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One-Step Multifunctionalization of Random Copolymers via Self-Assembly

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Abstract: A novel methodology for random copolymer functionalization based on a noncovalent, one-step, multifunctionalization strategy has been developed. Random copolymers possessing both palladated-pincer complexes and diaminopyridine moieties (hydrogen-bonding entities) have been synthesized using ring-opening metathesis polymerization. Noncovalent functionalization of the resultant copolymers is accomplished via (1) *directed self-assembly,* (2) *multistep self-assembly,* and (3) *one-step orthogonal self-assembly.* This system shows complete specificity of each recognition motif for its complementary unit, with no observable changes in the association constants regardless of the degree of functionalization.

Introduction

The next generation of highly functionalized materials for potential applications in molecular scale memory, photorefractives, displays, sensing, and drug delivery will require fast synthesis, functionalization, and fabrication as well as rapid device optimization.[1,2] Furthermore, the ability to control the structure and properties of the materials is key to their development. Current methodologies for the synthesis of complex materials such as multifunctionalized homo- and copolymers either lack this control or are synthetically challenging and require lengthy syntheses. Herein, we introduce a novel methodology to multifunctionalize random copolymers in one simple self-assembly step.

Motivated by Nature's simple yet elaborate approach to biomaterials,[3] this methodology relies upon noncovalent interactions to fabricate polymers with function, diversity, and complexity.[4,5] In contrast to covalent syntheses, noncovalent synthetic strategies are highly desirable due to the spontaneous formation of selective, simple, reversible, and self-healing, but sufficiently strong linkages. Such interactions include hydrogen bonding, metal coordination, Coulombic interactions, and hydrophobic interactions. Nature's ability to utilize parallel self-assembly processes has thus far been unmatched in materials design.[4b,c] Inspired by Nature, the methodology presented herein utilizes two recognition motifs, hydrogen bonding[4] and metal coordination,[5] to densely multifunctionalize random copolymers in one simple self-assembly step via a controlled noncovalent functionalization strategy thereby introducing tunable functional diversity.

Research Design. Random copolymers are the basis for our research design, an important class of materials with a wide variety of potential applications including photorefractive materials.[6,7] The copolymers introduced here can be viewed as "universal polymer backbones" (UPBs) and are based on two monomers containing terminal metal-coordination or hydrogen-bonding recognition motifs (Figure 2).[4k,5] Both monomers encompass three design elements: (1) norbornene as the polymerizable unit, which propagates in a living fashion via ring-opening metathesis polymerization (ROMP);[8,9] (2) a spacer molecule to increase solubility and to decouple the polymer backbone from the recognition unit;[10] and (3) the recognition units (a) Pd-pincer complexes that allow for the coordination

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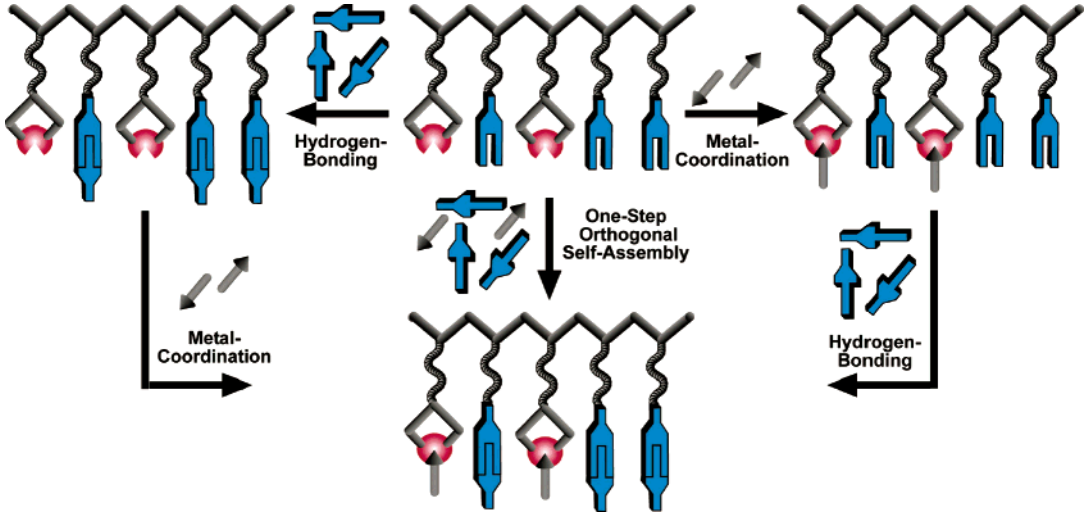


Figure 1. A cartoon depicting the formation of complex copolymers using stepwise and one-step, noncovalent multifunctionalization strategies.

