Towards a Universal Polymer Backbone: Design and Synthesis of Polymeric Scaffolds Containing Terminal Hydrogen-Bonding Recognition Motifs at Each Repeating Unit

Ludger P. Stubbs and Marcus Weck*[a]

Abstract: Polymers containing terminal hydrogen-bonding recognition motifs based on diaminotriazine and diaminopyridine groups in their side chains for the self-assembly of appropriate receptors have been prepared by ring-opening metathesis polymerization (ROMP) of norbornenes. A new synthetic method for the preparation of norbornene monomers based on pure alkyl spacers is introduced. These monomers show unprecedented high reactivity using ROMP. To suppress self-association of diaminotriazine-based polymers, polymerizations were run in presence of *N*-butylthymine. The butylthymine acts as a protecting group via self-assembly onto the hydrogen-bonding sites of the polymeric scaffold, thereby solubilizing the polymer. Diaminopyridine monomers do not require the presence of a protecting group due to their low propensity to dimerize. In addition, they exhibit a high affinity for hydrogen-bonded receptors on both monomeric and polymeric level. These polymers present our first building blocks towards the design and synthesis of a "universal polymer scaffold".

Keywords: hydrogen bonds · metathesis · receptors · self-assembly

Introduction

The design of supramolecular structures and self-healing materials based on the self-assembly of smaller subunits is desirable due to the parallel nature of the self-assembly step.[1] On the macromolecular scale, the self-assembly of molecules to corresponding recognition units of a polymer strand is the basis of DNA replication and the biosynthesis of proteins. Inspired by nature's efficiency in creating complex materials on the basis of a small number of building blocks by self-assembly, we are developing a new methodology in polymer science by designing and synthesizing polymer backbones with multiple recognition sites in their side chains that can be functionalized via non covalent interactions, such as hydrogen bonding, ionic forces, or metal coordination (Scheme 1). Such a "universal polymer scaffold" could allow for the rapid and reversible functionalization with suitable receptors to create materials for a wide range of applications in electronics, sensoring, or biochemical engineering.

Hydrogen bonding by way of acid–base interactions has been utilized in the last decade to self-assemble mesogens to polymer backbones for the preparation of side-chain liquid crystalline polymers.[2] Other approaches include the design of polymers with switchable phase transitions by self-assembly of alkylphenol side-chains to a polyvinylpyridine backbone[3] and the self-assembly of biological receptors and small molecules such as electroactive guests on partially diaminotriazine-substituted polystyrenes.[4]

A major disadvantage with many current side-chain functionalized polymer systems based on hydrogen bonding is the lack of recognition motif density, or the lack of stability of the hydrogen bond due to the use of only a single hydrogen bond per side-chain. To overcome these shortcomings, we decided to base our methodology on diaminotriazine- and diaminopyridine units. It has been shown that efficient hydrogen-bonding to receptors by donor–acceptor–donor interactions can be achieved by incorporation of these recognition units into the polymer backbone.[5, 6]

Complete control of the polymer architecture, ranging from statistical- to block copolymerization, is desirable to precisely define the material properties. Ring-opening metathesis polymerization (ROMP) initiated by ruthenium catalysts has proven to be an excellent method for the preparation of complex polymer architectures due to its compatibility with most functional groups and the possibility to be living, a necessary prerequisite for block copolymers.[7] In this paper we report the design, synthesis, and polymerization of diaminotriazine- and diaminopyridine-functionalized norbornenes as part of an approach towards a "universal polymer scaffold".

