rise to P(NH<sub>2</sub>-Leu-HEMA) (2). Among the synthetic routes followed for obtaining different polymeric salts *via* anion exchange reactions from 1a and 2, few typical examples are chronicled below.

**2.4.1. Synthesis of P(NTf<sub>2</sub><sup>-</sup>NH<sub>3</sub><sup>+</sup>-Leu-HEMA) (1b).** To a 20 mL glass vial equipped with a magnetic spin bar, 200 mg of 1a was added and the pH was tuned to 5.0 with 1 N HCl. To the vial was added a freshly prepared solution of LiNTf<sub>2</sub> (1.179 g in DI water) dropwise with stirring, until precipitation occurred. The solution was drained carefully and the precipitate was washed four times with DI water and dried under vacuum at 45  $^{\circ}$ C for 6 h, producing 1b.

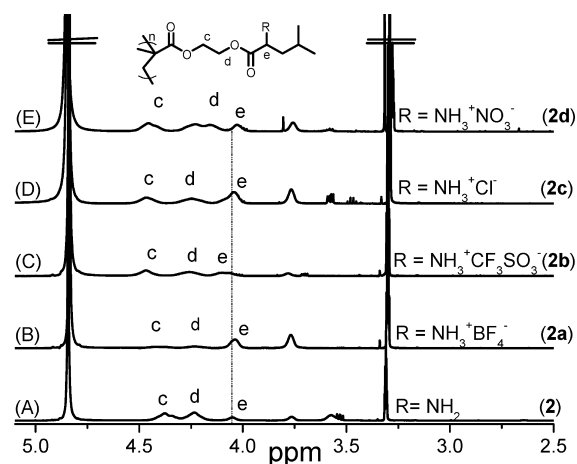
**2.4.2. Synthesis of P(PF<sub>6</sub><sup>-</sup>NH<sub>3</sub><sup>+</sup>-Leu-HEMA) (1c).** A 200 mg portion of 1a was placed in a 20 mL glass vial, and 1 N HCl was used to adjust the pH to 4.0. To this acidic solution, added freshly prepared KPF<sub>6</sub> solution under constant stirring. After 24 h, the resulting solution was dialyzed against DI water using a 1000 g/mol molecular weight cutoff (MWCO) dialysis bag (Spectrum Laboratories, Inc.) to remove unreacted KPF<sub>6</sub> and other low molecular weight impurities, followed by lyophilization, giving rise to the product 1c.

**2.4.3. Synthesis of P(Cl<sup>-</sup>NH<sub>3</sub><sup>+</sup>-Leu-HEMA) (2c).** A 200 mg portion of 2 was placed in a glass vial containing a small magnetic spin bar, and 2 N HCl was added dropwise under constant stirring. The reaction was allowed to stir for 24 h. The reaction mixture was then solubilized in methanol and precipitated using diethyl ether, followed by

centrifugation, and the precipitate was dried overnight under vacuum at 45  $^{\circ}$ C to obtain 2c. Similar methods were adopted for the synthesis of 2a, 2b, and 2d.

### 3. RESULT AND DISCUSSION

**3.1. Anion Exchange Reactions.** Conventional anion exchange reactions enabled synthesizing different PEs (Scheme 1). The PEs from 1a were directly synthesized by anion exchange reactions, whereas the PEs from 2 were synthesized by protonation prior to the anion exchange reactions.<sup>24</sup> The successful synthesis of the various PEs were confirmed by <sup>1</sup>H NMR and FT-IR spectroscopy. The <sup>1</sup>H NMR resonance signal of the proton of the chiral carbon atom adjacent to the -NH<sub>3</sub><sup>+</sup> cation is highly influenced by the electronic effect of the counteranion. <sup>1</sup>H NMR spectroscopy of all the PEs was performed in methanol-*d*<sub>4</sub> to check how noncovalent interactions sacrifice the electron density around the ionic center [Figures 1 and S1 (Supporting Information)]. For 2b



**Figure 1.** <sup>1</sup>H NMR spectra of neutral polymer 2 and PEs derived from it in methanol-*d*<sub>4</sub>: (A) 2, (B) 2a, (C) 2b, (D) 2c, and (E) 2d.

(Figure 1C), 1c (Figure S1D, Supporting Information), and 2c (Figure 1D), having stronger noncovalent interactions *via* withdrawal of electron density from the ionic center, the -CH- proton H<sub>e</sub> moves toward the deshielding zone. In 1a, 1b, 1c, 2a, 2b, 2c, and 2d, the H<sub>e</sub> proton was found at 4.15, 4.11, 4.04, 4.03, 4.1, and 4.08 ppm, respectively. The rest of the peaks from the polymer backbone remained intact.

