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Side-Chain Supramolecular Polymers Employing Conformer Independent Triple Hydrogen Bonding Arrays

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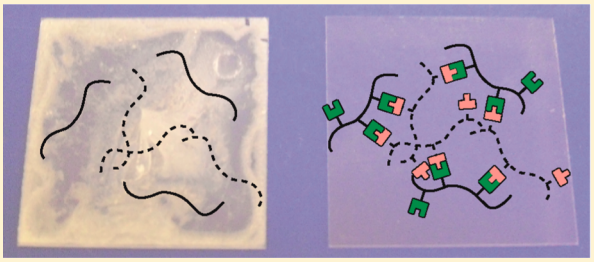
Supporting Information

ABSTRACT: Derivatives of thymine have been extensively used to promote supramolecular materials assembly. Such derivatives can be synthetically challenging to access and may be susceptible to degradation. The current article uses a conformer-independent acceptor−donor−acceptor array (ureidopyrimidine) which forms moderate affinity interactions with diamidopyridine derivatives to effect supramolecular blend formation between polystyrene and poly(methyl methacrylate) polymers obtained by RAFT which have been functionalized with the hydrogen bonding motifs.



INTRODUCTION

The synthesis of functional materials using noncovalent chemistry remains a major focus of supramolecular chemistry.[1,2] Recent high profile developments include self-healing materials,[3] supramolecular adhesives,[4] and scaffolds for tissue engineering.[5] Alongside these more applied developments, significant effort is focused on exploring the scope of molecular recognition in fundamental studies of materials synthesis (e.g., template directed synthesis)[6] and biomimetic processes requiring supramolecular aggregation (e.g., control of catalyst concentration).[7] Among noncovalent interactions, the use of hydrogen bonding for supramolecular materials assembly has found widespread use.[8,9] Underpinning the use of hydrogen bonding in supramolecular materials science[10] is the synthetic availability of linear arrays of hydrogen bonds.[11,12] A consideration where linear supramolecular condensation polymers are sought is the strength of association between supramolecular (macro)monomers,[13] which, in part, represents the stimulus for ongoing efforts to develop novel H-bonding motifs.[14−19] For side-chain-functionalized[20] and cross-linked supramolecular polymers,[21−23] however, the requirement for high affinity is tempered by multivalent effects, and so easy-to-synthesize systems capable of moderate to high affinity heterodimerization are attractive. In this context, nucleobases have found widespread use in supramolecular polymer assembly.[24−28] In particular, the diamidopyridine/diaminotriazine−thymine dyad (DAP/DAT·T) has been widely employed;[22,29−37] however, multistep syntheses of functionalized thymine derivatives are sometimes necessary, and these systems can be susceptible to oxidative degradation. Ureidopyridine derivatives, while synthetically accessible, exhibit poor association constants toward *acceptor−acceptor−donor* (AAD) arrays because they preferentially form an intramolecular hydrogen bond that retards intermolecular interaction.[38,39] Our group introduced the concept of conformer-independent hydrogen bonding[40] to circumvent this limitation, reporting on the design and synthesis of ureidoimidazole DDA arrays in which the six-membered pyridine ring was switched for a five-membered imidazole ring.[40−43] Subsequently, we illustrated that this motif could be useful for self-assembly of polyurethane-based elastomers.[44] In a similar manner, we reasoned that exchange of the pyridine of the ureidopyridine motif for a pyrimidine would generate a conformer-independent ADA array and that such a motif may represent an alternative to thymine derivatives; we previously described triple hydrogen bonded heterocomplex PUPY·DAP **1·2** for which an association K_a = 56 ± 20 M^{-1} was measured (Figure 1a).[45] We concluded that this moderate binding affinity was appropriate for side-chain supramolecular applications (Figure 1b), whereby several arrays may be incorporated into each macromonomer. This article describes incorporation of triple hydrogen bonding arrays based on model compounds **1** and **2** into monomer units of methyl methacrylate and styrene. The hydrogen bonding monomers are subsequently incorporated (at acceptably low stoichiometries) into macromonomer units using a controlled radical polymerization approach. The macromonomers are applied in preliminary studies to investigate the effect of the hydrogen bonding arrays upon miscibility between incompatible polymers.

