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Effect of Complementary Nucleobase Interactions on the Copolymer Composition of RAFT Copolymerizations

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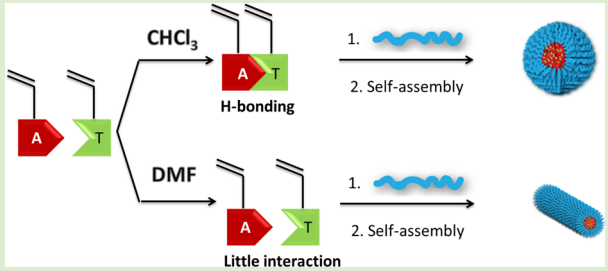
Supporting Information

ABSTRACT: Methacryloyl-type monomers containing adenine and thymine have been successfully synthesized with good yields. The homopolymerization and copolymerization of these two new functional monomers were carried out using RAFT polymerization. The reactivity ratios of monomer pairs were measured and calculated using a nonlinear least-squares (NLLS) method, and the results confirmed that the monomer reactivities were dependent on the solvent used for polymerization. The presence and absence of hydrogen bonding affected the resultant copolymer composition where moderate alternating copolymers had a tendency to be formed in $CHCl_3$, while in DMF, statistical copolymers were formed. Furthermore, the glass transition temperatures of the copolymers were investigated, and the self-assembly of block copolymers made in solvents with different polarity were studied.



Sequence-controlled polymerization is one of the fundamental processes in nature and allows access to biopolymers with enhanced function as a result of specific folding and structure. The defined sequence contained in biopolymers such as DNA, RNA strands, and proteins are responsible for the diversity, complexity, and adaptability of living organisms. By analogy, it is proposed that synthetic polymers with designed and controlled sequence will play an important role in materials science. Some promising approaches to control the sequence of synthetic polymers have emerged in recent years.[1,2] To date, solid phase synthesis, a method relying on step-by-step attachment of monomers, remains the most reliable approach to synthesize sequence-controlled polymers.[3−5] Alternatively, other facile and elegant methods have also been developed, such as tandem catalysis,[6−9] designed templates,[10−15] and chain copolymerization.[16,17] These have been applied to achieve precise polymerization with expected and specific sequences.

It is known that chain copolymerizations (e.g., ionic or radical polymerization) are generally statistical processes leading to statistical polymer structures.[1,18] However, in some particular cases, sequence can be controlled through manipulation of the reactivity of active chain ends. One way to achieve this manipulation is to shorten the distance between a chain end and a monomer or between monomers by specific covalent[12] or noncovalent interactions, such as host−guest interactions,[10] donor−acceptor interactions,[16,19] coordination bonding,[13] and hydrogen bonding of nucleobases.[20,21] Among these interactions, hydrogen bonding recognition interactions, as a fundamental property of nucleic acids, are of great interest.

Hydrogen bonding interactions of corresponding nucleobases play a key role in nature for synthesizing biopolymers with an exact complementary sequence and the same length as the original template and for mediating self-assembly of biomacromolecules to fold into one or more specific spatial conformations. Inspired by nature, synthetic nucleobase chemistry have been developed to control the polymers' tacticity,[22] to template a polymerization,[23−25] to achieve a biomimetic segregation/templating approach,[26] to drive the self-assembly,[27,28] and to manipulate the sequences.[20,21] This pioneering work has provided preliminary scope for further investigation into nucleobase materials.[29] However, to our knowledge, there has been little research into sequence-controlled polymerization driven by complementary nucleobases. Previous reports from the 1970s' have indicated that methacryloyl-type monomers containing nucleobases (in this work, uracil/thymine and adenine) can be polymerized using free radical polymerization to access alternating polymers.[20,21] Since these reports, no further work has explored this observation. Given the recent advances in characterization, polymerization, and monomer reactivity ratios, we have thus revisited this system.