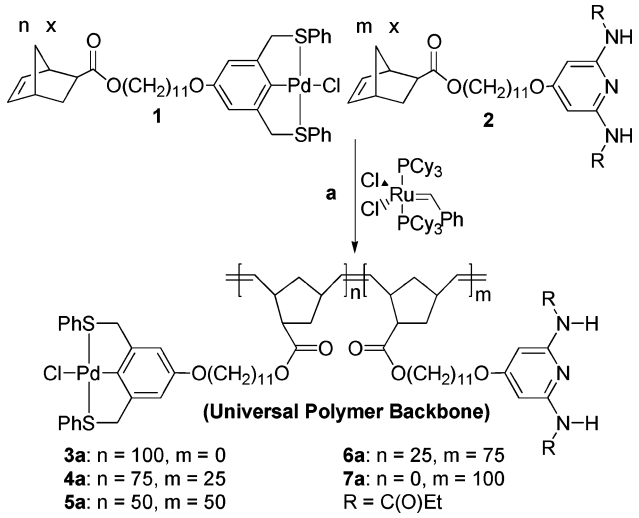
of pyridines, nitriles, or phosphines[5,11−12] and (b) diaminopyridines that are able to undergo three hydrogen bonds.[4c−f,k,13]

By appropriate design of these polymers, we envisaged a modular system for the noncovalent functionalization of the "universal polymer backbone" that allows for (1) directed self-assembly of one terminal recognition motive via either metal coordination or hydrogen bonding, (2) stepwise functionalization starting with either interaction, and ultimately (3) one step self-assembly in which both recognition motifs are spontaneously functionalized in the presence of complimentary recognition units (Figure 1).

Results and Discussion

UPB Synthesis and Characterization. Recently, we reported the synthesis, polymerization behavior, self-assembly properties, and materials properties of *exo*-**1** and *exo*-**2**.[5a] In both cases, self-assembly and ultimately materials fabrication are rapid and quantitative. ROMP of **1** and **2** can be carried out using $Ru(=Ph)Cl_2(PCy_3)_2$ as catalyst under mild reaction conditions in quantitative yields (Scheme 1). In addition, both monomers exhibit polymerization kinetics independent of the terminal recognition motif.[5a] This finding is an important prerequisite which allows for the formation of statistical copolymers. Furthermore, a linear relationship between molecular weight and monomer-to-initiator ratios has previously been established for **1** and **2**, allowing for stoichiometric control of copolymer molecular weights.[5a] Thus, by modifying the monomer feed ratios, the copolymer compositions are easily tailored. To examine the influence of monomer composition on the ability to noncovalently functionalize the resultant copolymers, a series of low polydisperse random copolymers were synthesized (Table 1). Furthermore, a series of copolymers composed of fifty percent of each monomer were synthesized with monomer-to-catalyst ratios of 10:1 (**8a**), 50:1 (**7a**), and 500:1 (**9a**) to study the effect of molecular weight on self-assembly. The resultant copolymers are all soluble in dichloromethane (DCM); however, streaking on the GPC columns was observed for copolymers possessing the diaminopyridine unit in this media. Generally, it was found that the extent of streaking increases proportionally with an increase in diaminopyridine composition. To circumvent this problem, a more polar solvent, THF, was employed for the characterization of **5a**−**8a**.

Scheme 1. Universal Polymer Backbone (UPB) Synthesis[a]



[a] (a) Grubbs catalyst, $CHCl_3$, rt, 1 h, 100%. Copolymer compositions are expressed as percentages.

