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Multiple Hydrogen Bonding for the Noncovalent Attachment of Ionic Functionality in Triblock Copolymers

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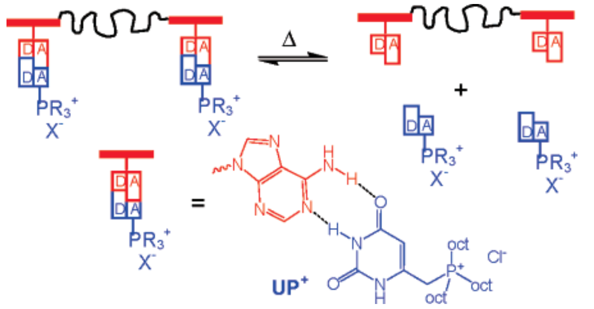
The introduction of electrostatic interactions to diverse macromolecular architectures has received significant attention for several decades.[1−4] Ionomers, which are defined as a class of lightly charged (≤15 mol %) ion-containing polymers, possess electrostatic interactions with enthalpies near ∼200 kJ/mol.[3] The Coulombic forces enable the formation of nanometer-scale aggregates,[4] resulting in improved thermomechanical properties, increased toughness, and improved chemical resistance. A further advantage of ion-containing polymers is the ability to conduct ions, which suggests applications in ion-conducting membranes, fuel cells,[5] electromechanical devices, water purification membranes, and breathable textiles for protection from chemical and biological reagents.

Despite the attractive physical properties of ionomers, melt processing often suffers due to relatively high viscosities that are attributed to ionic aggregates (which can persist to temperatures exceeding 300 °C).[6] Earlier efforts have attempted to address this potential limitation, and for example, the processability of sulfonated poly(ethylene-*co*-propylene-*co*-diene) (EPDM) improved upon the addition of zinc stearate, which "plasticized" the ionic aggregates.[7] Herein, we provide the first report of nucleobase hydrogen bonding as a noncovalent linkage for attachment of phosphonium cations to block copolymers (Scheme 1). This paper demonstrates the general concept of noncovalent ionic site attachment to block copolymers, which would enable dissociation from the block copolymer above the dissociation temperature for hydrogen bonding.

Hydrogen bonding, in contrast to nondirectional electrostatic interactions, exhibits lower enthalpies (10−40 kJ/mol) and greater specificity, which enables molecular recognition and lower melt viscosities using multiple hydrogen-bonding arrays such as ureido pyrimidones (UPy) and nucleobase pairs.[8−15] This paper describes the synergy of complementary hydrogen bonding in nanostructured block copolymers with guest molecules containing electrostatic interactions. Earlier researchers have reported coordination of metal sulfonates to pyridine-containing block copolymers;[16] however, the potential synergy of complementary hydrogen bonding with electrostatic interactions was not reported. Nucleobase functional block copolymers were also previously reported.[13,17,18] Other researchers have reported the attachment of neutral guest molecules via hydrogen-bonding interactions,[19−26] and for example, noncovalent attachment of mesogens resulted in supramolecular liquid crystalline assemblies. The attachment of single ionic sites to dendrimers[25] and small molecule hosts[26] was reported, but in these cases, the ionic portion was part of the hydrogen bonding array and nucleobases were not included.

Scheme 1. Noncovalent Attachment of UP$^+$ Phosphonium Salt to Complementary Nucleobase-Functionalized Block Copolymers



Phosphonium cations have received recent attention in our laboratories due to higher thermal stabilities relative to ammonium analogues. Earlier evidence indicates that the onset of decomposition of tetraoctylammonium bromide occurs at 170 °C due to Hofmann elimination, whereas the analogous phosphonium salt exhibits thermal stability to 260 °C.[27] Despite bulky organic substitution on the phosphonium cation, others have recently reported random copolymers containing covalently bound phosphonium cations, which result in nanoscale ionic aggregation and concomitant thermoplastic elastomeric behavior.[28]

Novel hydrogen-bonding triblock copolymers containing adenine were synthesized via nitroxide-mediated polymerization. A novel difunctional initiator, which does not introduce hydrolytically unstable ester linkages that lead to molecular weight loss, permitted the formation of symmetric outer blocks, reduced the number of subsequent monomer additions, and enabled a single crossover reaction.

