Noncovalently Functionalized Poly(norbornene)s Possessing both Hydrogen Bonding and Coulombic Interactions

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ABSTRACT: Random copolymers containing both hydrogen bonding and charged ionic sites have been synthesized by the ring-opening metathesis polymerization of norbornene monomers containing either an ionic quaternary ammonium group or a 2,6-diaminopyridine functionality. All copolymers were functionalized subsequently via self-assembly using hydrogen bonding and Coulombic interactions. The hydrogen bonding interactions between 2,6-diaminopyridine and *N*-butylthymine were studied in the presence of the ionic quaternary ammonium group and its subsequent self-assembly with three different charged anionic species to investigate the influence of the Coulombic interactions on the strength of hydrogen bonding. It was found that hydrogen bonding was independent of the nature and presence of the Coulombic interactions. These results prove that the studied hydrogen bonding interactions are orthogonal to the Coulombic interactions and that both interactions can be used independently of each other in the same system to noncovalently functionalize polymer backbones.

Introduction

Polymer functionalization through noncovalent chemistry has several distinct advantages over covalent functionalization strategies, such as fast and facile functionalization, reversibility, and self-reparability.[1−3] This area of supramolecular polymer chemistry has made significant strides,[4−6] with examples including the synthesis of supramolecular liquid crystalline polymers,[7] thermo- and chemoreversible cross-linked gels,[8] and supramolecular photoactive molecules.[9] In these studies, a wide variety of recognition motifs have been employed, including metal coordination,[10,11] Coulombic interactions,[12] and hydrogen bonding.[13,14] By using single or multiple noncovalent interactions, polymer properties have been precisely tailored and complex architectures have been easily synthesized.[8,15] One example from the work of Ikkala et al. demonstrates that, by combining metal coordination and ionic interactions with polymer science, highly controlled and functionalized nanostructures can be synthesized in a straightforward fashion.[16]

Coulombic interactions are among the most widely encountered noncovalent interactions rivaled only by hydrogen bonding and van der Waals interactions in their frequency. Each of these noncovalent interactions has unique bond strength and distinct advantages and disadvantages.[17] The most important example of using Coulombic interactions in materials science is in the field of "ionomers" which are tailor-made materials. Ionomers are widely used commercially due to their unique physical properties such as enhanced impact strength, toughness, and thermal reversibility.[18] Other examples of Coulombic interactions in polymeric systems include block copolymers containing charged segments,[19−21] ionically cross-linked polymers,[22] self-assembled dendrimers,[23,24] functionalized telechelics,[25] main-chain ionically functionalized polymers,[26] ionically linked main- and side-chain liquid crystalline polymers,[27,28] artificial molecular machines,[29] ionic polyamphiphiles,[30] and ionically self-assembled fluorescent materials.[31] While these examples clearly demonstrate the importance of Coulombic interactions in materials science, they have only used these interactions in the absence of other noncovalent interactions.

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One important strategy for noncovalent multifunctionalization[32,33] would be the controlled employment of ionic interactions along with other noncovalent interactions within the same polymeric system. Such a strategy would allow for the tailoring of materials properties by exploiting the differences in the nature of these reversible interactions as well as multifunctionalization.[8,34] However, a prerequisite for the use of multiple interactions in such a system is that all noncovalent interactions have to be orthogonal to each other, or at least the effects of one interaction in the presence of another one must be clearly understood. Recently, we have reported detailed investigations into the orthogonality of hydrogen bonding and metal coordination[34,35] where we have proven that these two interactions can be used in an orthogonal fashion, expanding the possibility to design polymers that can be utilized as precursors for a variety of materials applications through simple self-assembly based functionalization.[8,34] Although there have been some reports where Coulombic interactions have been used in the presence of hydrogen bonding in polymeric systems, a study of the interdependence of these two interactions with a quantitative evaluation is lacking.[7,28] Furthermore, Rotello et al. have used hydrogen bonding and Coulombic self-assembly in micropatterning surfaces; however, the recognition units were present on separate polymer backbones.[36] This contribution will demonstrate the efficiency of direct copolymerization via ring-opening metathesis polymerization (ROMP) of functionalized monomers as a convenient route to multifunctionalized polymers having both hydrogen bonding and Coulombic self-assembly sites. A qualitative as well as quantitative study of the interdependence of these two noncovalent interactions was carried out to fully understand this unique multifunctionalization system.

ROMP is a highly functional group tolerant polymerization technique, which can synthesize polymers with controlled architectures.[8,37−39] While ROMP of charged metal complexes such as ferrocene[37,40−43] and in ionic liquids[44] has been carried out, there are only few reports of polymerizing charged monomers.[45−47] The vast majority of reports utilize postpolymerization modifications to yield polyelectrolytes.[48−52] However, such postpolymerization modifications can involve side

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reactions such as hydrolysis, chain degradation, or cross-linking, thereby leading to ill-defined structures.[53] By directly copolymerizing a charged monomer, postpolymerization steps can be avoided, giving a straightforward and robust method to make functional materials such as ionomers and polyelectrolytes. In this contribution, we describe the first report to synthesize a highly functionalized polymer by copolymerizing a charged norbornene monomer with a norbornene monomer containing a terminal hydrogen bonding motif using ROMP followed by a detailed investigation into the noncovalent functionalization of the resulting copolymers.

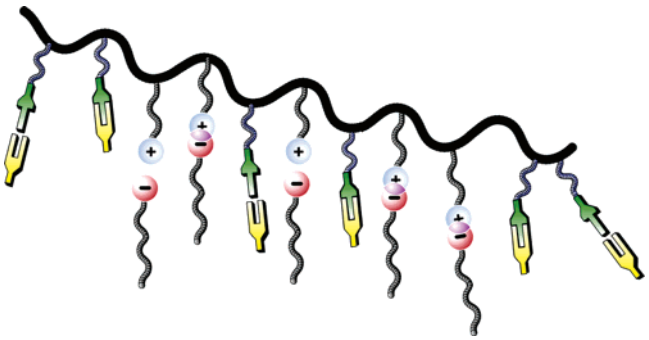


Figure 1. A cartoon depiction of a random copolymer noncovalently multifunctionalized by complementary sets of recognition units based on hydrogen bonding and Coulombic self-assembly.

Experimental Section

General. All reagents were purchased from Acros Organics, Aldrich, or Strem Chemicals and used without further purification unless otherwise noted. Triethylamine (TEA), methylene chloride, and deuterated chloroform ($CDCl_3$) were distilled over calcium hydride. Grubbs' third-generation initiator was synthesized as reported.[54] Monomer **4**,[55] *N*-butylthymine,[56] isomerically pure *exo*-norbornene acid,[55,57] and sodium 4-(dodecyloxy)phenolate (SDP)[58] were synthesized according to published procedures. Sodium benzene dodecylsulfonate (SDS) and sodium stearate (SS) were used as received. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were taken using a Varian Mercury Vx 300 spectrometer. All spectra are referenced to residual proton solvent. Abbreviations used include singlet (s), broad singlet (bs), doublet (d), triplet (t), quartet (q), and unresolved multiplet (m). Mass spectral analyses were provided by Georgia Institute of Technology's Bioanalytical Mass Spectrometry Facility on a VG-70se spectrometer using the fast atom bombardment ionization method (FAB). HRMS denotes high-resolution mass spectrum. Elemental analyses were performed on a Perkin-Elmer Series II 2400 CHNS/O analyzer. Gel-permeation chromatography (GPC) analyses were carried out using a Shimadzu pump and a Shimadzu UV detector with tetrahydrofuran (THF) or dimethylformamide (DMF) as eluant and a set of American Polymer Standards columns (100, 1000, 100 000 Å linear mixed bed). The flow rate for all measurements was 1 mL/min. All GPC measurements were calibrated using poly(styrene) standards and were carried out at room temperature. M_w, M_n, and PDI represent the weight-average molecular weight, number-average molecular weight, and the polydispersity index, respectively. IR analyses were performed on a Shimadzu IR spectrometer. The samples were dissolved in dry CH_2Cl_2 and cast as a thin film on a NaCl disk.