[a] Prof. Dr. M. Weck, Dr. L. P. Stubbs
School of Chemistry and Biochemistry
Georgia Institute of Technology
Atlanta, GA (USA) 30332-0400
Fax: (+1) 404-894-7452
E-mail: marcus.weck@chemistry.gatech.edu

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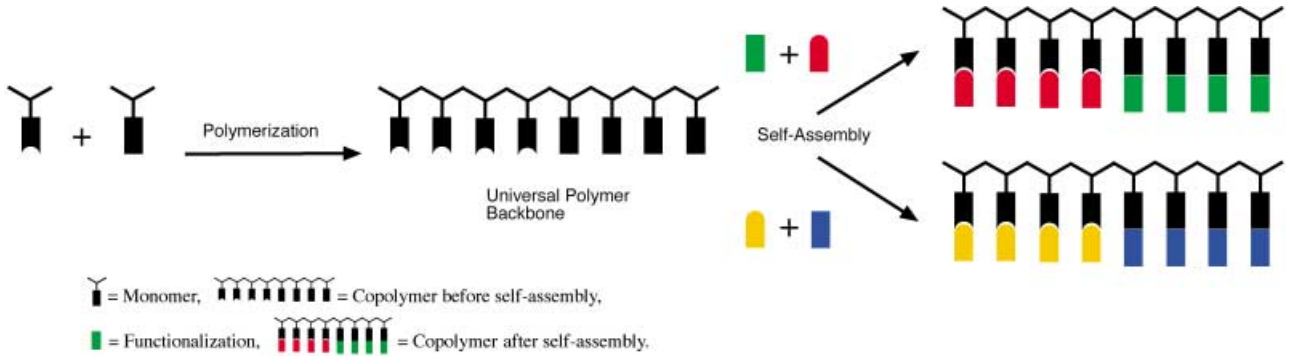


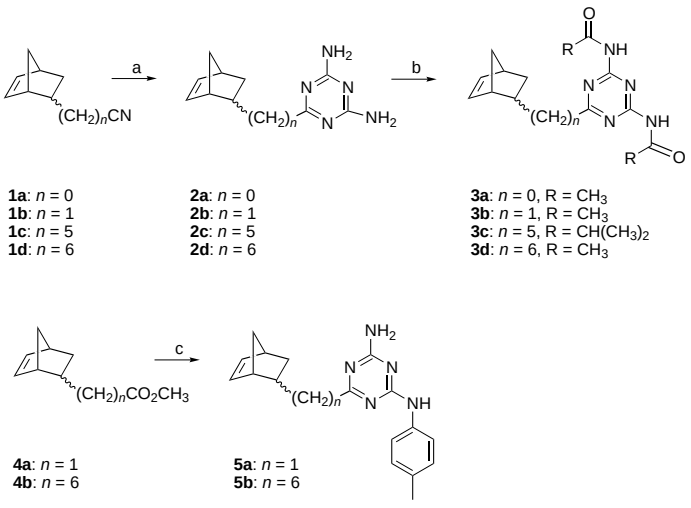
Scheme 1. Schematic representation of the design of a "universal polymeric scaffold". Monomers are polymerized in a controlled fashion to yield well-defined copolymers (schematic representation of a diblock copolymer shown) that can be functionalized through an orthogonal self-assembly methodology to yield highly functionalized copolymers in one simple step. The same polymer can be used for a variety of applications.

Results and Discussion

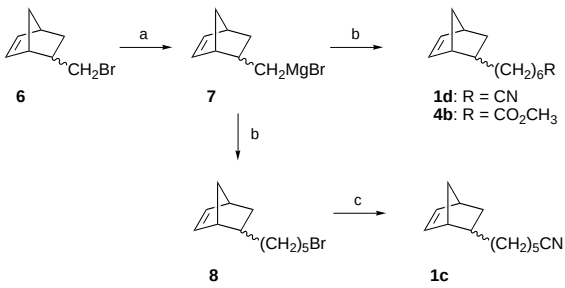
Monomer synthesis: A series of monomers with varying alkyl spacers $[(CH_2)_n$ with $n = 0,1,5,6]$, amine substitutions (aryl, acyl), and heterocycles (triazine, pyridine) were synthesized to study the influence of the nature and the proximity of the heterocyclic functionality on the polymerization and self-assembly behavior.

All diaminotriazines were prepared by condensation of the corresponding nitriles with dicyanodiamide[8] and subsequent acylation. Mono-aryl-substituted substitutions were achieved by condensation of carboxylic esters with *p*-tolylbiguanide[9] (Scheme 2). Triazine ring formations take place under strongly basic conditions. Therefore, the absence of any hydrolyzable functional groups other than the nitrile or esters in the starting materials is mandatory.