Comparison of the FT-IR spectrum of the polymeric ionic salts with the mother polymers gave insights into the generation of additional bond formation [Figures 2 and S2 (Supporting Information)]. The -N-H bond stretching at 2948 cm<sup>-1</sup> is red-shifted in all the salts, which arises due to the formation of -NH<sub>3</sub><sup>+</sup> (Figure S2, Supporting Information). In addition to the shifting in the bond-stretching frequencies, corresponding counterion stretching frequencies were also observed (Figure 2). In the FT-IR spectrum of 2a, the bond-stretching frequency corresponding to B-F was observed at 1036 cm<sup>-1</sup>. For 2b, peaks at 1274 and 1029 cm<sup>-1</sup> corresponds to -SO<sub>3</sub> and C-F bond stretching. 2c showed a characteristic C-Cl stretch at 1251 cm<sup>-1</sup>, and for 2d, the -NO<sub>3</sub> symmetric stretch at 1390 cm<sup>-1</sup> and asymmetric stretching at 1601 cm<sup>-1</sup> were observed.<sup>25</sup> The FT-IR signals corresponding to the counteranion are observed in Figure S2 (Supporting Information) as well: for 1a, peaks at 1751 and 1027 cm<sup>-1</sup> are due to the carboxylate group and C-F, and 1b gave rise to



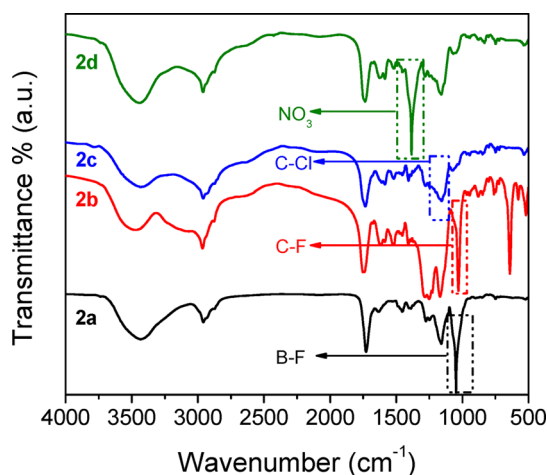


Figure 2. FT-IR spectra of the polymeric ionic salts 2a–d.

peaks at 1194 and 1053  $\text{cm}^{-1}$  because of N–S and  $-\text{SO}_2$  bond stretching. The characteristic P–F bond stretching of **1c** was gained at 751  $\text{cm}^{-1}$ .<sup>26</sup> These results confirmed successful anion exchange in each anion-exchanged polymer.

**3.2. Solubility.** The ionic groups dissociate in aqueous solution, resulting in generation of charges on the polymer, leading to the formation of PE. In solution, neutral polymers tend to follow entangled dynamics, while the linear PE follows untangled dynamics in the lower concentration regime, and again due to surface charge density, the PE chains will repel each other *via* double layer forces, which in turn can lead to a rigid rodlike conformation.<sup>2</sup> Polymers **1** and **2** were hydrophobic in nature (Table 1), and introduction of ionic character by anion exchange resulted in generation of a class of PEs with improved hydrophilicity. In fact, owing to the higher translational entropy, counterions can move freely in the solution of the PEs. Migration of the charges along the polymer chain of a PE can lead to lowering of the solubility compared to a PE having the same fraction of nonmigrating charged groups.<sup>27</sup> Among the synthesized PEs, **1a**, **2b**, **2c**, and **2d** were found to be soluble in the aqueous medium. This solubility of PEs in aqueous solution is the outcome of ionic hydration for charged groups and counterions, hydrogen bonding to polar groups, and hydrophobic hydration around alkyl main and side chains.<sup>28</sup> Among the water-soluble PEs, **1a** and **2b** have their advantage over forming the hydrogen bonding by disturbing the intermolecular hydrogen bonding of water. This process is favored by entropy, and thus, the PEs become soluble in water. Later PEs having smaller sized anions are hence favored by the electrostatic interaction because the higher surface charge density results in enhanced hydrophilicity.<sup>29</sup> The 50/50 (v/v)  $\text{H}_2\text{O}$ /methanol mixture served as a common solvent for all the PEs synthesized. An amassed effect of counterion condensation in solubility is perceptible when the distance between the two charged monomers along the polymer chain backbone is smaller than the Bjerrum length ( $\lambda_B$ );<sup>30</sup>  $\lambda_B = e^2/4\pi\epsilon\epsilon_0 k_B T$  ( $\sim 7.20$  Å for water), where  $e$ ,  $\epsilon_0$ ,  $\epsilon$ ,  $k_B$ , and  $T$  are elementary charge, vacuum permittivity, dielectric constant, Boltzmann's constant, and absolute temperature, respectively. The minimization of electrostatic attraction between opposite charges deteriorates the condensation effects, which lead to the enhanced solubility of **1a**, **2b**, **2c**, and **2d** in DI water.

It is also observed that as a result of migration of charges, the solubility of a polymer is lower than the solubility of the

corresponding PE bearing the same fraction of nonmigrating charged groups.<sup>31</sup> The fact that all the PEs synthesized were soluble in methanol and DMSO is a consequence of the minimization of the counterion effect in organic polar solvents. The increase of hydrophobicity of fluorine-substituted counterions, curtailing of favorable noncovalent interactions, and decreased surface charge density together contribute to the poor solubility of **1c**, **2a**, and **1b** in water.