10-Hydroxydecyl-*exo*-bicyclo[2.2.1]hept-5-ene-2-carboxylate (1). *exo*-Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (5 g, 0.036 mol) and 1,10-decanediol (12.6 g, 0.072 mol) were suspended in anhydrous toluene (100 mL). A catalytic amount of *p*-toluenesulfonic acid (0.37 g, 0.002 mol) was added, and the mixture was refluxed at 110 °C for 4 h. After cooling and filtering off the excess diol, the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, eluant: hexanes:EtOAc, 3/1, v/v) and dried to yield **1** as a colorless liquid (6.12 g, 60%). ^{1}H NMR ($CDCl_3$): δ = 6.01 (m, 2H, CH═CH), 3.97 (t, 2H, J = 6.70 Hz, −$COOCH_2$−), 3.49 (t, 2H, J = 6.70 Hz, −CH_2−OH), 2.92 (s, 1H, norbornene signal), 2.81 (s, 1H, norbornene signal), 2.75 (s, 1H, norbornene signal), 2.12 (m, H, norbornene signal), 2.17 (m, 1H, norbornene signal), 1.90 (m, 1H, norbornene signal), 1.67−1.55 (m, 4H, −$(CH_2)_2$−), 1.51−1.25 (m, 10H, −$(CH_2)_5$−). ^{13}C NMR ($CDCl_3$): δ = 176.5, 138.1, 135.8, 64.7, 62.7, 46.4, 46.7, 43.3, 41.7, 32.8, 30.4, 29.6, 29.5, 29.3, 28.8, 26.0, 25.9. HRMS (FAB+) [M + 1] calcd for $C_{18}H_{31}O_3$: 295.22732, found: 295.22962. Anal. Calcd for $C_{18}H_{30}O_3$: C, 73.43; H, 10.27. Found: C, 70.20; H, 10.49.

10-(4-(Dimethylamino)benzoyloxy)decyl-*exo*-bicyclo[2.2.1]-hept-5-ene-2-carboxylate (2). Compound **1** (1.0 g, 0.003 mol) and triethylamine (1.71 g, 0.016 mol) were dissolved in anhydrous CH_2Cl_2 (100 mL) and cooled to 0 °C. Then, 4-(dimethylamino)benzoyl chloride (0.64 g, 0.003 mol) was added slowly to the stirred solution. After 1 h, the temperature was allowed to rise to room temperature followed by reflux for 12 h. The reaction mixture was then cooled to room temperature and washed with 1 N HCl (100 mL) followed by saturated $NaHCO_3$ solution (100 mL). The organic phase was then dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (SiO_2, eluant: hexanes:EtOAc, 1/2, v/v), and dried to yield **2** as a colorless liquid (0.80 g, 56%). ^{1}H NMR ($CDCl_3$): δ = 7.90 (d, 2H, J = 9.95 Hz, Ar), 6.63 (d, 2H, J = 9.95 Hz, Ar), 6.11 (m, 2H, CH═CH), 4.24 (t, 2H, J = 6.70 Hz, −CH_2−OCO−Ar), 4.08 (t, 2H, J = 6.72 Hz, −$COOCH_2$−), 3.02 (s, 6H, −$N(CH_3)_2$), 3.00 (s, 1H, norbornene signal), 2.88 (s, 1H, norbornene signal), 2.31 (t, 2H, J = 7.08 Hz, −CH_2−), 2.17 (m, 1H, norbornene signal), 1.90 (m, 1H, norbornene signal), 1.67−1.55 (m, 4H, −$(CH_2)_2$−), 1.51−1.25 (m, 10H, −$(CH_2)_5$−). ^{13}C NMR ($CDCl_3$): δ = 176.5, 167.2, 153.4, 138.2, 136.0, 131.4, 117.5, 110.8, 64.8, 64.8, 46.8, 46.5, 43.4, 41.8, 40.2, 30.5, 29.6, 29.5, 29.4, 29.1, 28.9, 26.3, 26.1. HRMS (FAB+) [M + 1] calcd for $C_{27}H_{40}NO_4$: 442.295, found: 442.293. Anal. Calcd for $C_{27}H_{39}NO_4$: C, 73.43; H, 8.90; N, 3.17. Found: C, 73.47; H, 9.16; N, 3.39.

4-((10-(*exo*-Bicyclo[2.2.1]hept-5-enecarbonyloxy)decyloxy)-carbonyl)-*N*,*N*,*N*-trimethylbenzenaminium Iodide (3). Compound **2** (1.74 g, 0.003 mol) was dissolved in excess iodomethane (5.5 g, 0.039 mol) and stirred at 30 °C for 2 days. The excess iodomethane was removed under reduced pressure to give the crude product as a yellow solid. The solid was suspended in ice-cold diethyl ether, stirred for 30 min, and filtered. Then, the product was washed repeatedly with ice-cold hexanes and dried to yield the pure product **3** (1.71 g, 98%) as a pale yellow solid. ^{1}H NMR ($CDCl_3$): δ = 8.28 (d, 2H, J = 9.95 Hz, Ar), 8.13 (d, 2H, J = 9.95 Hz, Ar), 6.10 (m, 2H, CH═CH), 4.24 (t, 2H, J = 6.70 Hz, −CH_2−OCO−Ar), 4.08 (t, 2H, J = 6.72 Hz, −$COOCH_2$−), 4.05 (s, 9H, −$N(CH_3)_3$), 3.03 (s, 1H, norbornene signal), 2.90 (s, 1H, norbornene signal), 2.31 (m, 2H, J = 7.08 Hz, −CH_2−), 2.17 (m, 1H, norbornene signal), 1.90 (m, 1H, norbornene signal), 1.67−1.55 (m, 4H, −$(CH_2)_2$−), 1.51−1.25 (m, 10H, −$(CH_2)_5$−). ^{13}C NMR ($CDCl_3$): δ = 176.5, 164.7, 150.2, 138.2, 135.9, 133.0, 132.2, 120.9, 110.8, 66.2, 64.7, 62.1, 58.1, 46.8, 46.5, 43.4, 41.8, 40.3, 30.5, 29.6, 29.4, 28.8, 26.1. HRMS (FAB+) [M − I + 1] calcd for $C_{28}H_{42}NO_4$: 456.311, found: 456.311. Anal. Calcd for $C_{28}H_{42}INO_4$: C, 57.63; H, 7.25; N, 2.40. Found: C, 57.35; H, 7.25; N, 2.51.