The difunctional alkoxyamine initiator, which is depicted as DEPN$_2$ in Figure 1, was synthesized from *N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl)-*N*-oxyl (DEPN) and diethyl-2,5-dibromoadipate using conventional atom transfer radical addition techniques.[29−31] The chemical structure of DEPN$_2$, which consists of a mixture of diastereomers, was confirmed using NMR spectroscopy and mass spectrometry, and the *meso* diastereomer was isolated in a crystalline form, which allowed structural determination using X-ray crystallography (Figure 1).

In situ FTIR spectroscopy was used to probe the kinetics of DEPN$_2$-initiated homopolymerization of *n*-butyl acrylate. As expected for the difunctional initiator, the polymerizations exhibited typical pseudo-first-order kinetics and linear molecular weight vs conversion profiles (Figure 2) with narrow molecular weight distributions ($M_w/M_n \sim 1.10$). The difunctional nature of DEPN$_2$ was demonstrated via polymerization of *n*-butyl acrylate using mixtures of DEPN$_2$ and a monofunctional alkoxyamine initiator (Styryl-DEPN[31]). Bimodal molecular weight distributions with a ratio of peak molecular weights of 2:1 were observed, which was consistent with both monofunctional and difunctional species.

An adenine-functionalized styrenic monomer, 9-vinylbenzyladenine (9-VBA), was introduced after isolation of the telechelic DEPN-functionalized poly(*n*-butyl acrylate) (Figure 3). ^{1}H NMR spectroscopy was used to verify the presence of the adenine-containing repeat units and allowed quantification of the degree

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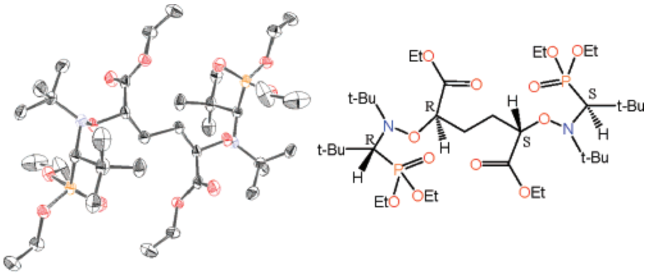

Figure 1. ORTEP X-ray crystal structure of DEPN$_2$ difunctional alkoxyamine initiator (hydrogen atoms omitted for clarity).

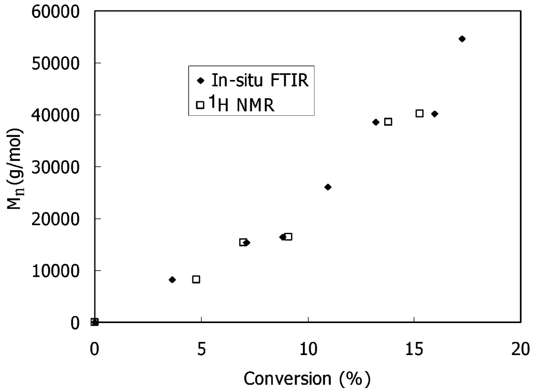

Figure 2. Number-average molecular weight as a function of monomer conversion for the polymerization of *n*-butyl acrylate with DEPN$_2$.

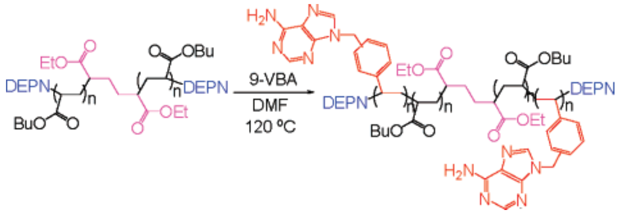

Figure 3. Synthesis of adenine-containing triblock copolymers from DEPN$_2$-initiated poly(*n*-butyl acrylate).

of polymerization of the outer blocks. Block molecular weights of 1.5K−16.5K−1.5K were calculated from ^{1}H NMR data, assuming an accurate SEC molecular weight for the rubber block ($M_n = 16\,500$, $M_w/M_n = 1.26$). Size exclusion chromatography (SEC) in tetrahydrofuran revealed a narrow molecular weight distribution and monomodal traces for the final triblock copolymer, which was consistent with a well-defined polymerization process. SEC was not suitable for the determination of hydrogen-bonding block molecular weights due to the relatively short block lengths. Thus, ^{1}H NMR was used to calculate the molecular weight for the shorter hydrogen-bonding outer block.