**3.3. pH Responsive Property.** The pH responsive property of **1a** and its block copolymers was well-studied and documented in the previous report from our group.<sup>21,32</sup> The conformations and mutual interactions are regulated by the charge density along the PE chains.<sup>33</sup> In a solution of binary monovalent electrolytes, the anticipated change in pH is proportional to the square root of the total electrolyte concentration, as long as the Debye–Huckel theory is effective. Herein, we are demonstrating the influence of the counteranion on the pH responsiveness of the PEs in the aqueous medium. The pH of the solution controls the degree of protonation/deprotonation of the acidic or basic groups of the weak PEs, and in the studied PEs, pH responsiveness is expected due to the presence of an ionizable primary amine group, which gets protonated at a certain pH. The turbidity test was performed using UV–vis spectroscopy at 500 nm by analyzing the percent transmittance (%T) of the PE solution as a function of pH at room temperature.<sup>34</sup> The polymer salts (2 mg/mL) were solubilized in DI water, and the initial pH of the PE solutions **1a**, **2b**, **2c**, and **2d** were noted as 4.17, 4.11, 5.36, and 4.19, respectively. The pH of the solution was adjusted using 0.1 N HCl or 0.1 N of NaOH, as required. As the pH of the solution is increased, the quaternary amine groups get deprotonated and the solution becomes turbid, leading to precipitation. The phase transition pH is defined as the pH at which reduction of 50%  $T$  of the polymer solutions is observed. The phase transition pH for the different PEs **1a**, **2b**, **2c**, and **2d** were determined to be 6.55, 6.21, 6.60, and 6.69, respectively (Figure 3). The transition pH of the PEs varied in accordance with the

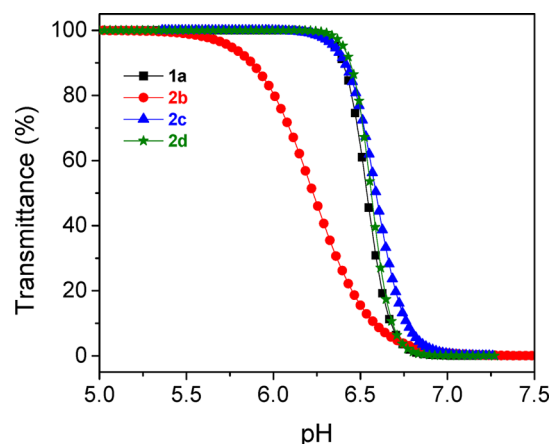


Figure 3. pH-dependent transmittance of the PEs in aqueous medium at 500 nm (0.2 wt % of polymeric ionic salt in aqueous medium).

bulkiness of the counteranions. With  $\text{OTf}^-$  being bulkier than other counteranions, the precipitation due to lower immobility of charge took place at a lower pH. At the same time,  $\text{Cl}^-$ -carrying PEs are predicted to have more mobility, shown as a higher transition pH.

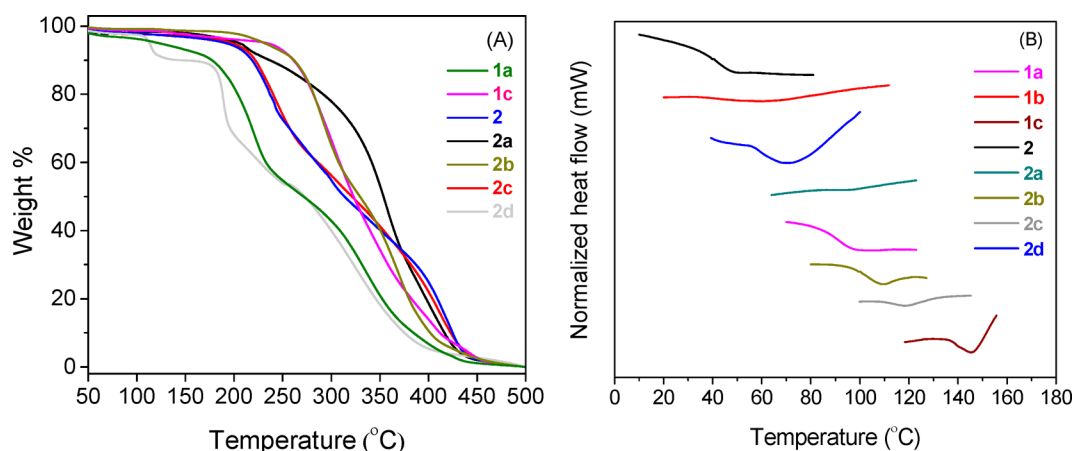


Figure 4. (A) TGA thermograms and (B) DSC traces of the neutral polymer (2) and various PEs.

**3.4. Thermal Properties.** The dependence of the charge density and bulkiness of the counteranions can significantly influence the thermal properties and, in particular, the  $T_g$  of PEs.<sup>17</sup> To elucidate the influence of the counteranions on the thermal properties of the polymeric salts, they were subjected to TGA and DSC analysis. TGA thermograms (Figure 4A) revealed that the polymers carrying the less coordinating and less nucleophilic counteranion, 1c and 2b, have the higher thermal stability. Whereas, the higher nucleophilicity of  $\text{NO}_3^-$  and  $\text{Cl}^-$  made 2c and 2d thermally unstable.<sup>29</sup> DSC studies demonstrated that the counteranions dramatically influenced the  $T_g$  of the PEs (Figure 4B). In contrast to the neutral polymer 2, all polymeric salts showed higher  $T_g$ . Typically, a polymeric salt with  $\text{PF}_6^-$  counteranion showed unusually high  $T_g$ , which could be due to the hydrogen-bonding interactions between the cation and anion.<sup>14</sup> Due to the greater extent of ionic aggregation of the small-sized anion, PE salt with  $\text{Cl}^-$  counteranion showed a much higher  $T_g$  of 117 °C. The reduced nucleophilicity and basicity due to the nonpolar nature of the  $\text{NTf}_2^-$  counteranion make the interaction with polycation modest, and the  $T_g$  of the corresponding polymeric salt was observed to be low. The  $T_g$  was found to be decreasing in the order  $\text{PF}_6^-$  (140 °C) >  $\text{Cl}^-$  (117 °C) >  $\text{OTf}^-$  (103 °C) >  $\text{TFA}^-$  (94 °C) >  $\text{BF}_4^-$  (82 °C) >  $\text{NO}_3^-$  (74 °C) >  $\text{NTf}_2^-$  (45 °C) (Figure 4B). Therefore,  $T_g$  values of side chain leucine containing PEs can be tuned by suitable anion choice.