Whereas the preparation of short alkyl spacer nitriles **1a**,**b** and ester **4a** is documented in the literature,[10] we had to devise a synthetic route to norbornene compounds with long alkyl spacers and terminal functional groups. This new class of monomers is accessible by a copper-catalyzed Grignard coupling of bromomethylnorbornene **6** with the corresponding ω-bromo functionalized compounds. Nitriles **1c**, **d**, ester **4b**, and bromoalkyl-norbornene **8** were prepared in 66–89% yields (Scheme 3). The *endo*/*exo*-isomer ratios are 1:1 for **3a** and 4:1 for all other monomers.



Scheme 2. Synthesis of diaminotriazine monomers **3a–d** and **5a–b**. a) Dicyanodiamide, KOH, n-propanol, reflux, 12 h, 57–70%. b) Acetic anhydride, pyridine, 120 °C, 1 h, 27–65% (**3a**, **b**, **d**); isobutyryl chloride, pyridine, 90 °C, 2 h, 70% (**3c**). c) *p*-Tolylbiguanide, MeOH, $NaOCH_3$, 90 °C, 96 h, 41–45%.



Scheme 3. Synthesis of monomer precursors with long alkyl spacers. a) Mg, THF, 25 °C, 95%. b) 2 mol% Li_2CuCl_4, THF, −10 to 25 °C, **1d**: 6-bromohexanenitrile, 71% **4b**: 6-bromomethylhexanoate, 89%, **8**: 1,4-dibromobutane, 67%. c) NaCN, DMSO, 80 °C, 3 h, 90%.

Unsubstituted diaminotriazines **2a–d** are only soluble in highly polar solvents such as alcohols or DMSO. However, after acetylation, monomers **3a**, **b**, and **d** are highly soluble in chloroform. Monomer **3c** was substituted with isobutyryl groups to study the influence of bulkier substituents on the self-assembly properties. The solubility of N-aryl-substituted monomers **5a** and **b** in chloroform is sufficiently high for the polymerization and self-assembly experiments.

It is known that in comparison to acylated diaminotriazines, diaminopyridines show a lower tendency towards dimerization and higher association constants with suitable receptors such as uracils or thymines.[11] These properties would be beneficial for the proposed application of a polymeric scaffold. Therefore, we also investigated the synthesis and self-assembly behavior of diaminopyridine functionalized norbornenes. Monomers bearing the diaminopyridine motif were prepared by converting diethyl chelidimate **9** to the *o*-benzylated hydrazide **10**, followed by conversion to the azide and Curtius rearrangement to yield 4-benzoxydiaminopyridine (**11**). Acylation with isobutyl chloride and subsequent deprotection gave phenol **12** that was coupled with bromoalkyl-norbornene **8** to yield monomer **13**. The bulky

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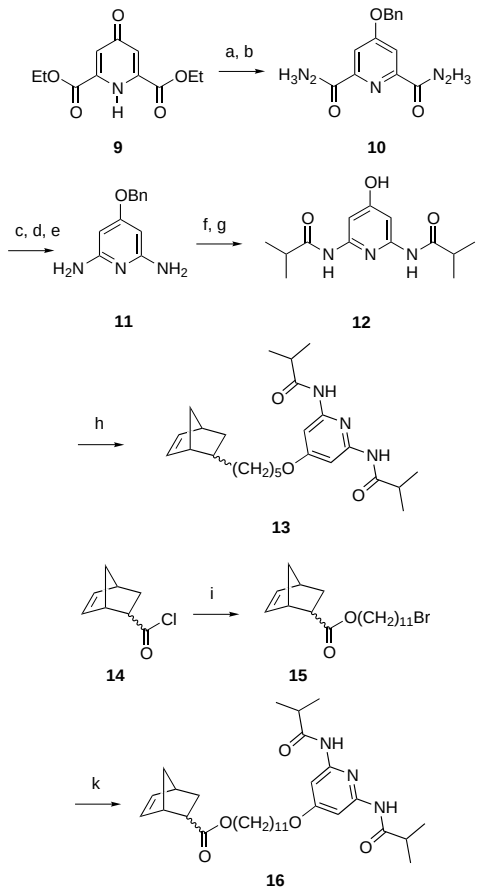
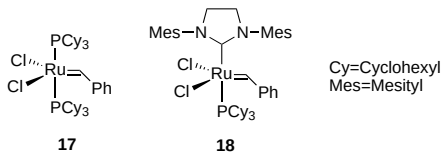
isobutyl substituents were chosen to further decrease the possibility of dimerization. In order to compare the polymerization properties of monomers with pure alkyl-chain spacers and the more commonly employed spacers based on norbornene-2-carboxylic esters, we synthesized compound **15** from norbornene acid chloride **14** and bromoundecanol and coupled it with phenol **12** to give monomer **16** in 65% yield (Scheme 4).