Table 1. Copolymer Characterization Data

polymer	polymer composition 1:2	[M]/[I]	GPC eluant	M_n (10^{-4})	M_w (10^{-4})	PDI
3a	100:0	50	DCM	7.3	8.0	1.10
4a	75:25	50	DCM	4.5	5.3	1.18
5a	50:50	50	THF	3.0	3.5	1.15
6a	25:75	50	THF	2.7	3.2	1.19
7a	0:100	50	THF	3.6	4.4	1.22
8a	50:50	10	THF	0.56	0.69	1.23
9a[a]	50:50	500				

[a] GPC results are not reported due to insolubility in THF.

Noncovalent Functionalization. Copolymers **4a**−**6a** provide the foundation for our main goal, the one-step multirecognition site functionalization of random copolymers via hydrogen bonding and metal coordination. To achieve this goal, several requirements must be realized, including strong self-assembly,

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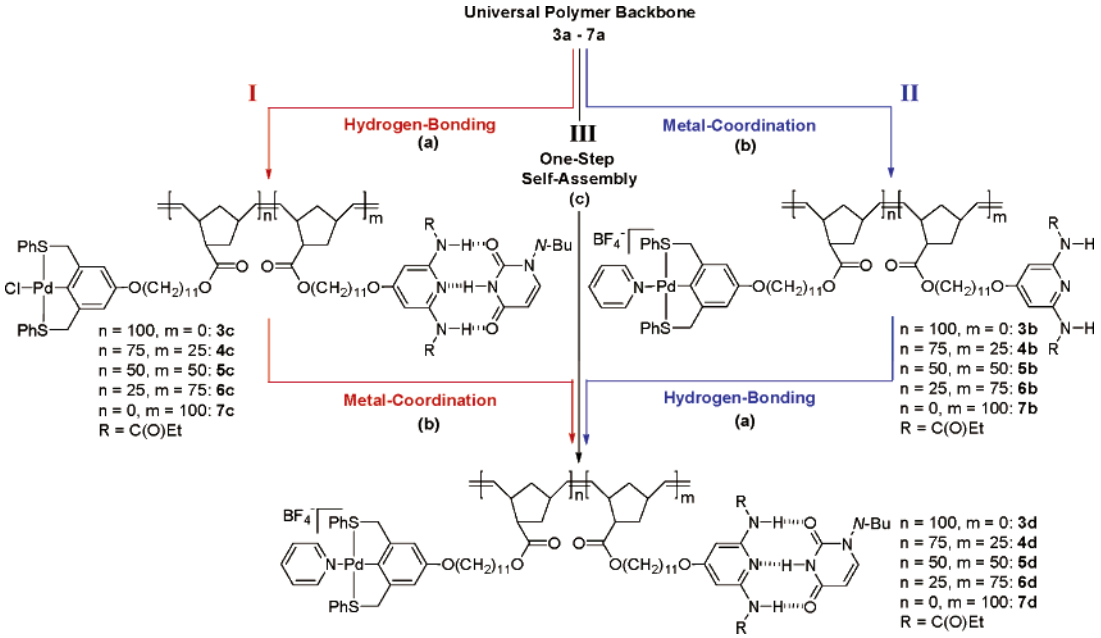
Scheme 2. Noncovalent UPB Functionalization Strategies[a]



[a] (I) Stepwise functionalization beginning with hydrogen bonding (II) with metal coordination and (III) one-step multirecognition site self-assembly. (a) *N*-butylthymine, CH_2Cl_2; (b) pyridine, $AgBF_4$, CH_2Cl_2; (c) *N*-butylthymine, pyridine, $AgBF_4$, CH_2Cl_2.

full solubility of all copolymers, and no interference of the two recognition motifs with each other. To address these concerns, a synthetic scheme was developed and executed that examines the stepwise self-assembly of "functional" anchoring units to each polymer, the effect of functionalization on the solubility, the strength of each self-assembly step, thermal properties of the resultant copolymers, and, ultimately, the one-step orthogonal random copolymer functionalization (Scheme 2).