**3.5. Solution Conductivity.** The higher solution conductivity of the PEs is an advantage in framing artificial membranes,<sup>5</sup> electrochemical devices,<sup>6</sup> and reaction medium.<sup>35</sup> Therefore, ionic conductivity measurements for hydrophilic and hydrophobic salts were respectively performed with a molar concentration of 0.05 mol repeat unit/L in DI water and 50/50 (v/v)  $\text{H}_2\text{O}$ /methanol mixture at various temperatures. The influence of the counteranions and the  $T_g$  of the PEs on the solution conductivity of the PE was investigated by variable temperature conductivity measurements. The solution conductivity, resistivity, total dissolved solids (TDS), and salinity index of the PEs at 298 K are tabulated in Table 2. The PE 2c at a concentration of 0.05 mol repeating unit/L showed very high solution conductivity on the order of 2.1 mS/cm at 298 K in DI water. The conductivity arises predominantly from the anions, since the main chain polycation has low mobility.<sup>36</sup> Although the ionic conductivity and the solution conductivities reported for the polyelectrolytes are in the range from  $10^{-7}$  to  $10^{-4}$  S/cm, the ionic conductivity of 2c is very high when

Table 2. Solution Conductivity Measurements of PEs at 298 K<sup>a</sup>

PEs	conductivity (mS/cm)	resistivity ( $10^2 \Omega \text{ cm}$ )	TDS	salinity (ppt)	$E_a$ (kJ/mol) <sup>d</sup>
1a <sup>b</sup>	1.93	5.18	966	0.98	3.0
2b <sup>b</sup>	0.85	11.7	556	0.55	3.4
2c <sup>b</sup>	2.10	4.76	739	0.86	2.7
2d <sup>b</sup>	1.81	5.53	790	0.79	2.3
1a <sup>c</sup>	0.86	11.7	428	0.42	3.6
1b <sup>c</sup>	0.50	20.2	248	0.24	3.6
1c <sup>c</sup>	0.34	29.6	168	0.16	2.7
2a <sup>c</sup>	0.30	33.4	150	0.14	4.7
2b <sup>c</sup>	0.59	17.1	293	0.28	

<sup>a</sup>Concentrations of PEs were 0.05 mol repeat unit/L. <sup>b</sup>Measured in DI water. <sup>c</sup>Measured in 50/50 (v/v) mixture of DI water/methanol. <sup>d</sup> $E_a$  is calculated by Arrhenius fitting of Figures 5A and 6A.

compared to previously reported values.<sup>37</sup> Long and co-workers reported a value of 1.7 mS/cm for PDMAEMA- $\text{Cl}^-$  polyelectrolyte at a concentration of 0.15 mol repeating unit/L.<sup>14</sup> Poly(*N*-vinylimidazole) when quaternized with *n*-butyl bromide showed a solution conductivity of  $5 \times 10^{-2}$  mS/cm.<sup>38</sup> We are extending our studies by framing thin films to explore the solid-state conductivity through impedance spectroscopy where the amino acid moiety in the polymer side chain is also varied.

The formation of ion pairs separated by the solvent is believed to play a crucial role in determining the ion conductivity,<sup>14</sup> and anions undergoing greater dissociation in solution give higher conductivity values. The PEs with larger and weakly coordinated anions required less thermal energy to dissociate ionic interactions, leading to tailored thermal behavior. The ionic conductivity obtained at 298 K varied from the  $T_g$  order, and in DI water it decreases in the order  $\text{Cl}^- > \text{TFA}^- > \text{NO}_3^- > \text{OTf}^-$ . The highest ionic conductivity at 298 K for 2c is due to the enhanced ionic mobility and polar nature of the smaller anion.<sup>14</sup> The mobility of the charge is more for 1a, as it underwent dissociation to a greater extent, leading to exceptionally high conductivity. The intra- and intermolecular hydrogen-bonding interactions in 1a weaken the specific cation–anion interactions, which reduces viscosity and increased conductivity.<sup>39</sup> The charge on the  $\text{NTf}_2^-$  anion is highly delocalized, which engenders lowered electrostatic attraction with the polymer backbone and reduced hydration compared with  $\text{PF}_6^-$  anion in a polar protic solvent,