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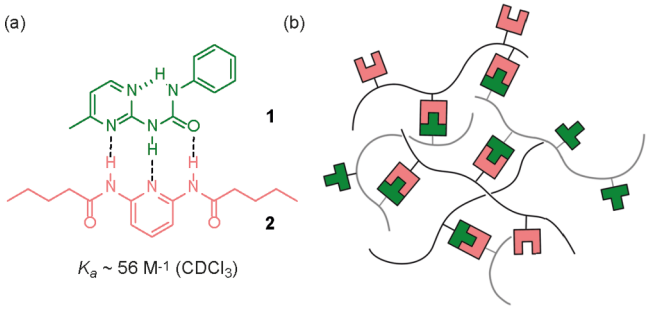


Figure 1. The use of hydrogen bonding motifs for multivalent cross-linking of macromonomers: (a) the ureidopyrimidine·diamidopyridine **1·2** complex and (b) schematic depicting the assembly of a cross-linked network promoted by heterocomplementary hydrogen bonding motifs.

EXPERIMENTAL SECTION

Gel-Permeation Chromatography (GPC). Analysis was performed on a Holland Spark instrument (fitted with a Shimadzu UFLC autosampler with Polymer Laboratories gel 5 μm mixed C column) with an LC1120 HPLC pump, using a flow rate of 1 mL min^{-1}, at a column pressure of 6.5−6.8 MPa. Samples were run against PS and PMMA standard calibration ranges accordingly, with all analyzed samples displaying retention times within the calibration range. Samples were prepared in HPLC grade THF at a concentration of 3 mg mL^{-1}. Results were processed using Cirrus GPC/SEC software (version 3.0). All reported M_n values are reported in g mol^{-1} and are rounded to the nearest 100 g mol^{-1}, and $Đ$ values are reported to the nearest 0.01.

Differential Scanning Calorimetry (DSC). Samples were run on a DSC Q200 V24.9 build 121 instrument and processed with TA Instruments Universal Analysis 2000 software. TZero pans and lids were used for all samples. Analysis was performed over a temperature range of 25−100 °C in a cyclic manner (two cycles per sample) with an isothermal stage of 5 min. The instrument was modulated to FE type, with a cell constant of 0.9708 without correction. Sample film preparation was performed by mixing the required polymers (if necessary) in equal weight ratios, before dissolving in $CHCl_3$. Solvent was evaporated over a stream of nitrogen for 10 min and residual solvent was removed under reduced pressure, to provide a glassy solid which was analyzed directly.

Atomic Force Microscopy (AFM). Topographical surface imaging of the polymer blends produced was carried out under ambient laboratory conditions using amplitude modulation (AM) feedback control. Tapping mode AFM was performed on a Multimode 8 platform (Bruker) using rectangular silicon cantilevers model TESPA (Bruker). These have a nominal spring constant range of 20−80 N/m, and the resonant frequency of those used was ~330 kHz. The free excitation amplitude was approximately 25 nm, and the imaging set point was kept to ~90% or more of the free amplitude. Images were acquired from 0.5 to 3 μm scan size at sampling of up to 512 × 512 pixels and a line rate of 2 Hz.

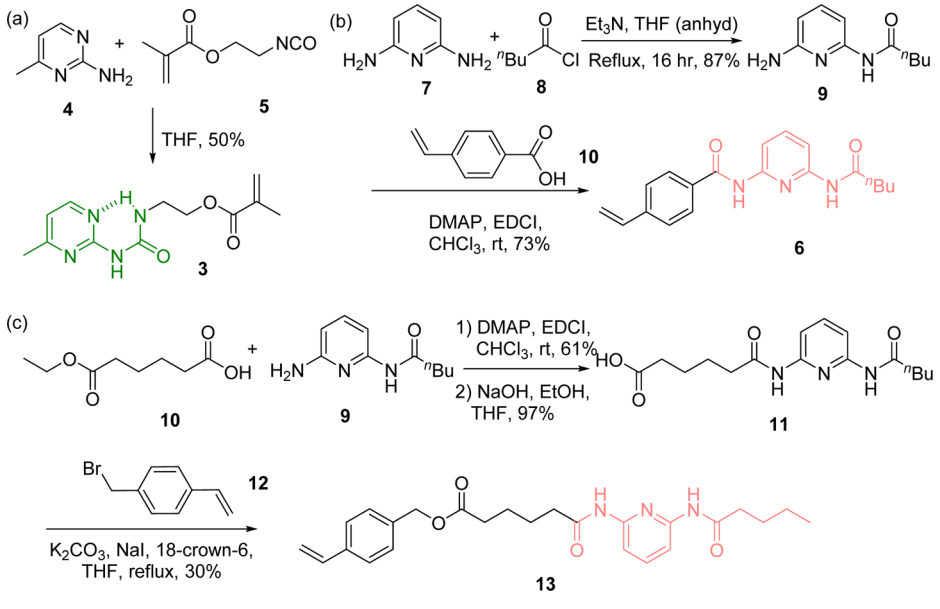
Procedure for PS-*co*-PS-DAP Polymerization. The required amounts of styrene, S-DAP comonomer (if required), and cyanomethyldodecyl trithiocarbonate were transferred to an ampule with stirrer bar under a nitrogen atmosphere. The reaction mixture was thoroughly degassed by purging with nitrogen for 20 min, followed by three freeze−pump−thaw cycles. The reaction mixture was placed into a preheated oil bath at 110 °C and stirred for 16.5 h. After this time, the flask was immediately cooled to 0 °C to prevent any further polymerization. Precipitation (minimum amount of THF vs a 100-fold excess of MeOH at 0 °C) twice followed by removal of residual solvent under reduced pressure provided the title material as a flocculent colorless solid.