For ease of characterization, pyridine and *N*-butylthymine have been employed as "functional" complementary recognition units for the Pd^{II} complexes and the diaminopyridine moieties, respectively.[4k,5] Copolymers **4a**−**6a** were functionalized using three distinct methodologies: (1) *directed self-assembly* of pyridine to the Pd^{II} complexes or *N*-butylthymine to the diaminopyridine units providing monofunctionalized copolymers **4b**−**6b** and **4c**−**6c**, respectively; (2) *stepwise functionalization* starting with either hydrogen bonding (Scheme 2I) or metal coordination (Scheme 2II) via two-step sequential addition yielding **4d**−**6d**; and (3) *orthogonal functionalization* by simple addition of both pyridine and *N*-butylthymine (Scheme 2III) providing the fully functionalized copolymers **4d**−**6d** in a simple, one-step process. In all cases, the self-assembly of the pyridine is quantitative with strong binding interactions between the diaminopyridine units and *N*-butylthymine. All copolymers are fully soluble in CH_2Cl_2 with the exception of **6b**, which is solubilized by a 75:25 CH_2Cl_2/nitromethane mixture. Addition of *N*-butylthymine to **6b** restores the CH_2Cl_2 solubility of the fully functionalized copolymer **6d**. No diffusion or solubility limitations to this methodology were observed for high or low molecular weight polymers **9a**−**d** and **8a**−**d**, respectively.

The self-assembly behavior of the stepwise functionalization route beginning with metal coordination can be characterized by monitoring characteristic changes in chemical shifts using ^{1}H NMR spectroscopy.[4k,5b,11−12] Figure 2A−C demonstrates the selectivity of the pyridine anchoring unit for the palladated-pincer ligand. As depicted, only the α-pyridyl signal at 8.58 ppm shows a characteristic upfield shift to the coordinated species at 8.00 ppm.[5b,11] Notably, the amide signals of the diaminopyridine moiety at 7.93 ppm (Figure 2B) remain unaffected (Figure 2C) by the transformation from **5a** to **5b**. However, following addition of 1.5 equiv of *N*-butylthymine, a dramatic downfield shift of the amide signal to 9.66 ppm (Figure 2E) is observed in addition to a weaker downfield shift of the imide signal of the *N*-butylthymine from 10.04 ppm (Figure 2D) to 10.53 ppm (Figure 2E).[4k] These results confirm the selectivity of each anchoring unit for its respective recognition motif.

Similarly, Figure 3A−E illustrate the stepwise functionalization of **5a** beginning with hydrogen bonding and ending with metal coordination. Beginning with addition of 1.5 equiv of *N*-butylthymine, we observe by comparison of Figure 3A−C only the diagnostic shifts of the hydrogen bonding amide (7.93 ppm to 9.66 ppm) and imide protons (10.04 ppm to 10.53 ppm) with no observed change of the signals for the aromatic pincer complexes. Once functionalized with *N*-butylthymine, the addition of 1 equiv of pyridine and $AgBF_4$ resulted in the fully functionalized copolymer **5d** (Figure 3E) whose spectrum is identical to Figure 2E.

Finally, the one-step multifunctionalization of **5a** was evaluated via ^{1}H NMR spectroscopy. A large number of significant chemical shifts are visible for the orthogonal transformation of **5a** to **5d**. Most notably, three major shifts occur when comparing Figure 4A, B, and C to Figure 4D: (1) the α-pyridyl signals at 8.58 ppm (Figure 3A) show the characteristic upfield shift to 8.00 ppm (Figure 3D) following coordination, (2) the amide signals of the diaminopyridine moiety at 7.93 ppm (Figure 3C) give a downfield shift to 9.66 ppm (Figure 3D) upon hydrogen bonding, and (3) a significant downfield shift from 10.04 ppm (Figure 3B) to 10.53 ppm (Figure 3D) is observed for the imide signal for *N*-butylthymine upon association. Again, the final spectra for this one-step process are identical to those obtained via the stepwise routes. Thus, ^{1}H NMR spectroscopy provides