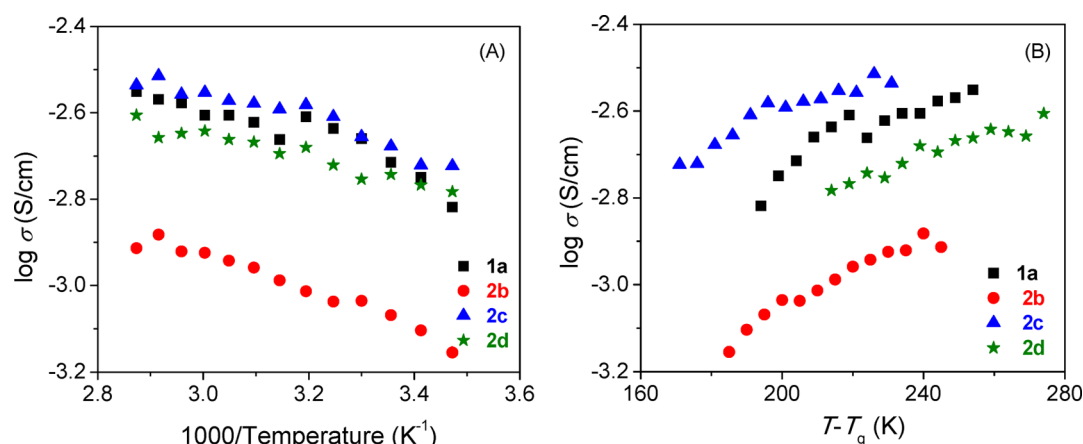


Figure 5. Ionic conductivity correlation with temperature (A) and  $T_g$  (B) of water-soluble PEs 1a, 2b, 2c, and 2d.

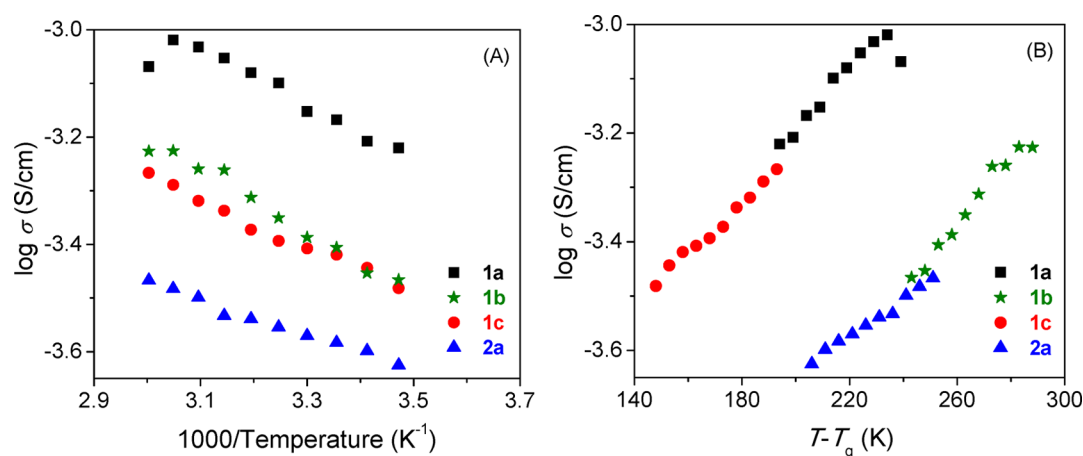


Figure 6. Ionic conductivity correlation with temperature (A) and the  $T_g$  (B) of 1a, 1b, 1c, and 2a.

occasioning its higher conductivity. **1b** showed lower conductivity than **2b** due to its larger size and the lower mobility of  $\text{NTf}_2^-$ .<sup>40</sup> Apparently,  $\text{PF}_6^-$  should show lesser mobility and conductivity as compared to  $\text{BF}_4^-$  because of its larger size, but the discrepancy in the result can be explained by virtue of the noncomplexing and lower coordinating ability of  $\text{BF}_4^-$  when compared to  $\text{PF}_6^-$ .<sup>36</sup>

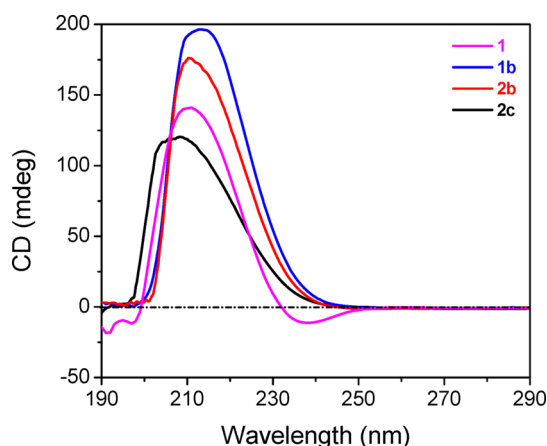
The presence of an organic solvent such as MeOH considerably decreases the conductivity of PEs (Table 2), since the ions dissociate to a lesser extent in MeOH. In Table 2, the activation energy ( $E_a$ ) for charge migration by the thermally activated process of **1a** in two different solvent systems has been given. There occurs a decrease in  $E_a$  when organic solvent (methanol) was added as the cosolvent to the system. This can be attributed to the higher resistivity to ionic mobility and the decrease in conductivity of the same salt in the different environment.<sup>36</sup> With the delocalization of charge being more or less the same in  $\text{OTf}^-$  and  $\text{TFA}^-$  anions, the size of the naked anion is perhaps the vital factor for its higher conductivity.<sup>41</sup>