Procedure for PMMA-*co*-PMMA-UP Polymerization. The required amount of MMA and MMA-UP comonomer (if required) was transferred to an ampule with stirrer bar under a nitrogen atmosphere. A 5 mL stock solution of 4-cyano-4-((dodecylsulfanylthiocarbonyl)sulfanyl)pentanoic acid and azobutyronitrile (AIBN) dissolved in methyl methacrylate monomer was also prepared, and the required aliquot of stock solution was added to the ampule by syringe addition. The reaction mixture was thoroughly degassed by purging with nitrogen for 20 min, followed by three freeze−pump−thaw cycles. The reaction mixture was placed into a preheated oil bath at 90 °C and stirred for 3 h. After this time, the flask was immediately cooled to 0 °C to prevent any further polymerization. Precipitation (minimum amount of THF vs 100-fold excess of petroleum ether at 0 °C) twice followed by removal of residual solvent under reduced pressure provided the title material as a flocculent colorless powder.

RESULTS AND DISCUSSION

In order to test the utility of the ureidopyrimidine motif in supramolecular materials assembly, we sought a suitable test

Scheme 1. Synthesis of Monomer Building Blocks for Copolymerization with Methacrylate Styrene Based Monomers



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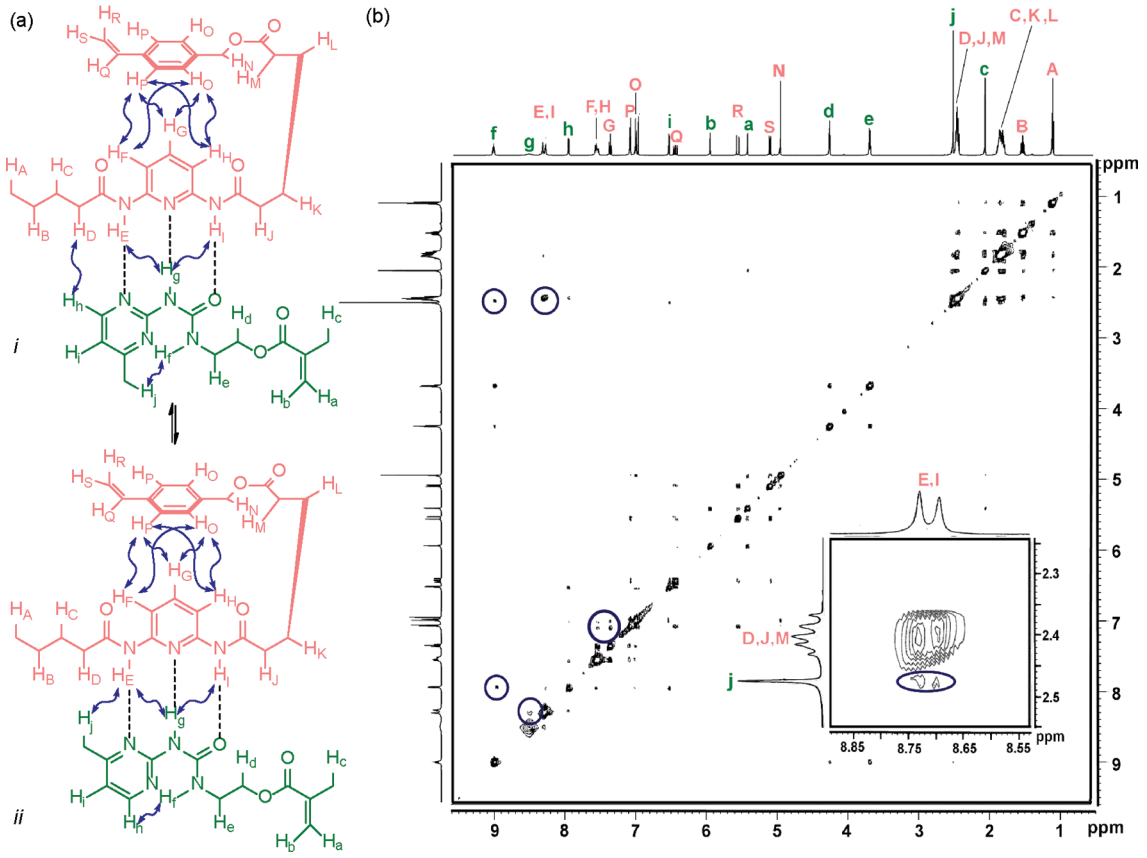