Scheme 4. Synthesis of diaminopyridine monomers **13** and **15**. a) BzBr, K_2CO_3, DMF, 80°C, 4 h, 78%. b) N_2H_4, EtOH, reflux, 12 h, 92%. c) $NaNO_2$, HCl, 0°C, 20 min. d) EtOH, reflux, 12 h. e) EtOH/KOH (aq.), reflux, 18 h, 49% (overall). f) isobutyryl chloride, NEt_3, DCM, 25°C, 86%. g) H_2, Pd/C, EtOH, 100%. h) **8**, K_2CO_3, DMSO, 90°C, 4 h, 83%. i) Bromoundecanol, pyridine, THF, reflux, 2 h, 91%. k) **12**, K_2CO_3, DMSO, 90°C, 4 h, 65%.

Polymer synthesis: The polymerizations were performed using ruthenium initiators **17** and **18**.



The polymerizations were carried out using 0.2 M solutions of the monomers in deuterated chloroform at ambient temperatures with monomer to catalyst ratios of 20:1 – 200:1. The progress of the polymerizations was monitored by ^{1}H NMR spectroscopy. Under these conditions, monomers **3a**, **b**, and **5a**, containing short spacer groups, showed no conversion with catalyst **17** over prolonged periods of time (96 h). Raising the temperatures to 45°C or switching to CD_2Cl_2 as a solvent did not increase conversion. Apparently, the close proximity of the bulky triazine unit to the olefin severely constrains the reactivity of these monomers. We therefore switched to catalyst **18** which is known to be significantly more active in ROMP and ring-closing metathesis than **17**.[7, 12] Using catalyst **18**, monomer **1a** still showed less than 10% conversion within 24 h, whereas monomers **3a** and **5a** showed approximately 40% conversion.

In contrast to the short spacer monomers, compounds **3c**, **d**, **5b**, and **13**, containing at least a four carbon spacer, proved to be exceptionally reactive. In all cases, polymerizations initiated with catalyst **17** were completed in less than two minutes with monomer to catalyst ratios up to 200:1. This remarkable reactivity can be attributed to two factors: 1) The removal of the heterocyclic unit from the proximity of the olefin limits steric interference, as is evident in the increasing reactivity of the series **1a** < **1b** ≪ **1c**, **d**, and **4a** ≪ **4b**. 2) The absence of any functional group in the spacer dramatically increases reactivity. Under the same reaction conditions (monomer to catalyst ratio 50:1, $CDCl_3$, 25°C), monomer **13** with a pure alkyl spacer polymerized completely within two minutes, whereas monomer **16** containing an ester group in the 2-position of the norbornene took more than 24 h to go to completion. These results suggest that the ester carbonyl oxygen in the predominant *endo* isomer retards the reaction by interfering with the catalyst either by chelation or steric constraint.