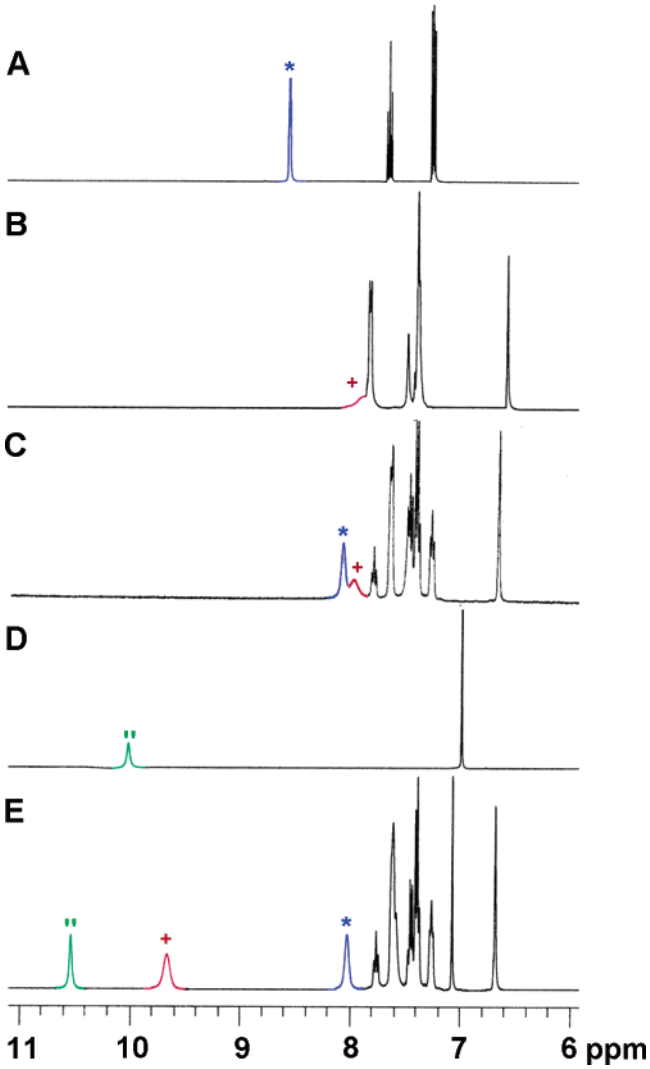


Figure 2. Aromatic region of the ^{1}H NMR spectra depicting the stepwise functionalization (metal coordination followed by hydrogen bonding) of **5a**. (A) Pyridine (* = α-pyridyl protons), (B) copolymer **5a** (+ = amide protons), (C) copolymer following directed metal coordination (**5b**), (D) *N*-butylthymine (" = imide proton), and (E) fully functionalized copolymer **5d**.

Table 2. Thermal Data for Functionalized Copolymers

entry	**3** T_g/T_{dec} (°C)	**4** T_g/T_{dec} (°C)	**5** T_g/T_{dec} (°C)	**6** T_g/T_{dec} (°C)	**7** T_g/T_{dec} (°C)
a	78/269	74/271	69/275	65/307	62/367
b	69/260	77/271	67/277	78/280	
c		62/248	48/221	42/217	31/214
d[a]		59/242	47/219	35/215	

[a] Values are independent of chosen functionalization route.

strong evidence for strong and selective binding of the complimentary recognition units and shows that the final, fully functionalized materials are identical, independent of the chosen functionalization route.

In addition to selectivity, it is essential that the strength of the noncovalent interactions remain unaltered throughout the course of all functionalization steps. To probe this parameter, ^{1}H NMR spectroscopy was employed to measure the hydrogen bonding association constants (K_a).[4k] In all cases, K_a remains constant within the error ranges with values of 474 ± 45 M^{-1}, 447 ± 80 M^{-1}, 537 ± 97 M^{-1}, 501 ± 98 M^{-1} for **2**, **7a**, **5a**, and **5b**, respectively. This implies that the hydrogen bonds are unaffected by the polymer backbone and the presence of the functionalized metal centers.