Figure 2. NMR based evidence for conformer independent interaction between **3** and **13**. (a) Observed through-space correlations (shown by blue lines) for **3** (green) and **13** (pink) for conformations i and ii. (b) 2D ^{1}H−^{1}H NOESY spectrum ($CDCl_3$, 300 MHz, 20 mM for each component **3** and **13**). Key correlations are circled in blue.

system. We did not consider that the ureidopyrimidine/diamidopyridine interaction was of sufficient affinity to support assembly of linear polymers in dilute solution and hypothesized that their use in cross-linking would be more plausible; we identified assembly of a blend as a suitable goal. The formulation of homogeneous mixtures of immiscible polymers represents an active area of research in materials science; several groups have reported methods of covalent modification to polymer structures to overcome interfacial energies between components and hence reduce the propensity for immiscibility.[46−50] The use of hydrogen bonding arrays to inhibit phase separation[51] and promote blend formation has been previously exploited[23,52−65] and is appealing because it provides the possibility to achieve miscibility on the molecular level even at low temperatures (on account of the reversible association between hydrogen bonding units). Initially, we needed to obtain polymerizable monomers functionalized with the ureidopyrimidine and diamidopyridine motifs. Methacrylate-functionalized ureidopyrimidine **3** was obtained in one step (Scheme 1a), while styrene-functionalized monomer **6** was similarly obtained in two synthetic steps (Scheme 1b). Subsequent polymerization studies with **6** revealed the monomer to undergo preferential incorporation in random copolymerizations, presumably due to the radical stabilization conferred by the conjugated electron withdrawing carboxamide group. Therefore, we synthesized monomer **13** (Scheme 1c) using a slightly longer route, but crucially introducing a spacer so as to retard this behavior.

We then performed several NMR based experiments to illustrate that the additional functionalization on the hydrogen bonding motif does not interfere with molecular recognition. Specifically, ^{1}H NMR experiments at different **3**·**13** ratios reveal complexation induced shifts in the concentration range expected (see Supporting Information for data) while ^{1}H−^{1}H NOESY confirms the presence of conformer-independent binding (Figure 2). Through-space correlations were observed from H_g to H_E and H_I, indicating complexation via the intended heterocomplementary triple array. Correlations from H_j to H_f, and H_h to H_D show the presence of heterodimer association with the methyl functionality of **3** pointing away from the hydrogen bonding face, while correlations H_j to H_E and H_h to H_f show the methyl pointing in the same orientation as the hydrogen bonding face. Interestingly, the ^{1}H−^{1}H NOESY data also provided structural information about the conformation of **13**. Correlations from H_G to H_O and H_P along with H_F and/or H_H (which could not be distinguished due to overlap of resonances) to H_O and H_P showed the presence of a folded conformation, whereby the aryl vinyl styrene moiety of **13** lies adjacent to the diamidopyridine functionality. This is perhaps favored by $\pi-\pi$ interactions between the styrene phenyl ring and the *ortho*/*para* protons of the pyridyl ring.

Several studies[21,23,61] have employed radical polymerization to provide macromonomer components presenting heterocomplementary hydrogen bonding arrays along polymer backbones. Such approaches are advantageous in that macromonomers can be synthesized on scale and also because they allow the possibility of structural modification of existing

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Scheme 2. Synthesis of Polymers Using RAFT Polymerization

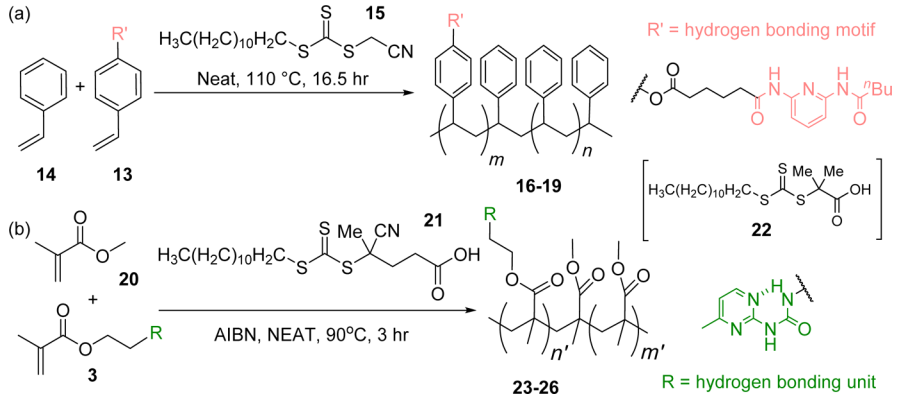

Table 1. Analytical Data on Macromonomers for Supramolecular Side-Chain Studies[a]