Among the living radical techniques, reversible addition−fragmentation chain transfer polymerization (RAFT) appears to be the most versatile process in terms of the mild reaction conditions, the variety of monomers that can be polymerized and the feasibility for the incorporation of various function-

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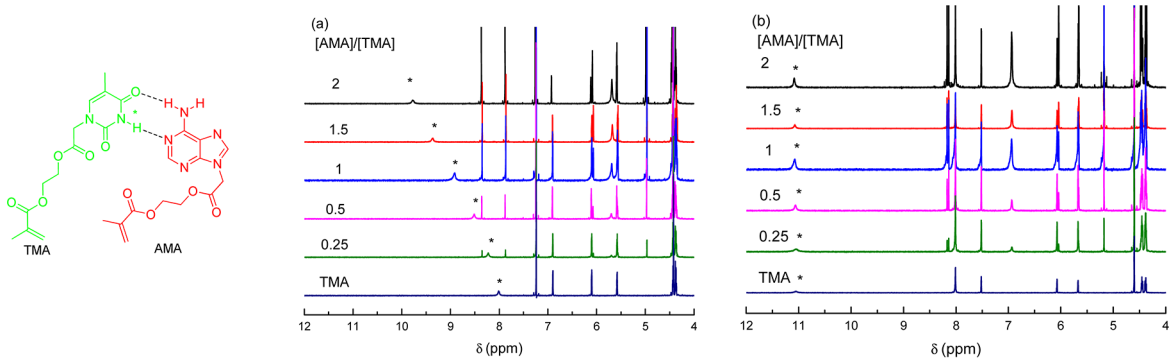

Figure 1. Expected hydrogen bonding interactions of the adenine–thymine pair is shown where the key imine signal used in the ^{1}H NMR spectroscopy study is indicated with a *; ^{1}H NMR spectra of the AMA and TMA mixtures with varying concentrations of AMA; [TMA] = 10 mM, [AMA] = 0, 2.5, 5, 10, 15, 20 mM. (a) $CDCl_3$, at 60 °C; (b) DMF-d_7, at 60 °C.

alities.[30−32] However, there have been few reports where RAFT has been used to make polymers containing nucleobases directly.[22,26] Hence, a goal is to study the synthesis of polymers containing nucleobase functionalities via RAFT. In addition, copolymerization behavior of the nucleobase monomers were studied in solvents with different capability of hydrogen-bonding tolerance ($CHCl_3$ and DMF). The reactivity ratios of the two monomers in both $CHCl_3$ and DMF were estimated. Moreover, the physical properties and the self-assembly behavior of the copolymers synthesized in different solvents were also investigated.

Both monomers were synthesized according to a modified literature procedure (Supporting Information, Scheme S1)[33] and high yields were obtained. One of the most important features of nucleobases is their ability to hydrogen bond to each other forming a base–base interaction pair. For adenine and thymine, this is the result of hydrogen bonding interactions between the purine and pyrimidine functionalities (Figure 1). To investigate the hydrogen bonding interactions between the synthesized nucleobase monomers, AMA and TMA, mixtures at varying ratios of the two were studied by ^{1}H NMR spectroscopy at different temperatures. $CDCl_3$ and DMF were selected as target solvents due to their different polarities and the established differences in ability to suppress or promote hydrogen bonding interactions. The ^{1}H NMR investigations were carried out at room temperature (25 °C) and at higher temperature (60 °C) to explore the strength of these interactions at the temperatures used for polymerization (Figure 1, Supporting Information, Figure S4). In $CDCl_3$, it was observed that increasing the concentration of AMA resulted in a downfield shift of the imine proton of TMA (labeled * in Figure 1, from 8.28 to 11.27 ppm at 25 °C, from 8.02 to 9.80 ppm at 60 °C). The downfield shift at 25 °C was more prominent than at 60 °C, indicating that the hydrogen bonding interactions are weaker at elevated temperatures. Nevertheless, hydrogen bonding interactions still occur at elevated temperatures. In contrast, in DMF little or no shift of the imide proton of TMA was observed at 25 or 60 °C. This is indicative of the lack of nucleobase interactions which is independent of temperature. The weaker hydrogen bonding interactions is a result of the more polar nature of DMF.[34,35] The stoichiometry of the hydrogen-bonding complex was evaluated by Job's method under conditions similar to those for further copolymerizations (Supporting Information, Figure S5). The results show the formation of a 1:1 complex between AMA and TMA.[36] Moreover, the association constant between the two monomers was calculated using Hildebrand–Benesi model (Supporting Information, Figure S6).[37,38] The calculated association constants were 20 M^{-1} in $CDCl_3$ at 60 °C and 1 M^{-1} in DMF-d_7 at 60 °C. These studies further reveal that the hydrogen-bonding interactions between the two monomers are indeed solvent dependent.