A novel uracil-containing phosphonium salt (UP$^+$) was synthesized in a single step from 6-chloromethyluracil and trioctylphosphine. UP$^+$ exhibited an onset of weight loss at 280 °C using thermogravimetric analysis (TGA) as well as solubility in a wide range of common organic solvents. In blends of the phosphonium salt with adenine-containing block polymers solution-cast from chloroform, crystallization of the phosphonium salt was absent from differential scanning calorimetry (DSC) thermograms. Furthermore, the solution-cast films were optically clear. In sharp contrast, solution-cast films of the phosphonium salt with nonfunctionalized poly(*n*-butyl acrylate) homopolymer resulted in opaque, macrophase-separated, films. The hydrogen-bonding association between the uracil phosphonium salt and 9-VBA monomer was verified through ^{1}H NMR spectroscopic measurements, and shifting of the adenine NH$_2$ protons was observed (Supporting Information). In the case of the adenine-functionalized block copolymer, lack of visibility of the adenine functional blocks in CDCl$_3$ prevented the analogous experiment. This phenomenon was reported previously for associating polymers.[32]

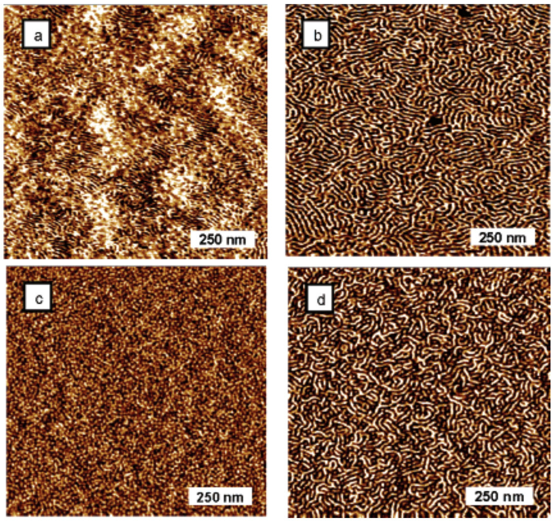

Figure 4. Tapping mode AFM phase images of 1.5K−16.5K−1.5K adenine triblock UP$^+$ blend (A:U 1:1) annealed at (a) 155, (b) 170, and (c) 200 °C. (d) Pure adenine triblock copolymer annealed at 155 °C. Set point ratio = 0.6. All samples spin-coated on silicon and annealed for 18 h under vacuum. Silicon surfaces were cleaned via chloroform rinsing and drying with high-pressure nitrogen. Film thickness values were ∼100 nm.

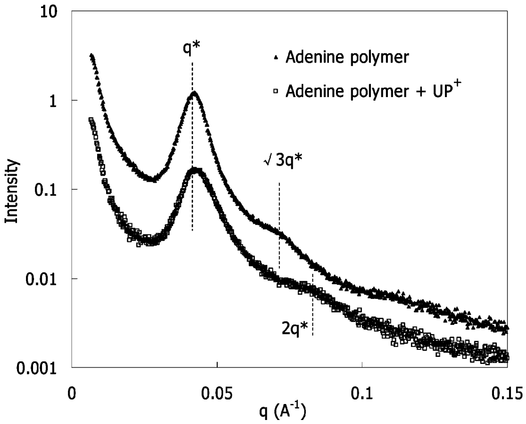

Figure 5. Small-angle X-ray scattering (SAXS) of 1.5K−16.5K−1.5K adenine triblock and UP$^+$ blend (A:U 1:1) annealed 155 °C for 18 h under vacuum.