polymer	polymer composition	M_n (10^3)	$Đ$	yield (%)	theor mol % comonomer	actual mol % comonomer	F	DP
16	PS	22.0	1.26	60	0	0	0	211
17	PS-*co*-PS-DAP	22.4	1.35	30	0.8	1.1	2.3	199
18	PS-*co*-PS-DAP	21.0	1.24	75	3.0	3.4	6.7	194
19	PS-*co*-PS-DAP	21.6	1.30	60	6.0	5.8	10.1	175
23	PMMA	13.6	1.13	60	0	0	0	136
24	PMMA-*co*-PMMA-UP	10.2	1.24	30	3.0	3.6	3.5	96
25	PMMA-*co*-PMMA-UP	10.4	1.26	30	6.0	8.8	8.0	91
26	PMMA-*co*-PMMA-UP	15.1	1.32	25	12.0	14.0	25.0	90

[a] M_n and $Đ$ values were determined by GPC analysis, while mol % comonomer was estimated based on relative integration from ^{1}H NMR ($CDCl_3$, 300 MHz). F refers to the estimated average number of arrays per macromonomer chain based on M_n and actual mol % comonomer. Degree of polymerization (DP) refers to the number of (co)monomers in an average chain, such that DP = $M_n/M_{w(monomer)}$ and was calculated from relative mole ratios of monomer/comonomer based on actual mol % values.

monomers to achieve incorporation of the desired hydrogen bonding arrays. However, kinetic equilibria of radical processes are often fast and can result in polymerization occurring in a nonuniform manner, such that inconsistent macromonomer chain lengths are produced. A consequence of this lack of "control" upon polymerization is that a degree of ambiguity is introduced when assigning emergent material properties that arise due to supramolecular self-assembly (it should also be noted that the manner in which functionalized monomers are distributed within a chain (e.g., random, block, or sequence controlled, will also be important). The development of predictable and highly controlled building block design is crucial for the continued growth of supramolecular polymers in commercial applications (such as biomedical applications).[66] Indeed, some of the earliest work on polymers incorporating hydrogen bonding motifs employed atom transfer radical polymerization (ATRP) to polymerize nucleobases.[27,28] We sought therefore to utilize RAFT[67] to obtain the hydrogen-bond-functionalized macromonomers. We selected benzyltrithiocarbonate as our chain transfer agent (CTA) for polystyrene (PS) polymer synthesis based on the literature precedent,[67] the synthesis of which was performed according to literature procedures;[68] however, this did not afford good control over polymerization when copolymerized with **13**. We therefore sought an alternative CTA from commercially available sources. Gratifyingly, we achieved success in generating PS (co)polymers with CTA **15** giving good $Đ$ and conversion (Scheme 2), following some optimizations. With these conditions in hand, we prepared a series of PS (co)polymers **16**–**19** incorporating various percentages of **13**. Using ^{1}H NMR analysis, we observed that comonomer **13** had been successfully incorporated into the macromonomer in a reasonably predictable manner. This demonstrated comonomer **13** was compatible for incorporation into PS macromonomers.

CTA agent **21** was synthesized for the synthesis of low molar mass dispersity poly(methyl methacrylate) (PMMA)-based (co)polymers according to literature procedures.[68] CTA agent **21** and a commercially available variant **22** were screened with the aim of synthesizing a PMMA standard and a series of (co)polymers PMMA-*co*-PMMA-UP incorporating a variety of stoichiometries of comonomer MMA-UP **3**. Azobutyronitrile (AIBN) was employed as a radical initiator component in all attempts according to the literature precident.[68] Controlled polymerization was achieved using the synthetic CTA **21** while CTA **22** gave polymers but with poor control over molecular weight and larger $Đ$s. In a similar manner to that applied to PS based macromonomers, we observed by ^{1}H NMR that comonomer **3** had been successfully incorporated into the macromonomer, in good agreement with the stoichiometries of **3** and **20** charged in the reaction. The samples and data from both series of monomers are collated in Table 1. Overall $Đ$s of 1.35 or below were measured for the selected PS and PMMA based macromonomers, suggesting the applied RAFT approach was successful in achieving controlled polymerization. Also, both series presented internally consistent molecular weights with only a narrow distribution of M_n values, allowing direct comparison of samples from each series without significant contributions of different molecular weight macromonomers upon self-assembly behavior.[61] For the current study we did not further study the monomer sequence distribution and assume a random distribution of monomers capable of hydrogen bonding within the polymer chain.