Homopolymerizations. The homopolymerization of monomer **3** is described as a representative example: Monomer **3** (22.1 mg, 0.037 mmol) was dissolved in 0.5 mL of $CHCl_3$. A stock solution of Grubbs' third generation initiator was prepared in $CHCl_3$, and an amount of the stock solution equaling 6.7 mg (0.379 mmol) of the initiator was added to the monomer solution. The solution was stirred, and the reaction was monitored by observing the olefinic signals of the monomer by ^{1}H NMR spectroscopy. Upon complete conversion, a drop of ethyl vinyl ether was added to terminate the polymerization. The polymer was isolated and purified by precipitation from ice-cold methanol, and repeated washings with ice-cold methanol and hexanes, followed by prolonged drying at room temperature under high vacuum.

Poly-2. ^{1}H NMR ($CDCl_3$): δ = 7.90 (d, 2H, J = 9.95 Hz, Ar), 6.63 (d, 2H, J = 9.95 Hz, Ar), 5.34−5.18 (m, 2H, CH═CH), 4.24 (br m, 2H, −CH_2−OCO−Ar), 4.01 (br m, 2H, −$COOCH_2$−), 3.02 (s, 6H, −$N(CH_3)_2$), 2.68 (br m, 2H), 2.48 (br m, 2H), 2.31 ( ), 2.02−1.91 (br m, 2H), 1.60 (br m, 5H), 1.41 (br m, 2H), 1.25 (br s, 14H). ^{13}C NMR ($CDCl_3$): δ = 176.1, 134−131, 120.0, 64.7, 50−49, 47.8, 43.2, 42.1, 41.3, 37.2, 36.4, 29.5, 28.9, 29.1, 25.5.

Poly-3. ^{1}H NMR (d_6-DMSO): δ = 8.16 (distorted d, 2H, Ar), 8.10 (distorted d, 2H, Ar), 5.33−5.17 (m, 2H, CH═CH), 4.24 (br m, 2H, −CH_2−OCO−Ar), 3.99 (br m, 2H, −$COOCH_2$−), 3.65 (br s, 9H, −$N(CH_3)_3$), 2.48 (br m, 2H), 2.31 (m, 2H), 2.02−1.91 (br m, 2H), 1.60 (br m, 2H), 1.48−1.26 (br m, 14H). ^{13}C NMR (d_6-DMSO): δ = 165.0, 151.1, 138.5, 136.3, 131.9, 122.0, 65.9, 64.6, 57.1, 46.6, 43.2, 30.5, 29.6, 29.4, 29.3, 28.7, 26.1.

Copolymerizations. Random copolymers of **3** and **4** were synthesized in a similar fashion as outlined above. The synthesis of **UPB-10%** is described as a representative example of random copolymerization of **3** and **4**: Monomer **3** (22.1 mg, 0.037 mmol) was dissolved in 0.5 mL of $CHCl_3$, to which a 0.5 mL solution of monomer **4** (200 mg, 0.38 mmol) was added. A stock solution of Grubbs' third generation initiator was prepared in $CHCl_3$, and an amount of the stock solution equaling 6.7 mg (0.379 mmol) of the initiator was added to the monomer solution. The solution was stirred, and the reaction was monitored by observing the olefinic signals of the monomers by ^{1}H NMR spectroscopy. Upon complete conversion, a drop of ethyl vinyl ether was added to terminate the polymerization. Purification of all polymers was performed by precipitating the polymers from ice-cold methanol and repeated washings with ice-cold methanol and ice-cold hexanes, followed by prolonged drying at room temperature under high vacuum.

UPB-10%. ^{1}H NMR (d_7-DMF): δ = 8.40 (br d, 2H, Ar), 8.21 (br d, 2H, Ar), 7.57 (s, 2H, pyridyl), 5.34−5.18 (m, 2H, CH═CH), 4.36 (t, 2H, J = 6.6 Hz,), 4.04 (m, 2H), 3.94 (s, 9H, −$N(CH_3)_3$), 2.48 (br m, 2H), 1.78 (br s, 2H), 1.61 (br s, 2H), 1.32−1.10 (br m, 2H), 1.08 (t, 6H, J = 7.7 Hz). ^{13}C NMR (d_6-DMF): δ = 173.2, 168.3, 164.9, 152.3, 151.2, 132−131, 121.9, 95.4, 68.2, 65.8, 64.3, 56.9, 37.2, 34.0, 26.0.

Self-Assembly Experiments. *Hydrogen Bonding*. The polymers (100 mg) were dissolved in CH_2Cl_2 (5 mL). Then a calculated amount of *N*-butylthymine was dissolved in CH_2Cl_2 (2−3 mL) and added in one portion, and the solution was stirred for 30 min after which the solvent was removed under reduced pressure to yield the hydrogen bonded polymer.

The synthesis of **UPB-2-10%** is described as a representative example: **UPB-10%** (222 mg, 0.379 mmol based on the 2,6-diaminopyridine functional groups along the polymer backbone) was dissolved in 5 mL of CH_2Cl_2. Then, 69 mg (0.379 mmol) of *N*-butylthymine was added, and the solution was stirred for 30 min. The solvent was evaporated, and the self-assembled polymer **UPB-2-10%** was dried under high vacuum.

Coulombic Self-Assembly. The polymers were dissolved in CH_2Cl_2 (5 mL) to get a homogeneous solution. Then, the calculated amount of **5**−**7**, dissolved in CH_2Cl_2 (2−3 mL), was added, and the solution was stirred for 30 min, after which the solvent was removed under reduced pressure to yield the self-assembled polymers.

The synthesis of **UPB-1-SDS-10**% is described as a representative example: **UPB-10%** (222 mg, 0.0379 mmol based on the quaternary ammonium iodide groups along the polymer backbone) was dissolved in 5 mL of CH_2Cl_2, then 13.2 mg (0.037 mmol) of compound **5** was added, and the reaction mixture was stirred for 30 min. The solution was dried under high vacuum to yield the self-assembled polymer **UPB-1-SDS-10%**.

Titration Experiments. Association constants (K_a) were measured by ^{1}H NMR spectroscopy titrations at room temperature of a 0.005 M solution of the copolymers (based on the hydrogen bonding moieties) in deuterated $CHCl_3$ with a 0.01 M solution of *N*-butylthymine. The chemical shifts of the amide protons for the 2,6-diaminopyridines were monitored during the titration. The data were evaluated by ChemEquili software to calculate the association constants.[59] All titrations were conducted in duplicate. The errors ranged from 10 to 15%.

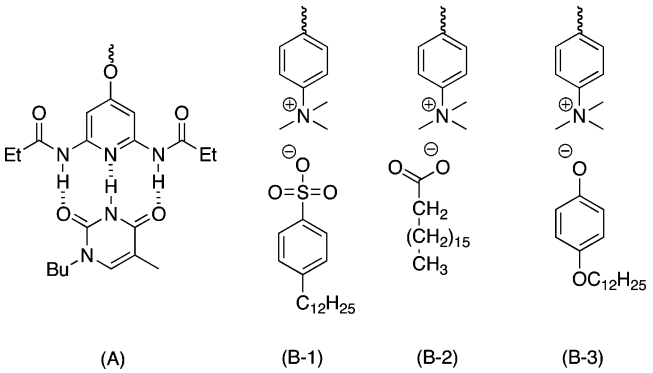


Figure 2. Self-assembly motifs used in this study: (A) three point hydrogen bonded complex between 2,6-diaminopyridine and *N*-butylthymine and (B) Coulombic self-assembly between the quaternary ammonium group and (B-1) sodium dodecyl sulfonate, (B-2) sodium stearate, and (B-3) sodium dodecyloxy phenolate.