NMR and GPC data indicate that the rate of propagation for monomers with pure alkyl spacers is higher than the rate of initiation of the catalyst, suggesting a non-living behavior. In ^{1}H NMR spectra of a 10:1 monomer **13** to catalyst **17** mixture, the signal at $\delta = 19.97$ ppm of the catalyst carbene was present even after complete conversion. In contrast, polymerization of **16** resulted in full conversion of the non-iniated carbene to a new signal at $\delta = 18.5$ ppm; this indicates full initiation of the catalyst and a living character of the polymerization. The non-living character of the polymerization of pure alkyl spacer monomers leads to broad molecular weight distributions with polydispersities higher than 1.4 (Table 1). To exclude the possibility that hydrogen-bonding is responsible for the broad molecular weight distributions, polymers of ester **4b** were prepared and found to have high polydispersities as well (PDI > 2).

Table 1. GPC data for selected polymers.[a]

Monomer	[M]/[C][b]	M_n	M_w (theor)	PDI[c]
3c	50	12095	20700	1.43
3d	45	8665	16740	1.48
4b	50	14737	11800	2.02
5b	50	12128	18875	1.67
13	75	22700	32047	1.75

[a] Eluent: THF [b] Monomer to catalyst ratio. [c] Polydispersity index. Reaction conditions: $CDCl_3$, 20 min. Conversion was quantitative by NMR for all monomers.

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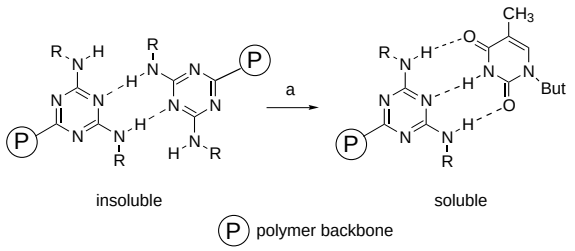
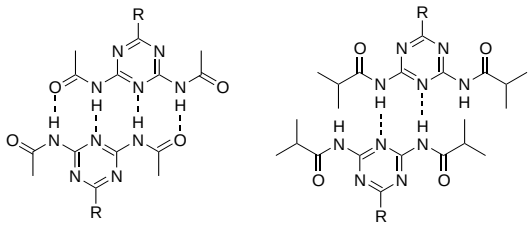
The diaminotriazine polymers immediately precipitated from solution following addition of the catalyst due to self-association. Wheras Rotello et al. have observed micellar-like folding into compact globules for polystyrenes that are partially functionalized with diaminotriazine units,[13] the much higher density of hydrogen-bonding units in our polymers renders them insoluble in solvents of low polarity. However, the precipitated polymers could be solubilized by heating and ultrasonification in the presence of N-butylthymine, which acts as a chloroform-soluble receptor for the diaminotriazine units and competes with the inter- and intramolecular self-association of the polymer chains by forming a triple hydrogen-bond interaction (Scheme 5).



Scheme 5. Reversible cross-linking of polymers by hydrogen bonds. a) 1-Butylthymine (excess), heat, ultrasound.

N-Acetyl diaminotriazines **3a**, **b**, and **3d** showed the strongest dimerization of all monomers. Polymers based on these compounds require at least three equivalents of butylthymine to dissolve, whereas one equivalent is sufficient for polymers based on N-isobutyryl substituted **3c**. These observations can be rationalized by assuming that acetylated diaminotriazines dimerize by quadruple hydrogen bonds in their favored *cis* conformation,[11] whereas steric interaction of the isobutyryl groups with the triazine ring possibly favors the *trans* conformation in **3c**,[14] with only two hydrogen bonds in the dimer that are weakened by steric repulsion (Scheme 6).



Scheme 6. Quadruple hydrogen bond of N-acetyl-diaminotriazines versus double hydrogen bond of N-isobutyryl-diaminotriazines in their preferred conformations.

Polymers based on N-aryl substituted monomers **5a** and **5b** also precipitated from solution, which was not to be expected from their low dimerization constant (see self-assembly experiments). Probably additional hydrogen bonds are formed in the polymer network between NH_2 protons and nitrogen atoms of the triazine rings. In contrast, diaminopyridine-based monomers **13** and **16** were polymerized without any precipitation or gelation. The low propensity of these monomers to self-associate allows for a homogeneous polymerization despite the high density of recognition units tethered to the backbone.