The temperature-dependent solution conductivity measurements were performed, and in Figures 5A and 6A we observed nice agreement with the Arrhenius model, with slight deviations for the higher temperature regime. In the Arrhenius model, conductivity is defined as  $\sigma = \sigma_0 \exp(-E_a/RT)$ , where  $E_a$  and  $T$  are the activation energy required for the mobility of anions regressed with conductivity and temperature, respectively.<sup>42</sup> The experiment conducted in DI water and 50/50 (v/v)

mixture of  $\text{H}_2\text{O}$ /methanol did not show much deviation from the model. The validity of the Vogel–Fulcher–Tamman (VFT) model was also checked. In the VFT model,  $\sigma = \sigma_0 \exp[-B/(T - T_0)]$  where  $T_0$  (K) is termed as the true  $T_g$ , which is 50 K lower than the experimental glass transition temperature.<sup>36</sup> VFT is validated from Figures 5B and 6B. From the mentioned figures, the deviations from the VFT model in Figure 5B are attributed to the higher intra- and intermolecular hydrogen bonding and electrostatic interactions, to disturbances in the local molecular environment, or to PEs in DI water.<sup>36</sup> However, the VFT model is well fit when the conductivity measurements were performed in a 50/50 (v/v) mixture of  $\text{H}_2\text{O}$ /methanol (Figure 6B). The  $T_g$ -independent behavior of ionic conductivity is reduced in the same way. The VFT model directly relates to the charge-hopping of the ions in PEs; hence, there could be a decrease in the charge carrier concentration and an increase in resistivity to the ionic mobility when methanol is applied as cosolvent, and the VFT model is in good agreement.<sup>43</sup> The highest  $T_g$ -independent ionic conductivity is for the PE having the most translational entropy. The activation energies (Table 2) for all the PEs were calculated from Arrhenius fitting.

### 3.6. Secondary Structure and Solution Conformation.

The chiroptical properties of the Boc-protected polymer and its corresponding PEs were examined by a CD spectroscopic technique from dilute polymer solution (1.0 mg/mL) in methanol [Figures 7 and S3 (Supporting Information)]. In our



**Figure 7.** CD spectra of **1**, **1b**, **2b**, and **2c** (0.1 wt % of polymer in methanol).

previous report, we have demonstrated that a Boc-protected chiral leucine moiety containing methacrylate polymer adopts a one-handed helical conformation.<sup>21,44</sup> The Cotton effect at 207–211 nm can be assigned to the  $n \rightarrow \pi^*$  transition of the carbonyl group of the ester chromophore. In addition to the transition mentioned above, a weak signal in the negative region at 237 nm of **1** can be attributed to the  $\pi_1 \rightarrow \pi^*$  transition from the amide chromophore, which is absent in all PEs due to the Boc group deprotection.<sup>45</sup> Intrachain hydrogen-bonding interactions among the chiral repeating units are responsible for such kind of rigid rodlike structure. Counterions play a significant role in maintaining the hydrogen bonding, thereby guiding the secondary structures. The ability of  $\text{NTf}_2^-$  and  $\text{OTf}^-$  anions to offer more intrachain hydrogen-bonding donation sites yields the higher CD value. The decrease in the CD value of **2a** and **1c** could be presumably due to the interplay of interchain hydrogen bonding by  $\text{BF}_4^-$  and  $\text{PF}_6^-$  anions. Nevertheless, from the CD spectra it is evident that all the PEs when solubilized in methanol tend to follow a specific conformation and retain the chiroptical properties.

#### 4. CONCLUSION

A new class of smart PEs having side chain amino acid moieties has been synthesized with remarkable ionic conductivity. Keeping the polycation the same, anions have been varied, and we observed interesting properties of multiple physical parameters, such as solubility, pH responsiveness, thermal properties, ionic conductivity, and chiroptical properties. Deterioration of counterion condensation in turn increases the solubility of PEs in aqueous medium, and the higher ionic mobility of  $\text{Cl}^-$  resulted in the higher ionic conductivity. The decrease in charge-hopping when methanol was introduced as a cosolvent while the temperature dependence of ionic conductivity was studied resulted in a tendency to follow the VFT model for **1a**, **1b**, **1c**, and **2a**. The phase transition pH of the PEs varied in accordance with the bulkiness of counteranions. Both charge density and the bulkiness of the counteranions significantly influenced the thermal properties and, in particular, the  $T_g$  of PEs. Polyelectrolytes with different counteranions showed chiroptical characteristics, although the ability of  $\text{NTf}_2^-$  and  $\text{OTf}^-$  anions to offer more intrachain hydrogen-bonding donation sites creates the higher ellipticity value. We are currently exploring the influence of counterions on the thin film conductivity<sup>4</sup> of the side chain amino acid

based polyelectrolytes and on the swelling/deswelling capability of their cross-linked three-dimensional networks.<sup>46</sup> The high ionic conductivity and expected biocompatibility for these positively charged PEs make these materials applicable to electrochemical membrane technology.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

<sup>1</sup>H NMR, FT-IR, and CD spectra of various PEs. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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##### Notes

The authors declare no competing financial interest.