The homopolymerizations of the two synthesized monomers AMA and TMA were explored using established RAFT methods.[26] RAFT polymerization was carried out using CTA 2 as the chain transfer agent (CTA), DMF or $CHCl_3$ as the solvent, and AIBN as the initiator (Scheme 1). The polymerization in DMF was found to be homogeneous, suggesting a strong interaction between the nucleobase functionalities and the solvent exists. However, when $CHCl_3$ was used as the solvent, the polymerization was found to be

Scheme 1. Synthesis of (a) Copolymers (PAMA-*co*-PTMA) Using CTA 1; (b) Copolymers (PAMA-*co*-PTMA) Using CTA 2; (c) Block Copolymers $PMMA_{220}$-*b*-($PAMA_x$-*co*-$PTMA_y$) in $CHCl_3$ or DMF

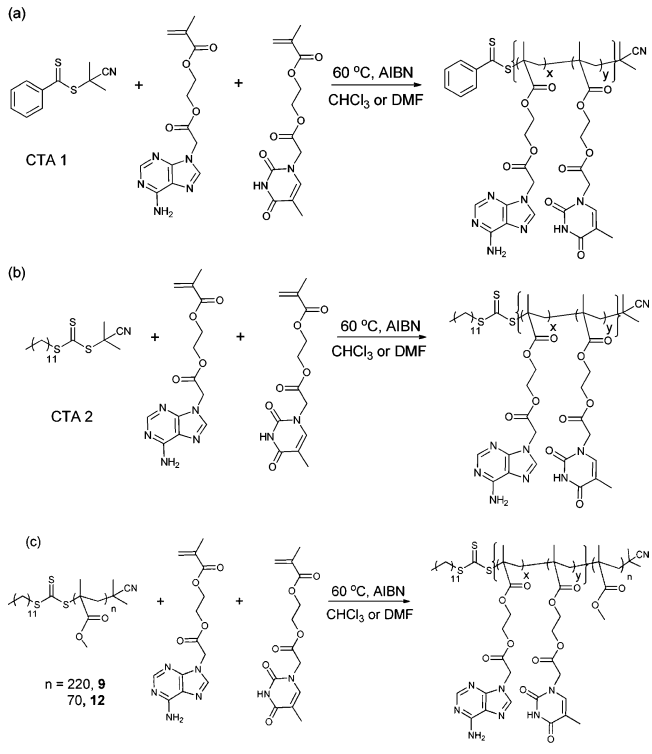

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Table 1. Polymerization Data for Polymers

polymer	CTA	solvent	AMA/TMA (before)[a]	AMA/TMA (after)[b]	conv.[c] (%)	$M_{n,\,th}$ (kDa)	$M_{n,NMR}$ (kDa)	$M_{n,GPC}$ (kDa)	$Đ_m$	copolymer composition (PAMA/PTMA)	T_g (°C)
1	1	$CHCl_3$	1:1	1.1:1	48, 50	5.7	7.9	10.8	1.23	~1:1	137
2	1	$CHCl_3$	2:1	2.9:1	39, 58	6.3	9.6	11.4	1.26	1.25:1	
3	1	DMF	1:1	1:1	43, 43	5.7	6.0	11.0	1.11	1:1	138
4	1	DMF	2:1	2:1	27, 27	3.7	5.4	10.7	1.12	2:1	
5	2	$CHCl_3$	1:1	1.1:1	70, 75	10.0	13.2	16.1	1.37	~1:1	120
6	2	$CHCl_3$	1.9:1	2.9:1	51, 68	7.6	18.0	21.3	1.38	1.4:1	
7	2	DMF	1:1	1:1	92, 92	12.7	14.1	17.0	1.22	1:1	115
8	2	DMF	2:1	2:1	60, 60	8.1	9.0	14.7	1.23	2:1	
9	2					22.6	22.0	22.1	1.20		
10	9	$CHCl_3$	1:1	1:1	90, 90	35.5	35.8	34.9	1.33	1:1	
11	9	DMF	1:1	1:1	99, 99	36.9	37.0	34.5	1.20	1:1	
12	2					7.2	7.0	7.0	1.17		
13	12	$CHCl_3$	1:1	1:1	95, 95	21.3	26.8	26.1	1.32	1:1	
14	12	DMF	1:1	1:1	95, 95	21.3	22.0	21.5	1.14	1:1	