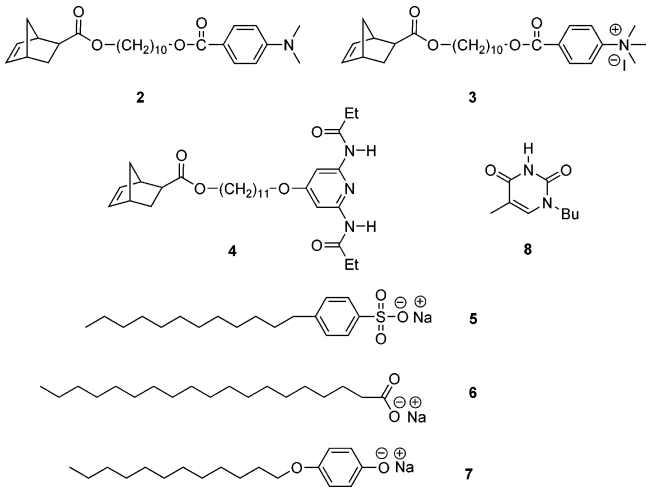


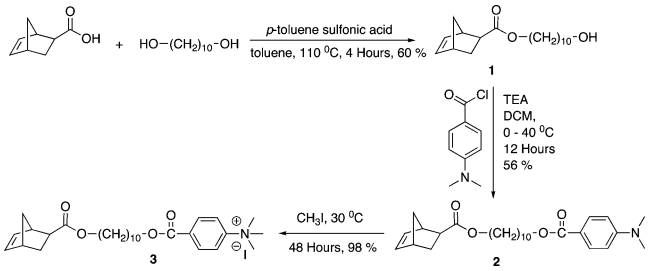
Figure 3. Monomers **2**−**4** and recognition units **5**−**8** used in this study.

Research Design. Our research design consists of multifunctional random copolymers having both hydrogen bonding and Coulombic recognition sites. These multifunctionalized copolymers can be viewed as "universal polymer backbones"[8,34] since a family of different functionalized polymeric materials can be obtained from a single polymer backbone by varying the complementary recognition units, i.e., the functionalization. These polymer backbones are based on monomers that are comprised of a norbornene moiety that can be polymerized using ROMP and a long alkyl spacer composed of either a C-10 or C-11 chain to improve solubility and to decouple the recognition units from the polymer backbone.

Three-point hydrogen bonding DAD−ADA arrays (D = hydrogen bonding donor, A = hydrogen bonding acceptor) are the most studied complementary hydrogen bonding receptors to date and have been utilized in this study.[60] In particular, functionalized 2,6-diaminopyridines (DAD) and *N*-butylthymine (ADA) (Figure 2) have been employed. The 2,6-diaminopyridine recognition units are anchored onto the polymer backbone with *N*-butylthymine being the complementary recognition unit. In a recent contribution, we have shown that higher K_a are achieved with the 2,6-diaminopyridines being attached to the polymer backbone as they have a lesser tendency to undergo self-association as compared to their complementary thymine counterpart.[35]

The components for the Coulombic self-assembly consist of quaternary ammonium iodides which can be self-assembled with three different complementary recognition units **5**−**7** (Figures 2 and 3). The recognition units are based on the sodium salts of long alkyl chain functionalized sulfonic acid (sodium dodecyl sulfonate, (SDS)), carboxylic acid (sodium stearate-SS), and phenol (sodium

Scheme 1. Synthesis of Monomer 3



dodecyloxy phenolate (SDP)). The long alkyl chains enhance the solubility of these salts in nonpolar solvents such as $CHCl_3$ and CH_2Cl_2 in which all self-assembly experiments were carried out. The three different anionic recognition units were chosen to study the effect of the hydrogen bonding acceptors (oxygen atoms) on the anionic moieties; each of the three anionic recognition units has a differing number of oxygen atoms, capable of disrupting the hydrogen bonding interactions between *N*-butylthymine and 2,6-diaminopyridine.

Results and Discussion

Synthesis of Monomers and Recognition Units. All monomers are derived from 100% isomerically pure *exo*-norbornene acid.[55,57] Monomer **3** was synthesized as outlined in Scheme 1. Esterification of *exo*-norbornene acid with an excess of 1,10-decanediol using *p*-toluenesulfonic acid as the catalyst in toluene gave the monoester alcohol **1**. Compound **1** was then esterified with 4-(dimethylamino)benzoyl chloride in CH_2Cl_2 to yield the tertiary amine monomer **2**.

Monomer **3** was then synthesized by quantitatively converting the tertiary amine group of monomer **2** to a quaternary ammonium group, which was achieved by reacting **2** with an excess of iodomethane at 30 °C for 48 h.[61] The quantitative quaternization of **2** was determined by ^{1}H NMR spectroscopy. Upon complete quaternization, the methyl signals showed a complete downfield shift from 3.00 to 4.00 ppm. Furthermore, because of the strong negative inductive effect of the quaternary ammonium group, the aromatic signals also showed significant shifts from 6.63 to 8.13 ppm and from 7.90 to 8.28 ppm. Isolation of the analytically pure monomer **3** was facile, as monomer **2** is a liquid and soluble in hexanes, whereas monomer **3** is a solid and insoluble in hexanes. As a result, filtration and repeated washing with ice-cold hexanes followed by prolonged drying under high vacuum yielded pure **3** as a pale yellow solid.

Homopolymerization Studies. Although monomer **2** could be polymerized using Grubbs' second and third generation initiators, monomer **3** could only be polymerized using Grubbs' third generation initiator which has been reported to have a high catalytic activity and functional group tolerance.[62] Quantitative conversions of monomer **3** could be achieved in less than 5 min at room temperature using $CHCl_3$ as the solvent as determined by ^{1}H NMR spectroscopy. **Poly-3** had limited solubility in solvents such as CH_2Cl_2, $CHCl_3$, and THF but was completely soluble in strongly polar solvents such as DMF and DMSO. Once Grubbs' third generation initiator was found to polymerize monomer **3**, we studied whether the polymerization is controlled. We conducted a series of homopolymerizations with monomer to initiator ratios (M/I ratios) ranging from 10:1 to 250:1. We found that molecular weights of the resulting polymers were independent of the M/I ratio used, indicating an uncontrolled polymerization. For all M/I ratios studied, the M_n was in the range of 8000−9000 with the PDI ranging from 1.2 to 1.3. (GPC analysis of **Poly-3** was carried out using DMF as the solvent and poly(styrene)s as standards.) To further probe the polymerization of **3**, we monitored the carbene signal during polymerization. Upon addition of **3** to the catalyst solution, complete disappearance of the uninitiated carbene signal at 19.09 ppm without any presence of either initiated or uninitiated carbene signals was observed, confirming the uncontrolled nature of this polymerization.