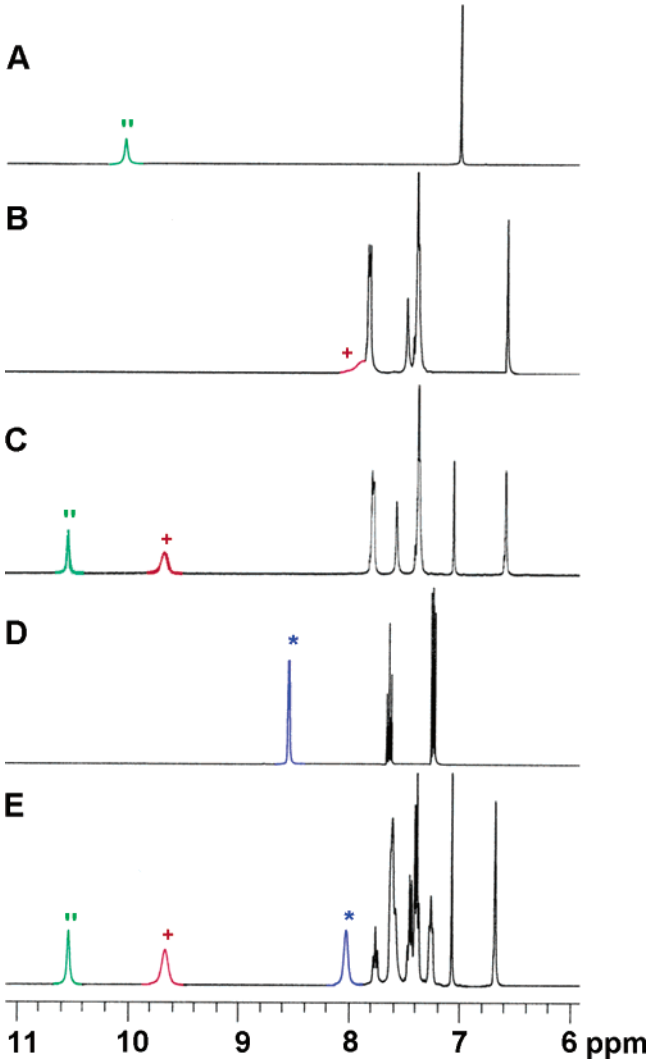


Figure 3. Aromatic region of the ^{1}H NMR spectra depicting the stepwise functionalization (hydrogen bonding followed by metal coordination) of **5a**. (A) *N*-Butylthymine (" = imide proton), (B) copolymer **5a** (+ = amide protons), (C) copolymer following directed hydrogen bonding (**5c**), (D) pyridine (* = α-pyridyl protons), and (E) fully functionalized copolymer **5d**.

Table 3. Thermal Data: Concentration Dependence of the Complimentary Hydrogen-bonding Unit

copolymer	plasticizer	0 equiv T_g/T_{dec} (°C)	0.5 equiv T_g/T_{dec} (°C)	1.0 equiv T_g/T_{dec} (°C)	1.5 equiv T_g/T_{dec} (°C)	2.0 equiv T_g/T_{dec} (°C)
9a	*N*-butylthymine	69/275	61/258	52/240	41/221	29/200
9b	*N*-butylthymine	69/277	63/262	50/248	43/219	36/181
9a	*N*-Me *N*′-butylthymine	69/275	49/250	28/226	20/197	
9b	*N*-Me *N*′-butylthymine	69/277	43/255	30/229	23/195	

Thermal Characterization. To examine the effect of functionalization on the thermal properties, glass-transition temperatures (T_g) and decomposition onsets (T_{dec}) were determined for all polymers (Table 2). These parameters were found to be dependent upon both changes in composition and functionalization. In general, nonfunctionalized copolymers showed a decrease in T_g with added thermal integrity as the concentration