[a]The ratio of monomers in initial feed. [b]The ratio of residual monomers after polymerization. [c]The final conversion of AMA (first number) and the final conversion of TMA (second number).

somewhat heterogeneous due to the insolubility of the polymer. The molecular weight of the resultant polymers were determined by ^{1}H NMR spectroscopy by comparing the integration of the backbone signals with those of the end group from the CTA. Furthermore, SEC (in DMF, with PMMA standards) was used to determine the molecular weight and molecular weight distribution.

Both homopolymerizations carried out in DMF were polymerized with good control over molecular weights and high conversion were obtained after 24 h (Supporting Information, Table S1). The SEC traces for both homopolymers (PAMA and PTMA) were found to be narrow, indicating a narrow molecular weight distribution. Additionally, RAFT chain end functionalities were analyzed by ^{1}H NMR spectroscopy (Table 1, Supporting Information, Figures S7–10), confirming good RAFT group chain end fidelity. Polymerizations carried out in $CHCl_3$ on the other hand, were found to be less controlled due to polymer precipitation during the polymerization process (Supporting Information, Table S1). Nevertheless, the polymers were found to be more controlled than those synthesized via traditional free radical polymerization methods.

It should be noted that the solubility of the resultant homopolymers is somewhat limited but they were found to be soluble in DMF, DMSO, DMAc, and *N*-methyl-2-pyrrolidone. An adenine containing methacrylate polymer which was prepared by free radical polymerization has previously been reported to be insoluble in DMF and pyridine,[20] but this study has shown that PAMA is fully soluble in DMF at relatively low molecular weights (i.e., <15 kDa). To explore the effect of solvent on the composition of the resulting copolymers, further studies were carried out in both $CHCl_3$ and DMF.

Two different CTAs were used for the copolymerizations of AMA/TMA (Scheme 1a,b) to confirm the observed results were in fact related to the different solvents (DMF and $CHCl_3$) used in the polymerization and not an effect of the CTA. Following polymerization, the final copolymers were dissolved in DMSO-d_6 or DMF-d_7 and the ratio of the two monomers in the copolymer was calculated using ^{1}H NMR spectroscopy (Table 1, polymers **1**–**8**). In the polymerizations where the initial feed mol fraction of the two monomers was 1:1, the resulting mol fraction in the copolymers (**1** and **3**) was very close to 1:1, regardless of the solvent used. However, when the mol fraction of the two monomers in the initial feed was changed to 2:1 (AMA/TMA, polymerizations **2** and **4**), a difference in the mol fraction in the resulting copolymers was observed. The final copolymer composition was found to be dependent on the solvent used in the polymerization. When the polymerization was carried out in DMF the final copolymer composition for **4** was found to be very close to 2:1. However, in $CHCl_3$ the ratio of the two monomers in the final copolymer **2** was found to be 1.25:1. These results indicate copolymers with different microstructures were synthesized in the two different solvents. Similar results were observed for the two different CTAs, indicating the final polymer composition is independent of the type of CTA used. Hence, in $CHCl_3$, regardless of the initial monomer ratios, the final polymers synthesized (**5** and **6**) tend to have a 1:1 composition of the two monomers. In contrast, in DMF the final polymer composition is the same as the initial monomer feed (for CTA 2, polymers **7** and **8**). As previously discussed, hydrogen bonding interactions were observed between AMA and TMA in $CHCl_3$ at 60 °C, while little or no interactions were observed in DMF at the same temperature. We propose that the presence or absence of such interactions between monomers during polymerization has an effect on the resulting copolymer composition.

It should be noted that CTA 1 was not stable in DMF, evidenced from examination of CTA 1 dissolved in DMF over time at room temperature. The color of the CTA/DMF solution changed from pink to orange after 1 day while the solution color stayed pink in $CHCl_3$. We hypothesize that this may be related to impurities in DMF such as amines or imines reacting with the CTA. Previous studies have reported that aminolysis of the thiocarbonylthio group commonly occurs in the presence of free primary and secondary amines.[39,40] Thus, although some insightful results have been obtained using CTA 1 in DMF, further studies have been carried out utilizing CTA 2 for polymerizations performed in DMF.