Copolymerization Studies. Monomers **2** and **4** could be quantitatively copolymerized using Grubbs' third generation initiator in less than 5 min. All copolymers based on **2** and **4** with varying composition were soluble in nonpolar solvents such as CH_2Cl_2 and $CHCl_3$.

Similarly **3** and **4** could be copolymerized using Grubbs' third generation initiator to yield copolymers having both hydrogen bonding and charged sites. GPC analysis of the resulting copolymers shows unimodal curves with PDIs around 1.2. However, the solubility of copolymers **3** and **4** was highly dependent upon the mole fraction of the charged monomer **3**. All copolymers having less than 20 mol % of monomer **3** were completely soluble in nonpolar solvents such as $CHCl_3$ and CH_2Cl_2. However, increasing the concentration of **3** above 20 mol % resulted in copolymers that phase-separated in these solvents but were completely soluble in polar solvents such as THF and DMF. Unfortunately, because of the competing nature of these solvents, they do not allow for formation of strong hydrogen bonds between 2,6-diaminopyridine and *N*-butylthymine, thereby eliminating these solvents for our self-assembly studies.

Noncovalent Functionalizations. The copolymers thus synthesized have both hydrogen bonding and ionic sites along the polymer backbone which after multifunctionalization can yield a family of functionally varied copolymers from a single polymer backbone.[8,34] Functionalization of the resulting copolymers using noncovalent interactions as well as investigation into the orthogonal character of all functionalization steps is the basis of this work. Therefore, we investigated the noncovalent functionalizations of all copolymers via hydrogen bonding and/or Coulombic self-assembly.

Monomer Studies. Qualitative Analysis: Hydrogen Bonding Interactions. One of the aims of this work was to determine whether the hydrogen bonding interactions between 2,6-diaminopyridine and *N*-butylthymine were affected by the presence of ionic charges and subsequent Coulombic self-assembly. To investigate this, we employed ^{1}H NMR spectroscopy to monitor the chemical shifts of the amide protons of 2,6-diaminopyridine and the chemical shifts of the imide proton of *N*-butylthymine during the hydrogen bonded complex formation both in the presence and in the absence of ionic charges and Coulombic self-assembly. For these qualitative analyses, we could not use copolymers based on **4** and **3** having equimolar amounts of the recognition units, as they were not completely soluble in $CHCl_3$. Hence, we conducted these qualitative analyses using monomers **3** and **4**, which were completely soluble in equimolar ratios in $CHCl_3$; this allowed us to accurately and reliably study the effect of ionic charges and self-assembly on the 2,6-diaminopyridine-*N*-butylthymine complex formation. Furthermore, we wanted to study whether the sequence of the hydrogen bonding and ionic self-assemblies would have any effect on the complex formation of 2,6-diaminopyridine and *N*-butylthymine. Therefore, we carried out these multiple self-assembly experiments in three distinct ways:

(A) Hydrogen Bonding Followed by Coulombic Self-Assembly. This investigation was carried out to study the effect of the ionic charges and the Coulombic self-assembly on the hydrogen bonded complex of **4** and **8**. In this experiment, **4** and **8** were first self-assembled to form the corresponding

Table 1. GPC Data of Unfunctionalized Homo- and Copolymers

entry	[M]/[I]	M_n (10^{-3})	M_w (10^{-3})	PDI
poly-2	50	5.3	6.7	1.26
poly-3	50	8.5	13.0	1.23
poly-4[a]	50	10.4	13.0	1.25
UPB-10%	50	7.1	9.0	1.26
UPB-15%	50	8.0	9.7	1.22
UPB-20%	50	8.7	10.6	1.21
control polymer	50	63.0	97.5	1.54

[a] Eluant: DMF. Polymer abbreviations are based on Scheme 3.

hydrogen bonded complex, after which an equimolar amount of **3** was added to the complex. It was found that the amide and the imide protons of the hydrogen bonded complex did not undergo any changes in their chemical shifts, indicating that the presence of ionic charges does not interfere with the hydrogen bonding interactions of **4** and **8**. Further, the effect of Coulombic self-assembly was investigated; monomer **3** in the above experiment was then self-assembled with **5**, **6**, and **7** individually. In each case we found that the proton shifts of the hydrogen bonded complex were not affected upon the Coulombic self-assembly. The NMR data are listed in Table 2. This clearly establishes that the hydrogen bonding between **4** and **8** is not disrupted by the presence of **3** and its subsequent Coulombic self-assembly.

(B) Coulombic Self-Assembly Followed by Hydrogen Bonding. In this functionalization mode, we first carried out the Coulombic self-assembly followed by hydrogen bonding. Monomer **3** was self-assembled with **5**, **6**, or **7** individually to form three distinct ionic complexes. Then an equimolar amount of **4** was added to the ionic complexes. We found that the amide protons of **4** did not undergo any changes in their chemical shifts. Furthermore, when **4** was self-assembled with an equimolar amount of **8**, the amide and the imide protons shifts of the complex of **4** and **8** were not affected by the self-assembled Coulombic complexes. These results clearly illustrate that the route of functionalization does not affect the hydrogen bonding between **4** and **8**.

(C) Simultaneous Multifunctionalizations. To investigate whether both ionic self-assembly and hydrogen bonding can be carried together simultaneously, we carried out multifunctionalization experiments. Monomers **3** and **4** were simultaneously self-assembled using ionic self-assembly and hydrogen bonding interactions, respectively. Here again we found that the amide and the imide protons shifts of the complex of **4** and **8** were independent; i.e., the hydrogen bonding interaction is not affected by the Coulombic self-assembly and was independent of the anionic recognition units **5**, **6**, and **7**.

Qualitative Analysis: Coulombic Self-Assembly. We were not able to characterize the Coulombic self-assembly via NMR spectroscopy since it involves only the exchange of the counter anions and no visible shifts of the chemical shifts of the protons (methyl protons attached to the quaternary nitrogen atom) as well as the protons of the aromatic nucleus and the methylene carbon atom adjacent to the aromatic nucleus that were not within the error range of the NMR instrument were detected. Also, no significant shifts in the ^{13}C spectra were observed upon Coulombic self-assembly, regardless of the fact that the carbon data would also be qualitative and not quantitative. Hence, the Coulombic self-assembly between **3** with **5**, **6**, and **7** was studied by using infrared spectroscopy by monitoring the distinct absorption bands around 3000 and 1500 cm^{-1} ($-N^+(CH_3)_3$ group), 1245 cm^{-1} (sulfonate group), around 1560 cm^{-1} (carboxylate group), and around 1235 cm^{-1} (phenate group).[24,63,64] The IR spectra can be found in the Supporting Information.

First, we investigated changes of the IR stretches during the hydrogen bonding. Upon self-assembly of **4** and **8**, the free amide vibration band of **4** at 3320 cm^{-1} was completely shifted to 3280 cm^{-1}, whereas the free imide vibration band of **8** was completely shifted to 3210 cm^{-1}.[65] Then, we investigated whether **5**, **6**, and **7** which have hydrogen bond acceptor oxygen moieties are able to interact with **4**. We monitored the vibrational frequencies of the amide group of **4** in the presence of **5**; no shifting of the amide frequency at 3320 cm^{-1} as well as the sulfonate frequency at 1245 cm^{-1} was detected, indicating the absence of any interactions between the sulfonate groups and the amide groups of **4**. Furthermore, when **4** and **8** were self-assembled in the presence of **5**, we observed the distinctive shifts of both the amide and the imide frequencies of **4** and **8** without any shifting of the sulfonate group at 1245 cm^{-1}. Next, we self-assembled **5** with **3** and found that the positions of the amide band of **4**, the imide band of **8**, and the sulfonate band of **5** were not altered. We carried out the same experiments using **6** and **7** and observed similar results indicating the absence of hydrogen bonding interactions between the amide groups of **4** with the carboxylate and the phenate groups, respectively. The detailed IR shifts are tabulated in Table 3.