Morphological investigations with atomic force microscopy (AFM) revealed unique surface textures for the UP$^+$ block copolymer blends compared with the pure adenine block copolymer annealed at the same temperature 155 °C (Figure 4a,d). Regions of the surfaces of the blends with UP$^+$ near the surface appeared to resemble a lamellar morphology to a greater extent than the pure adenine-containing block copolymer. Although AFM did not provide evidence of the bulk morphological effects of UP$^+$, additional X-ray scattering measurements elucidated bulk morphological changes upon blending. Corresponding SAXS data for samples annealed at 155 °C (Figure 5) revealed that the addition of the phosphonium salt resulted in a shift in morphology from cylindrical to lamellar structure. The addition of 1 equiv of phosphonium salt corresponded with a change in hard phase from 15 to 37 wt %. Transmission electron microscopy of the phosphonium salt adenine polymer

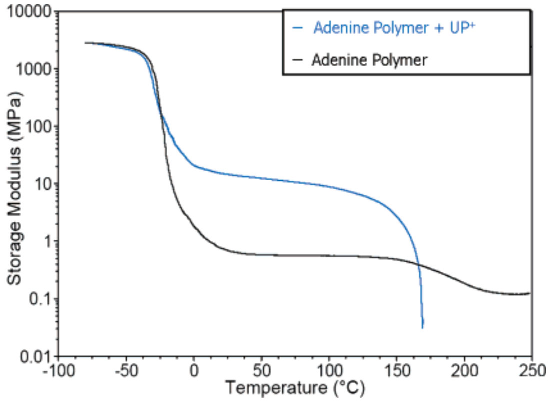

Figure 6. Dynamic mechanical temperature sweep for pure 1.5K−16.5K−1.5K adenine triblock copolymer and blend with 1 equiv of UP$^+$.

blend further supported the assignment of a lamellar morphology. Reducing the concentration of the phosphonium salt to less than stoichiometric levels (0.53 equiv) also resulted in a transition to a lamellar morphology according to SAXS. Annealing at greater termperatures (170, 200 °C) led to further changes in the surface morphology; however, these changes will be the subject of future reports.

Solution rheological studies of UP$^+$-modified adenine-containing triblock copolymers were conducted in chloroform, which favors hydrogen-bonding interactions due to a relatively low dielectric constant. An apparent 3.4-fold decrease in solution viscosity of the block copolymer solution (4.2 wt %, 25 °C) was observed upon the addition of 1 equiv of UP$^+$. This suggested a screening effect of the adenine−adenine self-association between polymer chains and further indicated the effectiveness of the hydrogen-bonding interaction.

Dynamic mechanical (DMA) studies on the adenine polymer UP$^+$ blends revealed that the glass transition temperature of the rubber phase did not change significantly (Figure 6). The rubber phase T_g of the blend was −32 vs −29 °C for the pure adenine polymer according to the maximum of the loss modulus curve, indicating selective incorporation of UP$^+$ into the hard phase. Furthermore, the rubbery plateau modulus increased from 0.7 to 14.6 MPa at 25 °C. This change in modulus is consistent with the increased hard phase volume fraction from 15 to 37 wt % but may also be possibly attributed to ionic aggregation, as reported by others.[28] Future studies will seek to determine the dominant mechanism of this modulus enhancement. Interestingly, for the blend with UP$^+$, the softening of the hard phase occurred at lower temperatures (160 vs 230 °C), suggesting that adenine−uracil hydrogen bonds remained intact at these temperatures, resulting in a screening effect of the adenine−adenine intermolecular hydrogen bonds.

In conclusion, this paper defines a novel general strategy for the introduction of thermally stable ionic sites to block copolymers via complementary hydrogen bonding. Novel adenine-containing block copolymer precursors were synthesized using a novel difunctional initiator. Subsequent blending with unique phosphonium cation containing complementary hydrogen-bonding guests was conducted. Influences on surface morphology, solution viscosity, and mechanical properties were observed.

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Supporting Information Available: X-ray crystallographic data for DEPN$_2$, synthetic procedures with characterization for DEPN$_2$, UP$^+$, and block copolymers, and spectroscopic evidence of association of UP$^+$ with 9-VBA. This material is available free of charge via the Internet at http://pubs.acs.org.

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