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#### ■ REFERENCES

- (1) Schmitz, K. S. *Macroions in Solution and Colloidal Suspension*; VCH Publishers: New York, 1993.
- (2) Dobrynin, A. V.; Rubinstein, M. Theory of Polyelectrolytes in Solutions and at Surfaces. *Prog. Polym. Sci.* **2005**, *30*, 1049–1118.
- (3) Netza, R. R.; Andelman, D. Neutral and Charged Polymers at Interfaces. *Phys. Rep.* **2003**, *380*, 1–95.
- (4) Bordin, F.; Colby, R. H.; Cametti, C.; Lorenzo, L. D.; Gili, T. Electrical Conductivity of Polyelectrolyte Solutions in the Semidilute and Concentrated Regime: The Role of Counterion Condensation. *J. Phys. Chem. B* **2002**, *106*, 6887–6893.
- (5) Matsumoto, K.; Endo, T. Synthesis of Ion Conductive Networked Polymers Based on an Ionic Liquid Epoxide Having a Quaternary Ammonium Salt Structure. *Macromolecules* **2009**, *42*, 4580–4584.
- (6) Lutkenhaus, J. L.; Hammond, P. T. Electrochemically Enabled Polyelectrolyte Multilayer Devices: From Fuel Cells to Sensors. *Soft Matter* **2007**, *3*, 804–816.
- (7) Bara, J. E.; Carlisle, T. K.; Gabriel, C. J.; Camper, D.; Finotello, A.; Gin, D. L.; Noble, R. D. Guide to  $\text{CO}_2$  Separations in Imidazolium-Based Room-Temperature Ionic Liquids. *Ind. Eng. Chem. Res.* **2009**, *48*, 2739–2751.
- (8) Tang, J.; Radosz, M.; Shen, Y. Poly(ionic liquid)s as Optically Transparent Microwave-Absorbing Materials. *Macromolecules* **2007**, *41*, 493–496.
- (9) Liu, K.-J. Specific Counterion Effects on the Viscosity Behavior of Protonated Poly(ethylenimine). *Macromolecules* **1968**, *1*, 390–393.
- (10) Bunton, C.A.; Nome, F.; Quina, F. H.; Romsted, L. S. Ion Binding and Reactivity at Charged Aqueous Interfaces. *Acc. Chem. Res.* **1991**, *24*, 357–364.
- (11) Wee, G.; Larsson, O.; Srinivasan, M.; Berggren, M.; Crispin, X.; Mhaisalkar, S. Effect of the Ionic Conductivity on the Performance of Polyelectrolyte-Based Supercapacitors. *Adv. Funct. Mater.* **2010**, *20*, 4344–4350.
- (12) Argun, A. A.; Ashcraft, J. N.; Hammond, P. T. Highly Conductive, Methanol Resistant Polyelectrolyte Multilayers. *Adv. Mater.* **2008**, *20*, 1539–1543.