Quantitative Analysis: Hydrogen Bonding Interactions. After performing the qualitative analysis, we conducted detailed quantitative analyses by measuring the K_a values of 2,6-diaminopyridine and *N*-butylthymine in the presence and absence of the charged ionic species. First, we carried out preliminary studies using monomer **4** and its complementary recognition unit **8**. Using ^1H NMR spectroscopy titration experiments, we determined that the K_a of the hydrogen bonded complex between **4** and **8** was 900 M^{-1}, which is comparable to published values.[35,65] Next we investigated whether the anionic recognition species **5**, **6**, or **7** would interfere in the hydrogen bonded complex formation between **4** and **8**. Therefore, we titrated monomer **4** against **8** in the presence of equimolar concentrations of **5**, **6**, or **7**. In all cases we found that the K_a values were identical to the K_a values for the hydrogen bonding between **4** and **8** without the presence of any

Table 2. Amide and Imide Proton Chemical Shifts in ppm Measured by ^1H NMR Spectroscopy of the Hydrogen Bonded Complex Between 4 and 8 Using Three Different Functionalization Routines: (A) Hydrogen Bonding Followed by Coulombic Self-Assembly, (B) Coulombic Self-Assembly Followed by Hydrogen Bonding, and (C) One-Step Multifunctionalization

(A) hydrogen bonding followed by Coulombic self-assembly			(B) Coulombic self-assembly followed by hydrogen bonding		
	chemical shift (ppm)			chemical shift (ppm)	
entry	amide protons of **4**	imide protons of **8**	entry	amide protons of **4**	imide protons of **8**
4	7.57	N.A.	**3 + 5 + 4 + 8**	9.16	10.54
8	N.A.	8.02	**3 + 6 + 4 + 8**	9.11	10.60
4 + 8	9.21	10.64	**3 + 7 + 4 + 8**	9.18	10.60
4 + 8 + 3	9.17	10.54	(C) simultaneous multifunctionalization		
4 + 8 + 3 + 5	9.21	10.56	**(4 + 3) + (8 + 5)**	9.11	10.63
4 + 8 + 3 + 6	9.15	10.61	**(4 + 3) + (8 + 6)**	9.13	10.62
4 + 8 + 3 + 7	9.17	10.61	**(4 + 3) + (8 + 7)**	9.14	10.56

Table 3. Wavenumbers of (1) N−H Stretch of 4 and 5 and (2) Counteranion A^-

	wavenumber (cm^{-1})				wavenumber (cm^{-1})		
entry	amide	imide	A^-	entry	amide	imide	A^-
4 + **5**	3320	N.A.	1245[a]	**4** + **8** + **6** + **3**	3280	3210	1560[b]
4 + **8** + **5**	3280	3210	1245[a]	**4** + **7**	3320	N.A.	1235[c]
4 + **8** + **5** + **3**	3280	3210	1245[a]	**4** + **8** + **7**	3280	3210	1235[c]
4 + **6**	3320	N.A.	1560[b]	**4** + **8** + **7** + **3**	3280	3210	1235[c]
4 + **8** + **6**	3280	3210	1560[b]				

[a] Sulfonate group. [b] Carboxylate group. [c] Phenate group.

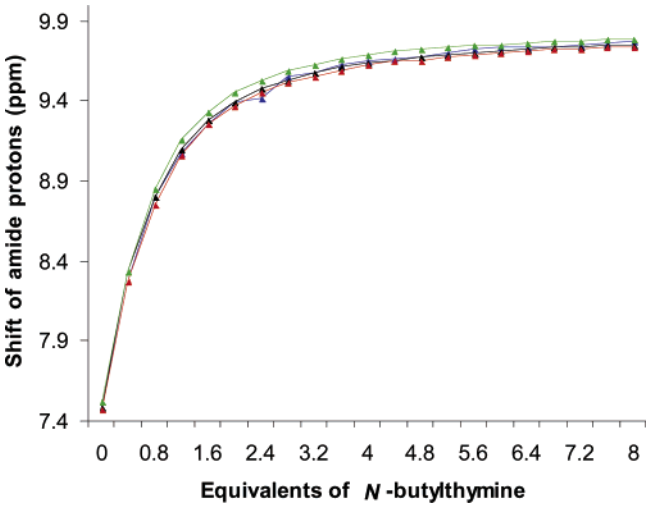


Figure 4. ^{1}H NMR spectroscopy titration curves for monomer **4** (blue), monomer **4** + **5** (black), monomer **4** + **6** (green), and monomer **4** + **7** (red) with *N*-butylthymine (**8**). The solutions (0.005 M, based on the hydrogen bonding moieties) were titrated against *N*-butylthymine (0.01 M) at room temperature in $CHCl_3$.

Table 4. K_a Values for the Self-Assembly via Hydrogen Bonding of Monomer 4 before and after Coulombic Self-Assembly

entry	K_a value[a] (M^{-1})	entry	K_a value[a] (M^{-1})
4 + **8**	900	**4** + **7** + **8**	895
4 + **3** + **8**	920	**4** + **3** + **5** + **8**	945
4 + **5** + **8**	885	**4** + **3** + **6** + **8**	822
4 + **6** + **8**	922	**4** + **3** + **7** + **8**	1000

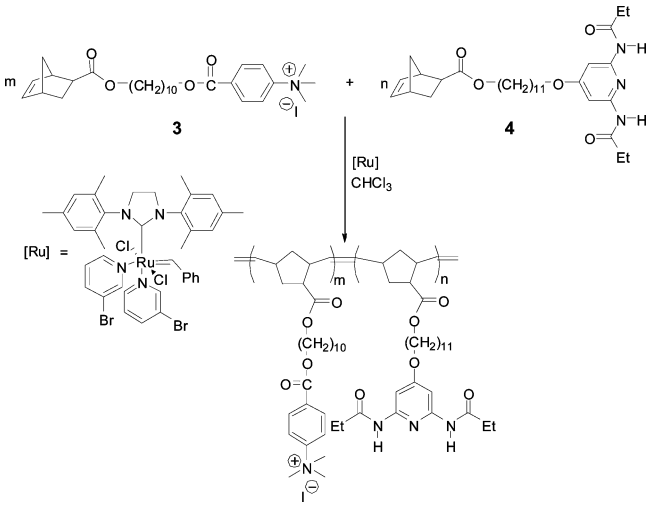
[a] Errors for all K_a measurements ranged from 10 to 15%.

salt, which indicates that the presence of anionic functional groups such as sulfonate, carboxylate, and phenolate does not appreciably interfere in the hydrogen bonding interactions between **4** and **8**. Figure 4 and Table 4 outline these results.