To further explore the behavior of AMA and TMA copolymerizations, the monomer reactivity ratios were investigated (Supporting Information, Tables S2–S4). Mol fractions of the two monomers in the initial feed and in the final copolymers were obtained by ^{1}H NMR spectroscopy. Plots of

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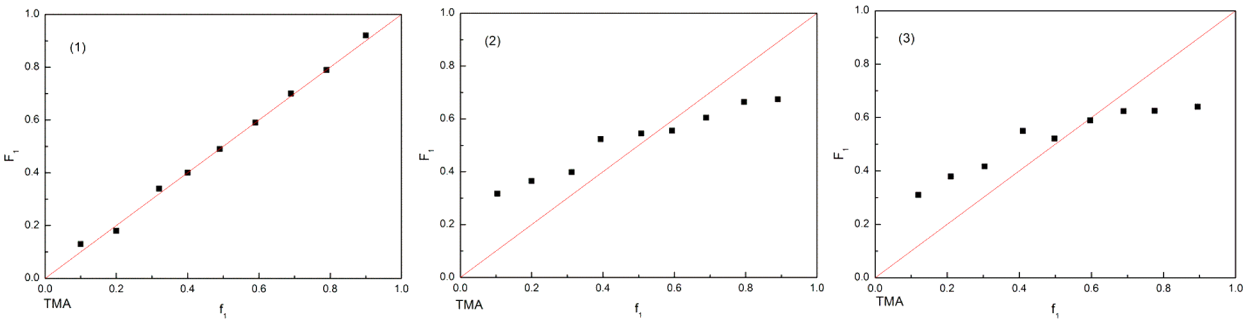

Figure 2. Plot of f_1 vs F_1 for the copolymerization of TMA and AMA using (1) CTA 2, in DMF; (2) CTA 2, in $CHCl_3$; (3) CTA 1, in $CHCl_3$ (the red line is the plot of f_1 vs F_1 for an ideal polymerization, where $r_1 = r_2 = 1$).

f_1 (f_1 = initial mol fraction of monomer 1, M_1) versus F_1 (F_1 = mol fraction of M_1 in the copolymer) are presented in Figure 2, highlighting the copolymer compositions. The reactivity ratios were calculated using Contour, a program based on a NLLS method developed by Van Herk.[41−44] The calculated monomer reactivity ratios are shown in Table 2. In $CHCl_3$, regardless of the CTA used the reactivity ratios are comparable and also close to zero. The results suggest that the copolymerizations carried out in $CHCl_3$ tend to form alternating polymers, shown by the shape of the F_1 versus f_1 plot and the reactivity ratios being close to zero. It should be noted that the alternating behavior of the copolymerization in $CHCl_3$ is not an extreme alternating behavior but a moderate alternating behavior. In DMF, on the other hand, the reactivity ratios are close to one, suggesting statistical copolymers are most likely synthesized. This is supported by the shape of the F_1 versus f_1 plot (Figure 2). The monomer reactivity ratio experiments further support that hydrogen bonding interactions between the two monomers (AMA and TMA) have a strong influence on the final polymer composition which may be tuned by the choice of solvent.

Table 2. Calculated Reactivity Ratios (r_1 and r_2) Using a Nonlinear Least Squares (NLLS) Method

CTA	solvent	M_1[a]	M_2[b]	r_1	r_2	$r_1 \cdot r_2$	error[c] (%)
2	DMF	TMA	AMA	0.89	0.88	0.78	5
2	$CHCl_3$	TMA	AMA	0.23	0.17	0.039	6
1	$CHCl_3$	TMA	AMA	0.21	0.17	0.036	6

[a]M_1 is monomer 1. [b]M_2 is monomer 2. [c]Total error given by the Contour program.