- (13) Matsumi, N.; Sugai, K.; Miyake, M.; Ohno, H. Polymerized Ionic Liquids via Hydroboration Polymerization as Single Ion Conductive Polymer Electrolytes. *Macromolecules* **2006**, *39*, 6924–6927.
- (14) Hunley, M. T.; England, J. P.; Long, T. E. Influence of Counteranion on the Thermal and Solution Behavior of Poly(2-(dimethylamino)ethyl methacrylate)-Based Polyelectrolytes. *Macromolecules* **2010**, *43*, 9998–10005.
- (15) Kooa, H.-J.; Velevalonic, O. D. Ionic Current Devices—Recent Progress in the Merging of Electronic, Microfluidic, and Biomimetic Structures. *Biomicrofluidics* **2013**, *7*, 031501-1–031501-10.
- (16) Jiang, R.; Anson, F. C. Association of Electroactive Counterions with Polyelectrolytes. 3. Electrochemistry of Cationic Counterions Associated with Poly(styrenesulfonate). *J. Phys. Chem.* **1991**, *95*, 5701–5706.
- (17) Strauss, U. P.; Woodside, D.; Winema, P. Counterion Binding by Polyelectrolytes. I. Exploratory Electrophoresis, Solubility and Viscosity Studies of the Interaction between Polyphosphates and Several Univalent Cations. *J. Phys. Chem.* **1959**, *61*, 1353–1356.
- (18) Moad, G.; Rizzardo, E.; Thang, S. H. Toward Living Radical Polymerization. *Acc. Chem. Res.* **2008**, *41*, 1133–1142.
- (19) Vandermeulen, G. W. M.; Klok, H. A. Peptide/Protein Hybrid Materials: Enhanced Control of Structure and Improved Performance through Conjugation of Biological and Synthetic Polymers. *Macromol. Biosci.* **2004**, *4*, 383–398.
- (20) White, J. D.; Wilker, J. J. Underwater Bonding with Charged Polymer Mimics of Marine Mussel Adhesive Proteins. *Macromolecules* **2011**, *44*, 5085–5088.
- (21) Bauri, K.; Roy, S. G.; Pant, S.; De, P. Controlled Synthesis of Amino Acid-Based pH-Responsive Chiral Polymers and Self-Assembly of Their Block Copolymers. *Langmuir* **2013**, *29*, 2764–2774.
- (22) Roy, S. G.; Bauri, K.; Pal, S.; De, P. Tryptophan Containing Covalently Cross-Linked Polymeric Gels with Fluorescence and pH-Induced Reversible Sol–Gel Transition Properties. *Polym. Chem.* **2014**, *5*, 3624–3633.
- (23) Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*; Longman Scientific & Technical Copublished in the United States with John Wiley & Sons, Inc: New York, 1989.
- (24) Helfferich, F. G. *Ion Exchange*; Dover Publications: New York, 1962.
- (25) Noh, T. H.; Ahn, J.; Na, Y. M.; Jung, O.-S. Anion Effects on Structure and Properties of Bis(3-methylimidazolium-1-yl) Salts. *Bull. Korean Chem. Soc.* **2011**, *32*, 2795–2798.
- (26) Hu, Z.-A.; Xie, Y.-L.; Wang, Y.-X.; Xie, L.-J.; Fu, G.-R.; Jin, X.-Q.; Zhang, Z.-Y.; Yang, Y.-Y.; Wu, H.-Y. Synthesis of  $\alpha$ -Cobalt Hydroxides with Different Intercalated Anions and Effects of Intercalated Anions on Their Morphology, Basal Plane Spacing, and Capacitive Property. *J. Phys. Chem. C* **2009**, *113*, 12502–12508.
- (27) Bokias, G.; Vasilevska, V. V.; Iliopoulos, I.; Hourdet, D.; Khokhlov, A. R. Influence of Migrating Ionic Groups on the Solubility of Polyelectrolytes: Phase Behavior of Ionic Poly(*N*-isopropylacrylamide) Copolymers in Water. *Macromolecules* **2000**, *33*, 9757–9763.
- (28) Collins, K. D. Sticky Ions in Biological Systems. *Proc. Natl. Acad. Sci. U. S. A.* **1995**, *92*, 5553–5557.
- (29) Marcilla, R.; Blazquez, J. A.; Fernandez, R.; Grande, H.; Pomposo, J. A.; Mecerreyes, D. Synthesis of Novel Polycations Using the Chemistry of Ionic Liquids. *Macromol. Chem. Phys.* **2005**, *206*, 299–304.
- (30) Manning, G. S. Limiting Laws and Counterion Condensation in Polyelectrolyte Solutions I. Colligative Properties. *J. Chem. Phys.* **1969**, *51*, 924–933.
- (31) Sabbagh, I.; Delsantia, M. Solubility of Highly Charged Anionic Polyelectrolytes in Presence of Multivalent Cations: Specific Interaction Effect. *Eur. Phys. J. E* **2000**, *1*, 75–86.
- (32) Bauri, K.; De, P.; Shah, P. N.; Li, R.; Faust, R. Polyisobutylene-Based Helical Block Copolymers with pH-Responsive Cationic Side-Chain Amino Acid Moieties by Tandem Living Polymerizations. *Macromolecules* **2013**, *46*, 5861–5870.
- (33) Lowe, A. B.; McCormick, C. L. Synthesis and Solution Properties of Zwitterionic Polymers. *Chem. Rev.* **2002**, *102*, 4177–4189.
- (34) De, P.; Li, M.; Gondi, S. R.; Sumerlin, B. S. Temperature Regulated Activity of Responsive Polymer–Protein Conjugates Prepared by Grafting-from via RAFT Polymerization. *J. Am. Chem. Soc.* **2008**, *130*, 11288–11289.
- (35) Prescher, S.; Polzer, F.; Yang, Y.; Siebenbürger, M.; Ballauff, M.; Yuan, J. Polyelectrolyte as Solvent and Reaction Medium. *J. Am. Chem. Soc.* **2014**, *136*, 12–15.
- (36) Chen, H.; Choi, J.-H.; Cruz, D. S.; Winey, K. I.; Elabd, Y. A. Polymerized Ionic Liquids: The Effect of Random Copolymer Composition on Ion Conduction. *Macromolecules* **2009**, *42*, 4809–4816.
- (37) Mecerreyes, D. Polymeric Ionic Liquids: Broadening the Properties and Applications of Polyelectrolytes. *Prog. Polym. Sci.* **2011**, *36*, 1629–1648.
- (38) Patachia, S.; Savin, G.; Luca, C.; Beldie, C. Study of Some Properties of Poly(*N*-vinyl imidazole) Partially Quaternized with *n*-Butyl Bromide Aqueous Solutions. *Eur. Polym. J.* **2002**, *38*, 1121–1127.
- (39) Allen, M. H., Jr.; Wang, S.; Hemp, S. T.; Chen, Y.; Madsen, L. A.; Winey, K. I.; Long, T. E. Hydroxyalkyl-Containing Imidazolium Homopolymers: Correlation of Structure with Conductivity. *Macromolecules* **2013**, *46*, 3037–3045.
- (40) Tsuzuki, S.; Tokuda, H.; Hayamizu, K.; Watanabe, M. Magnitude and Directionality of Interaction in Ion Pairs of Ionic Liquids: Relationship with Ionic Conductivity. *J. Phys. Chem. B* **2005**, *109*, 16474–16481.
- (41) Mayfield, H. G. Jr; Bull, W. E. Coordinating Tendencies of the Hexafluorophosphate Ion. *J. Chem. Soc. A* **1971**, 2279–2281.
- (42) MacCallum, J. R.; Vincent, C. A. *Polymer Electrolyte Reviews*; Elsevier Applied Science: London, 1987.
- (43) Florjanczyk, Z.; Bzducha, W.; Wiecek, W.; Zygadlo-Monikowska, E.; Krawiec, W.; Chung, S. H. Highly Conducting Lithium Polyelectrolytes Based on Maleic Anhydride–Styrene Copolymers. *J. Phys. Chem. B* **1998**, *102*, 8409–8416.
- (44) Bauri, K.; Pant, S.; Roy, S. G.; De, P. Dual pH and Temperature Responsive Helical Copolymer Libraries with Pendant Chiral Leucine Moieties. *Polym. Chem.* **2013**, *4*, 4052–4060.
- (45) Kumar, S.; Acharya, R.; Chatterji, U.; De, P. Side-Chain Amino-Acid-Based pH-Responsive Self-Assembled Block Copolymers for Drug Delivery and Gene Transfer. *Langmuir* **2013**, *29*, 15375–15385.
- (46) Roy, S. G.; Haldar, U.; De, P. Remarkable Swelling Capability of Amino Acid Based Cross-Linked Polymer Networks in Organic and Aqueous Medium. *ACS Appl. Mater. Interfaces* **2014**, *6*, 4233–4241.