To study the effect of the cationic quaternary ammonium salt group on the hydrogen bonding interactions, **4** was titrated against **8** in the presence of an equimolar concentration of **3**. No changes in the K_a values were observed, indicating that the presence of the quaternary ammonium salt does not interfere with the hydrogen bonding interactions. Furthermore, the quantitative effect of ionic self-assembly on hydrogen bonding interactions was investigated. Monomer **3** in the above experiment was self-assembled with **5**, **6**, or **7** individually, and subsequently we carried out ^{1}H NMR titration studies. In each case we observed that the K_a values (Table 4) did not show any significant deviations from the K_a values for the complex of **4** and **8** in the absence of any charged species. This clearly establishes that the hydrogen bonding between **4** and **8** is not disrupted by the presence of **3** and its subsequent Coulombic self-assembly.

These preliminary monomer studies indicate that the presence of anions such as sulfonate (**5**), carboxylate (**6**), and phenolate (**7**) containing three, two, and one oxygen atom, respectively, that are able to act as potential hydrogen bond acceptors does

Scheme 2. Random Copolymerization of Monomers 3 and 4

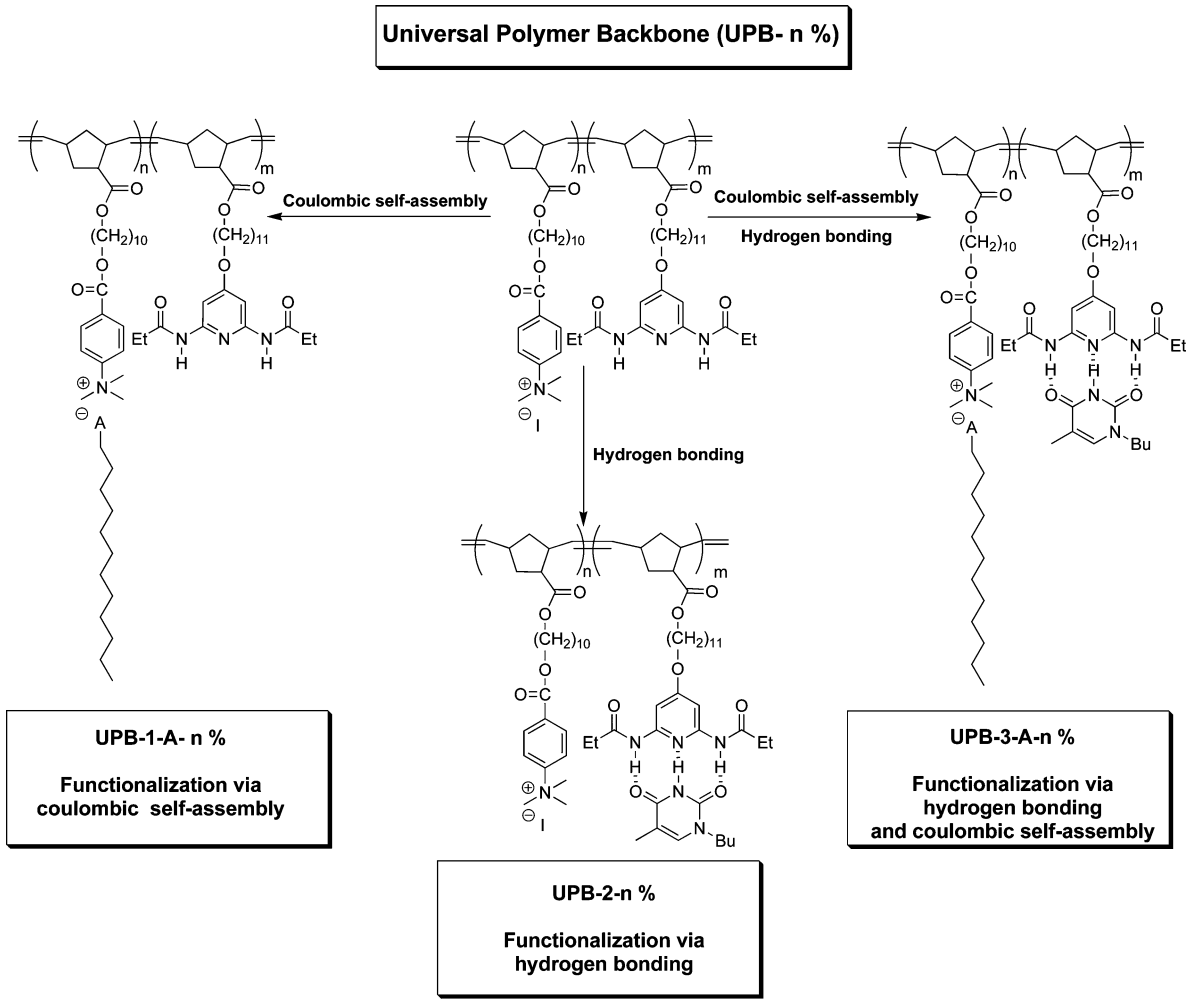


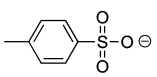
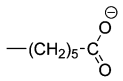
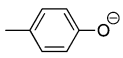
not disrupt the hydrogen bond complex formation between **4** and **8**. Furthermore, when these anions are complexed with **3**, the presence of the ionic complex does not cause any disruption of the hydrogen bonded complex formation of **4** and **8**. After these preliminary experiments, we carried out the self-assembly of all copolymers by using either hydrogen bonding or ionic self-assembly as well as the stepwise multifunctionalization beginning with the ionic self-assembly followed by hydrogen bonding, as depicted in Scheme 3

Polymer Studies. *Hydrogen Bonding*. All copolymers were easily self-assembled via hydrogen bonding by simply stirring the polymer solution in CH_2Cl_2 with the calculated amounts of **8** (based on the 2,6-diaminopyridine moieties along the polymers), followed by the removal of the solvent under reduced pressure. The K_a values for all copolymers measured by ^{1}H NMR spectroscopy titration experiments were found to decrease from 900 M^{-1} to around 500 M^{-1}. This result was expected since we previously reported similar decreases in the K_a values of hydrogen bonding monomers based on 2,6-diaminopyridines upon polymerization.[35,56]

To study the effect of copolymer composition on the K_a values, three different copolymers were synthesized having three different ratios of monomer **3** to monomer **4** (10:90, 15:85, 20:80 mol %). The K_a values (Table 5 and Figure 5) of these three different copolymers were identical within the experimental error, indicating that the copolymer composition has no effect on the K_a values. Furthermore, we synthesized a copolymer using monomers **2** and **4** as a control polymer (equimolar amounts of **2** and **4**, [M]/[I] = 50). This control copolymer does not contain any charged species along the polymer backbone and allowed us to easily compare the effect of the ionic charges. Again, we found that the K_a value (K_a = 520 M^{-1}) of the control copolymer was identical, within the error range, to those copolymers based on monomers **3** and **4**, indicating that the presence of the ionic sites along the polymer does not interfere

Scheme 3. Functionalization Strategies of the Random Copolymers



UPB	UPB-1-SDS UPB-3-SDS	UPB-1-SS UPB-3-SS	UPB-3-SDP UPB-3-SDP	UPB-2
$A^{\ominus}$				None

[a] Nomenclature: *n* % denotes the percentage of monomer **3**; UPB-1 indicates functionalization through Coulombic self-assembly; UPB-2 indicates functionalization through hydrogen bonding; UPB-3 indicates complete functionalization through both interactions; SDS, SDP and SS represent the anionic recognition units **5**, **6** and **7** respectively used for ionic self-assembly. Hence the polymer abbreviation **UPB-1-SDS-20%** would indicate a copolymer of **4** and **3** (20 mol %) which is functionalized by ionic self-assembly using **5**.