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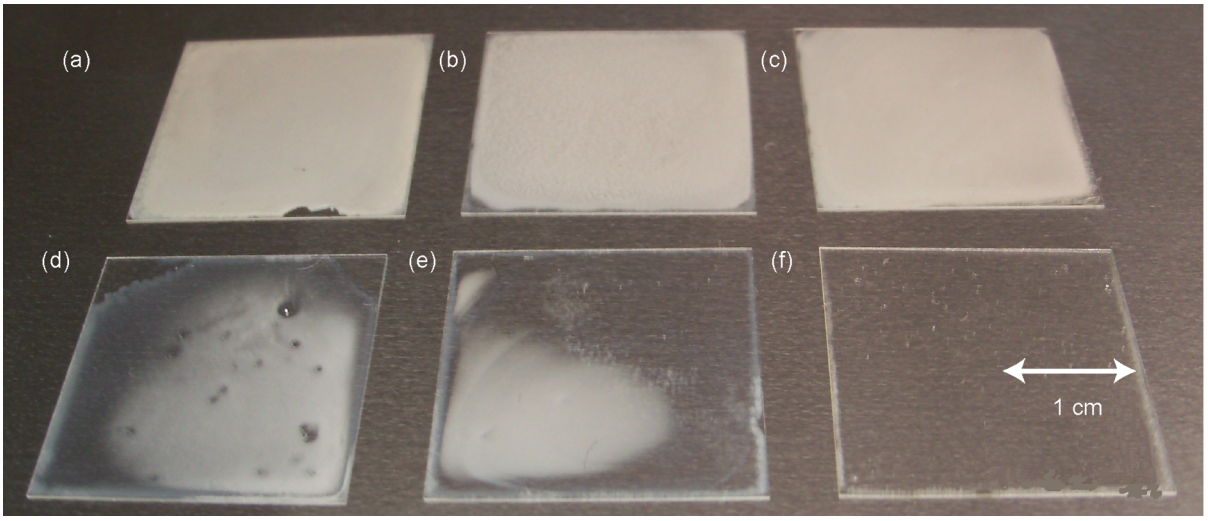

Figure 3. Polymer films prepared from slow drying of $CHCl_3$ solutions (20 mg mL^{-1} of each component) on mica surfaces. Controls include (a) PS **16** and PMMA **23**, (b) PS-*co*-S-DP **19** and PMMA **23**, and (c) PS **16** and PMMA-*co*-PMMA-UP **26**. Heterocomplementary macromonomer mixes are shown of (d) PS-*co*-PS-DAP **17** and PMMA-*co*-PMMA-UP **24**, (e) PS-*co*-PS-DAP **18** and PMMA-*co*-PMMA-UP **25**, and (f) PS-*co*-PS-DAP **19** and PMMA-*co*-PMMA-UP **26**.

We subsequently performed a series of preliminary experiments to study blend formation. A series of polymer films were prepared by solution casting onto glass surfaces (Figure 3). Films were prepared from 1:1 mixes of macromonomers in $CHCl_3$ solution (20 mg mL^{-1} of each component). A sample composed of **19** and **26** was prepared—thus presenting the highest proportion of heterocomplementary arrays. The resulting film (Figure 3f) is completely transparent and homogeneous in appearance. Control samples were composed of mixtures of **16** with **23**, **19** with **23**, and **26** with **16**. Their appearance (Figure 3a–c)—in stark contrast to the sample made using **19** and **26**—is a white, opaque layer which is consistent with immiscibility within the polymer mixture. This indicates that **19** and **26** form polymer blends due to enhanced affinity between macromonomers as a result of heterocomplementary association. Also, comparison of these films indicates that miscibility is not achieved by incorporating only one of the hydrogen-bond-functionalized macromonomers, suggesting that association occurs via the intended heterocomplementary arrays. Further films were prepared from mixtures of **17** with **24** and **18** with **25**, respectively, and therefore present lower fractions of hydrogen bonding components relative to the film formed using **19** and **26**. Interestingly, we observed white, semiopaque patches for these samples (Figure 3d,e). While these regions were less prominent than those observed in the controls (Figure 3a–c), they present a markedly different appearance to the sample composed with **19** and **26**. Presumably, this is due to the reduced number of hydrogen bonding associations between macromonomers, resulting in incomplete polymer blending. This is supported by the more pronounced imperfections observed for films comprising **17** and **24** relative to **18** and **25**.