The T_g of both homopolymers and copolymers were measured by DSC (Supporting Information, Figure S17). In general, the T_g of a copolymer is between the T_g of the two precursor polymers and can be predicted by Fox rule.[45] However, in terms of specific interactions within a copolymer, such as hydrogen-bonding interactions, higher T_gs would be predicted.[46] In this study, compared to the homopolymers prepared (for CTA 2, PAMA T_g = 105 °C, PTMA T_g = 87 °C), the copolymers exhibit strong hydrogen bonding interactions and therefore higher T_gs were observed as expected. However, due to the different molecular weights among the copolymers, the T_gs are not directly comparable although the nature of the CTA end group may have an effect on the polymers' T_g.[47]

Polymers with different sequences usually allow access to different polymeric microstructures. To further study the properties of the functional copolymers prepared in this study, block copolymers were synthesized and self-assembled in $CHCl_3$. However, due to the heterogeneous character of the polymerization involving the two functional monomers in $CHCl_3$ resulting in unreliable RAFT end group fidelity, chain extension starting from the functional copolymers was not ideal. Thus, the block copolymers were prepared by first synthesizing the nonfunctional block, in this case, PMMA followed by chain extension with the functional block, AMA and TMA. The characterization data for the final block copolymers are shown in Table 1, polymers **9**−**14**. It is evident that well-defined block copolymers with comparable molecular weight were obtained for both polymerizations, in $CHCl_3$ and DMF.

Polymers were self-assembled in $CHCl_3$ and the morphologies were characterized by TEM and DLS. Close to spherical structures of around 40 nm were observed for polymer **10** assembled in $CHCl_3$ by unstained TEM on graphene oxide grids[48] (Figure 3a). By comparison, a mixture of spherical micelles and elongated worm-like structures was observed by TEM (Figure 3b) under the same conditions when polymer **11** was assembled in $CHCl_3$. The sizes observed by DLS (84 and 69 nm, for **10** and **11** respectively, see Figure S20) correlated well with the approximate sizes determined by TEM analysis. Compared to polymers **10** and **11**, polymers **13** and **14** have a shorter PMMA block that leads to the formation of larger spherical micelles (which perhaps have internal structure) for polymer **13** assembled in $CHCl_3$ (Figure 3c), while more obvious worm-like micelles were observed from the self-assembly of polymer **14** (Figure 3d). We hypothesize that the different monomer sequence in the functional block and the

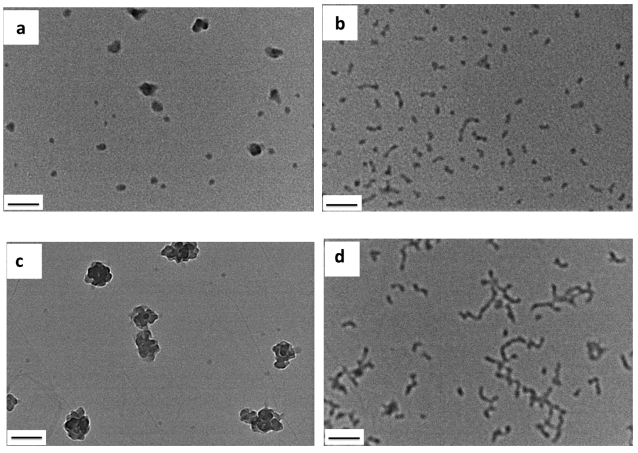

Figure 3. TEM images of self-assembled polymers on graphene oxide: (a) **10**; (b) **11**; (c) **13**; and (d) **14**; scale bar = 100 nm.

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resulting block copolymer solubilities are responsible for the different morphologies observed. The strength of the hydrogen bonding interactions within the copolymers is different and thus drives the copolymers into different morphologies. However, the exact cause for this behavior is unclear and further investigations are ongoing.

In conclusion, methacryloyl-type monomers containing adenine and thymine functionalities have been successfully synthesized. RAFT polymerization using these monomers were carried out with good control over molecular weight and end group fidelity. The difference in reactivity of the two monomers in DMF and $CHCl_3$ were investigated. The results indicate polymerizations carried out in $CHCl_3$, a solvent that promotes hydrogen bonding interactions between the nucleobase-based monomers, tend to give moderate alternating copolymers. However, polymerizations in DMF, a solvent that suppresses the interactions, tend to give statistical copolymers. These hydrogen bonding interactions between two monomers may be used to access copolymers with specific monomer sequences. Moreover, properties of the copolymers such as self-assembly behavior were investigated and were found to be greatly influenced by the presence or absence of hydrogen bonding between the two nucleobases.

■ ASSOCIATED CONTENT

Supporting Information

Experimental section, characterization data (NMR, SEC, DLS, TEM), association constant data, DSC, and reactivity ratio data and calculations. 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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