Table 5. K_a Values for the Self-Assembly via Hydrogen Bonding of Copolymers Based on Monomers 3 and 4 before and after Coulombic Self-Assembly[a]

entry	K_a value[b] (M^{-1})	entry	K_a value[b] (M^{-1})
UPB-10%	505	**UPB-1-SS-10%**	650
UPB-15%	415	**UPB-1-SS-15%**	550
UPB-20%	555	**UPB-1-SS-20%**	560
UPB-1-SDS-10%	450	**UPB-1-SDP-10%**	525
UPB-1-SDS-15%	535	**UPB-1-SDP-15%**	620
UPB-1-SDS-20%	505	**UPB-1-SDP-20%**	660

[a] Polymer abbreviations are based on Scheme 3. [b] Errors for all K_a measurements ranged from 10 to 15%.

with the hydrogen bonding interactions between 2,6-diaminopyridine and *N*-butylthymine.

Coulombic Self-Assembly. Functionalization of the quaternary ammonium salt was carried out by dissolving the copolymers in dry CH_2Cl_2 and then adding the calculated amount of the appropriate recognition unit **5**, **6**, or **7**. The solution was stirred for 30 min, after which the solvent was evaporated under reduced pressure.

*Stepwise Multifunctionalization*s. After establishing that (a) the Coulombic self-assembly of all copolymers can be carried out without interference of the hydrogen bonding recognition motifs and the hydrogen bonding based functionalization of the copolymers, (b) the strength of the hydrogen bonding interaction is independent of the copolymers used, and (c) the strength of the hydrogen bonding interaction is independent of the Coulombic recognition pair employed, we carried out studies toward our ultimate goal of multifunctionalization of polymer scaffolds. In particular, we investigated the hydrogen bonding strength via ^{1}H NMR spectroscopy titration experiments of copolymers that were first functionalized via Coulombic self-assembly. We used all three complementary recognition units **5**, **6**, and **7** for these studies. As shown in Figure 6 and Table 5, similar K_a

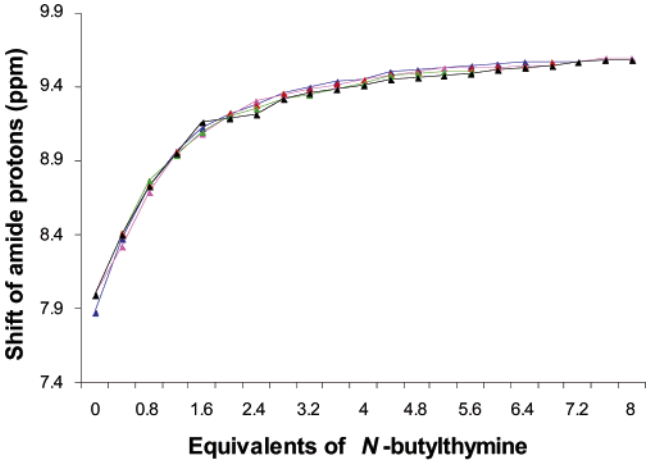


Figure 5. ^{1}H NMR spectroscopy titration curves for **Poly-4** (blue), control polymer (red), **UPB-10%** (orange), **UPB-15%** (green), and **UPB-20%** (black) with *N*-butylthymine. The solutions (0.005 M, based on the hydrogen bonding moieties) were titrated against *N*-butylthymine (0.01 M) at room temperature in $CHCl_3$.

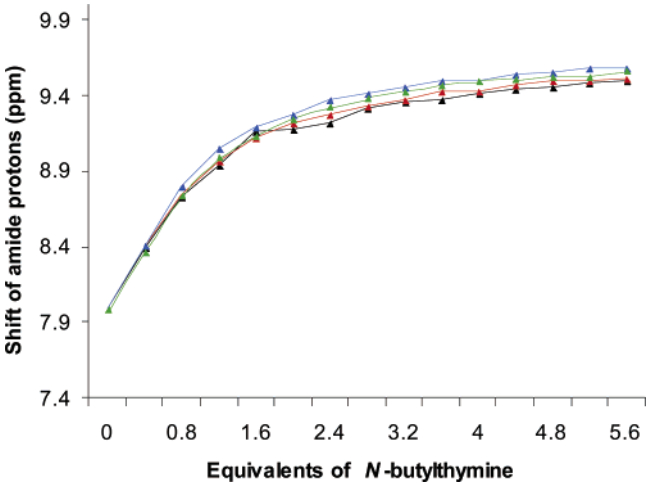


Figure 6. ^{1}H NMR spectroscopy titration curves for **UPB-20% (**black), **UPB-1-SDS-20%** (red), **UPB-1-SDP-20%** (blue), and **UPB-1-SS-20%** (green) with *N*-butylthymine. The solutions (0.005 M, based on the hydrogen bonding moieties) were titrated against *N*-butylthymine (0.01 M) at room temperature in $CHCl_3$.

values for the hydrogen bonding titration experiments for all copolymers self-assembled with **5**, **6**, and **7** were observed. Futhermore, the K_a values were also independent upon the composition of the copolymers functionalized by Coulombic self-assembly. These results clearly demonstrate that Coulombic self-assembly does not interfere with the hydrogen bonding functionalization; i.e., both recognition motifs are orthogonal to each other.

Summary and Conclusions

In this contribution, we have synthesized random copolymers possessing both hydrogen bonding and charged ionic recognition sites via ROMP. The hydrogen bonding recognition system consisted of substituted 2,6-diaminopyridine and *N*-butylthymine, whereas the Coulombic self-assembly system is based on a quaternary ammonium salt and sodium salts of long alkyl chain sulfonic acid, stearic acid, and phenol. The effect of copolymerization, copolymer composition, and last Coulombic self-assembly on the noncovalent functionalization via hydrogen bonding was studied in detail. None of these variables had any substantial impact on the stability of the hydrogen bonded complexes. Since the hydrogen bonding interactions between 2,6-diaminopyridine and *N*-butylthymine are highly sensitive to the solvent medium used, the multifunctionalizations were studied only in solvents such as chloroform or methylene chloride which offer superior solubility and do not disturb the hydrogen bonding interactions. Clearly the Coulombic interactions are also strongly solvent dependent, and all results described in this paper are only valid for the solvent systems studied. Nevertheless, these results demonstrate that the hydrogen bonding interactions are orthogonal to the Coloumbic interactions. Therefore, by combining a functional group tolerant polymerization route with noncovalent functionalization techniques, we have demonstrated that such a strategy allows for the fast synthesis of highly functionalized materials. Using noncovalent interactions such as hydrogen bonding and ionic self-assembly, we can synthesize from a single polymer backbone a large variety of functionally varied polymers which widely differ in their physical and chemical properties by simply altering the functionalization strategy. Such a strategy will be important in the synthesis of multifunctional materials for emerging advanced applications.

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Supporting Information Available: IR spectra of the qualitative investigations of Coulombic interactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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