Differential scanning calorimetry (DSC) was performed on films of macromonomer samples in order to evaluate the effect of side-chain interactions upon phase transition characteristics (Figure 4). Controls PS **16** and a mixture of PS **16** and PMMA-*co*-PMMA-UP **26** both show distinctive transitions at 53 °C, while PMMA **23** alone exhibits no distinctive transitions in the temperature range measured (measurements were not recorded above 100 °C in order to avoid thermal radical initiation at higher temperatures—a property which was not considered in previous studies).[23] This allowed confident assignment of the transition observed at 53 °C to be due to unassociated PS/PS-*co*-S-DP macromonomer.

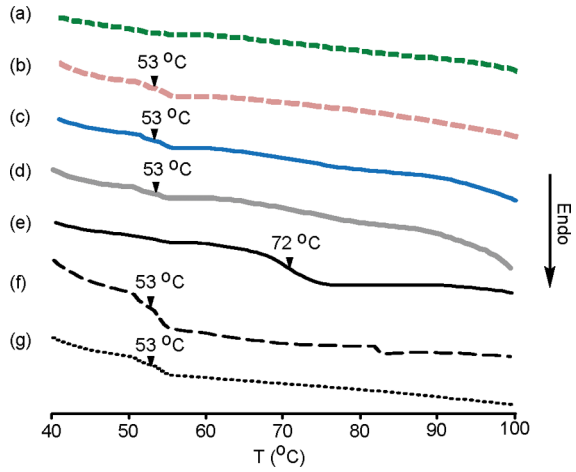

Figure 4. DSC thermograms of macromonomers: (a) PMMA **23** alone; (b) PS **16** alone; (c) PS **16** and PMMA-*co*-PMMA-UP **26**; (d) PS-*co*-PS-DAP **19** and PMMA-*co*-MMA-UP **26** prior to film formation; (e) PS-*co*-PS-DAP **19** and PMMA-*co*-PMMA-UP **26**; (f) PS-*co*-PS-DAP **17** and PMMA-*co*-PMMA-UP **24**; (g) PS-*co*-PS-DAP **18** and PMMA-*co*-PMMA-UP **25**.

For the sample containing both hydrogen-bond-functionalized macromonomers **19** and **26**, the transition corresponding to unassociated PS/PS-*co*-PS-DAP was replaced by a transition at 72 °C. This shows that the physical properties of unassociated PS-*co*-PS-DAP **26** are no longer observed and suggests polymer blend formation on a molecular level. Perhaps unsurprisingly, the DSC thermogram of the same sample prior to film formation (whereby equal portions of PS-*co*-PS-DAP **19** and PMMA-*co*-PMMA-UP **26** were added directly to the DSC pan without further mixing) shows retention of the transition at 53 °C, indicating a lack of blend formation when the two components are not adequately mixed. Retention of the transition at 53 °C was also observed for mixtures of **17** with

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24 (Figure 4f) and **18** with **25** (Figure 4g), indicating incomplete polymer blending. This is presumably related to the reduced proportion of hydrogen bonding arrays in the applied macromonomers.

In conclusion, the DSC analysis shows that miscible polymer blends are achievable by incorporation of higher mole percentages of triple hydrogen bonding comonomers (PS-*co*-PS-DAP **19** and PMMA-*co*-PMMA-UP **26**); however, retention of PS and PMMA characteristics is observed in samples with lower proportions of hydrogen bonding arrays. Conformation that hydrogen bonding plays a role in promoting miscibility was obtained from IR analysis on drop-cast samples of the PS-*co*-PS-DAP **19** and PMMA-*co*-PMMA-UP **26** blend. This IR analysis revealed a reduction in frequency ($\delta\nu \sim 10$ cm^{-1}) for the carbonyl stretch that we assign to the UP unit (Figure 5).

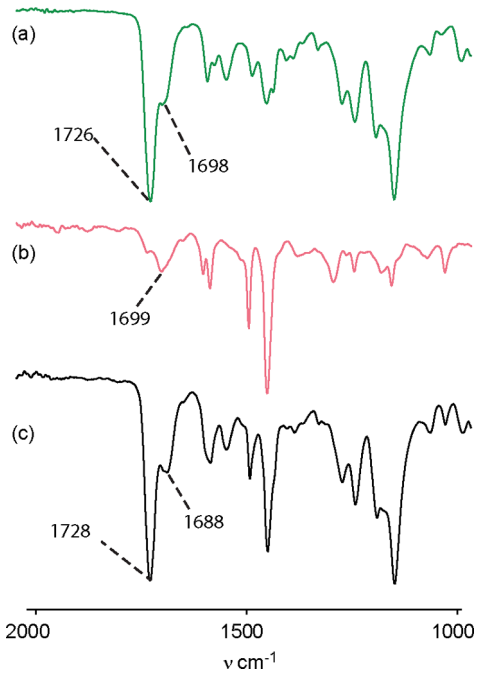

Figure 5. IR analysis of polymer blends obtained from drop-casting a solution (10 mg/mL $CDCl_3$) of PS-*co*-PS-DAP **19** and PMMA-*co*-PMMA-UP **26**: (a) PS-*co*-PS-DAP **19**; (b) PMMA-*co*-PMMA-UP **26**; (c) PS-*co*-PS-DAP **19** and PMMA-*co*-PMMA-UP **26**.