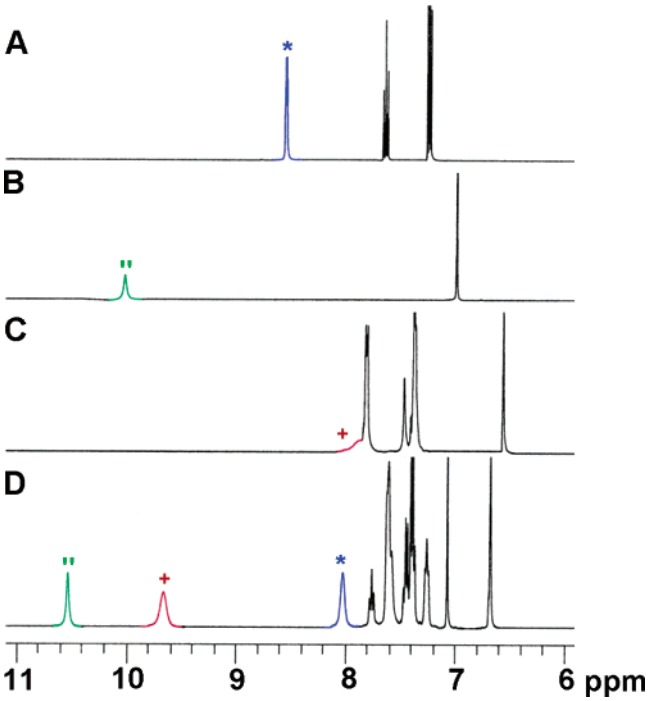


Figure 4. Aromatic region of the ^{1}H NMR spectra depicting the one-step multifunctionalization of **5a**. (A) Pyridine (* = α-pyridyl protons), (B) *N*-butylthymine (" = imide proton), (C) copolymer **5a** (+ = amide protons), and (D) fully functionalized copolymer **5d**.

of diaminopyridine was increased (Table 2, row a). In contrast to pyridine coordinated polymers (**3b**−**6b**), which showed only minor changes in T_g or T_{dec} upon coordination, *N*-butylthymine hydrogen-bonded polymers (**3c**−**6c**) always gave large decreases in T_g and lower decomposition temperatures (Table 2, row a vs c or d). It is interesting to note that the thermal properties are independent of molecular weight. Polymers possessing 500 (**8a**−**d**), 50 (**5a**−**d**), or 10 (**9a**−**d**) repeat units have identical thermal properties within ±5 °C of one another (T_g/T_{dec}(°C): **8a** = 69/275, **8b** = 69/277, **8c** = 46/220, **8d** = 44/215, **9a** = 70/275, **9b** = 70/277, **9c** = 41/218, **9d** = 43/219).

To further probe the plasticizer effect on the thermal properties of these materials, a series of copolymers possessing from 0 to 2 equiv of *N*-butylthymine and *N*-methyl *N*′-butylthymine were evaluated (Table 3). Structurally, the absence of imide protons in *N*-methyl *N*′-butylthymine eliminates the potential for hydrogen bonding (^{1}H NMR spectroscopy of **9a** and **9b** with *N*-methyl *N*′-butylthymine showed no evidence of amide-carbonyl hydrogen bonding). Therefore, a comparison between *N*-butylthymine and *N*-methyl *N*′-butylthymine should give insights into the influence of hydrogen bonding on the thermal behavior of our materials. To that end, the addition of *N*-butylthymine and *N*-methyl *N*′-butylthymine to copolymer **9a** and pyridine-coordinated copolymer **9b** both resulted in a linear decrease in the glass transition temperature and a consistent decrease in thermal integrity. The magnitude of this effect for the two additives was significant, with consistently lower T_g and T_{dec} values observed for *N*-methyl *N*′-butylthymine. Thus, the enhanced thermal integrity of the self-assembled *N*-butylthymine functionalized copolymers must be due to stabilization via hydrogen bonding.

Conclusion

Herein, we introduce a new methodology for random copolymer functionalization based on a noncovalent, one-step, multifunctionalization strategy. Copolymers containing both Pd-pincer complexes and diaminopyridine moieties were synthesized using ROMP. Functionalization of the resultant copolymers was accomplished via (1) *directed self-assembly*, (2) *multistep self-assembly*, and (3) *one-step orthogonal self-assembly*. This system shows complete specificity of each noncovalent interaction for its complementary recognition unit. This methodology allows for controlled copolymer functionalization in one simple step and will facilitate rapid development and optimization of random copolymer based functional materials.

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Supporting Information Available: Experimental procedures and spectral data for all new compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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