Such changes were not observed in the IR spectra of control samples PS **16** and PMMA **23** (see Supporting Information). We also attempted to illustrate the role of hydrogen bonding by ^{1}H NMR analysis of the PS-*co*-PS-DAP **19** and PMMA-*co*-PMMA-UP **26** blend in chloroform; while further broadening of the ^{1}H resonances was observed upon mixing, we were not overly surprised to observe only minimal changes in chemical shift given at a concentration of 20 mg/mL; the overall concentration of H-bonding motif in this experiment is around 2 μM, which is below the K_a for H-bond mediated dimerization (see Supporting Information).

Finally, in addition to the DSC experiments, we performed initial characterization of the surface topography of the thin films using AFM. Solutions containing mixtures of samples were drop-cast onto a mica surface to give a thin film as for the experiments described above and tapping mode AFM imaging performed. The PS **16** and PMMA **23** sample which is incapable of complementary hydrogen bonding interactions showed significant height variations including surface dome-like features indicating phase separation on the micrometer scale (Figure 6a). Both the PS-*co*-PS-DAP **18** and PMMA-*co*-PMMA-UP **25** and the PS-*co*-PS-DAP **19** and PMMA-*co*-PMMA-UP **26** samples with a higher fraction of H-bonding groups showed lower height variations, with lower roughness and finer structure on the submicrometer scale (Figures 6b,c). The rms roughness (Rq) values over a 1 μm^2 area for the three surfaces are (a) 4.43, (b) 2.19, and (c) 0.38 nm. These observations are consistent with the ability of the hydrogen bonding moieties to restrict phase separation of the polymers and increase miscibility with surface roughness decreasing as H-bond content increases.

CONCLUSIONS

In summary, we have shown that uriedopyrimidine represents an easily accessible conformer-independent ADA hydrogen bonding array that is complementary to the DAD array presented by diamidopyridine derivatives and that this motif can be readily incorporated into addition polymers via RAFT yielding PS/PMMA based (co)polymers with low molar mass dispersity ($Đ$ < 1.40). We have exemplified the utility of this motif through blend assembly of the resultant supramolecular macromonomers as shown by film formation, DSC, IR, and AFM analyses. Polymer blends were obtained for mixtures of PS and PMMA macromonomers containing higher proportions of hydrogen bonding arrays, while PS and PMMA in the absence of hydrogen bonding arrays were shown to be immiscible, thus highlighting a central role of the proportion of hydrogen bonding motifs in affecting blend formation. The association constant for the diamidopyridine−uriedopyrimidine dyad is comparable to that observed for the diamidopyridine−thymine dyad; therefore, the ease of synthesis of polymerizable uriedopyrimidine renders this motif a powerful addition to the arsenal of supramolecular synthons available for polymer materials assembly. Our own future work will focus on

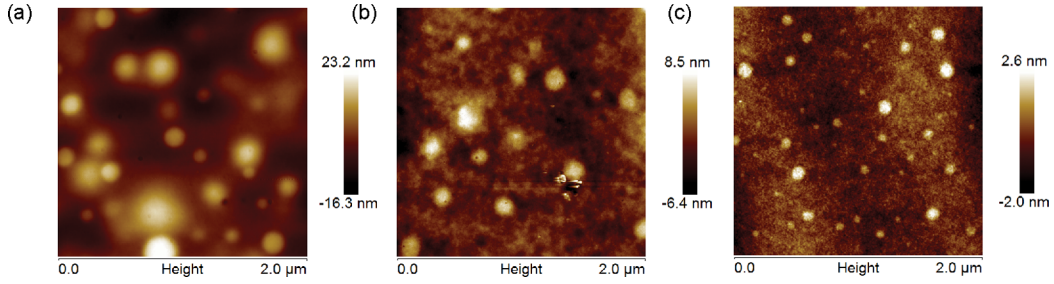

Figure 6. AFM analysis of polymer blends: (a) PS **16** and PMMA **23**; (b) PS-*co*-PS-DAP **18** and PMMA-*co*-PMMA-UP **25**; (c) PS-*co*-PS-DAP **19** and PMMA-*co*-PMMA-UP **26**.

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delineating further the role of these motifs in effecting supramolecular blend formation, further materials characterization, and the use of these motifs to construct healable and responsive materials.

■ ASSOCIATED CONTENT

Supporting Information

Details of further experimental procedures and polymer characterization. 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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