To overcome the problem of precipitation, we carried out the polymerizations of diaminotriazine monomers **3a–d** and **5a–b** in the presence of butylthymine (1–3 equivalents). The competitive self-assembly of the butylthymine to the recognition units during polymerization suppresses dimerization, and the solutions remained homogeneous. In analogy to organic chemistry, the butylthymine can be regarded as a protecting group for the diaminotriazine units. As a general strategy, it might be possible to carry out the synthesis of self-assembled diaminotriazine polymers by preforming a complex between monomer and receptor, utilizing the receptor as both a protecting group and a functionalization agent for the diaminotriazine units. However, this requires that the receptor does not interact with the polymerization catalyst. Whereas excess butylthymine did not affect the catalyst, this is not necessarily the case for highly functionalized receptors, and the method of self-assembly prior to polymerization is inferior to using a polymer backbone that does not show self-association behavior. Therefore, diaminopyridine monomers are clearly preferred to their diaminotriazine counterparts.

Self-assembly studies: To further quantify the self-association, dimerization constants for monomers **3c**, **3d**, **5b**, **13**, *N*-butylthymine, and poly-**13** were determined by measuring the ^{1}H NMR chemical shift of the amide protons as a function of concentration in chloroform solutions[15] (Figure 1, Table 2).

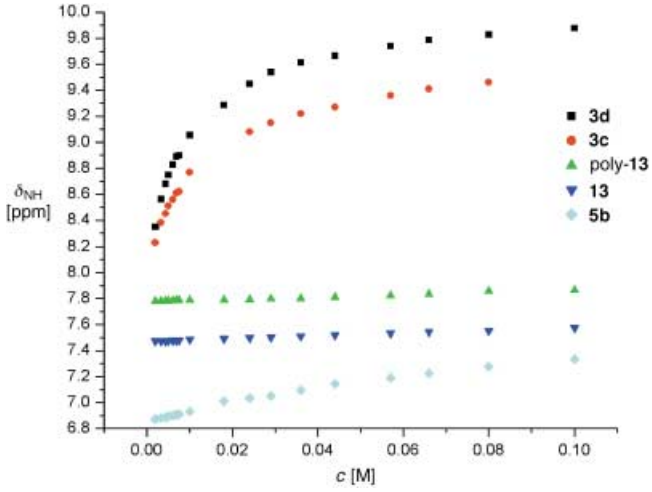


Figure 1. Chemical shifts of the amide protons of **3c**, **3d**, poly-**13**, **13**, and the *p*-tolylamino proton of **5b** as a function of the concentration in $CDCl_3$.

Table 2. Dimerization and association constants determined by ^{1}H NMR data.[a]

Compound	K_{dim} [M^{-1}][b]	K_a [M^{-1}][b, c]
3c	45 (±5)	–
3d	93 (±15)	–
5b[d]	2.6 (±0.2)	–
N-butylthymine	4.1 (±0.2)	–
13	0.31 (±0.15)	116 (±11)
poly-**13**	< 5	73 (±9)

[a] Binding constants were calculated by curve fitting with the computer program ChemEquili.[16] [b] Measured in $CDCl_3$ at 22 °C. [c] With receptor *N*-butylthymine. [d] Calculated for *p*-tolyl-NH.

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With the exception of monoarylated diaminotriazine **5b**, the values reflect the polymerization properties of the compounds, with the highest constant measured for the N-acyl diaminotrazine **3d** and negligible self-association observed for diaminopyridine **13**. The dimerization constant of poly-**13** could only be determined with a wider error range due to peak broadening of the amide protons, but is small with a K_{dim} of less than $5\,mol^{-1}$.

For an efficient self-assembly of receptors to the polymeric scaffold, it is mandatory that the binding constants of the monomers do not significantly change after polymerization. We therefore compared the association constants of monomer **13** and poly-**13**. The binding constants were determined by NMR titrations, using *N*-butylthymine as a model receptor (Figure 2). As shown in Table 2, the difference in binding strength is small and more likely due to limited accessibility of binding sites in the polymer than to competitive self-association. The binding constant of $116\,M^{-1}$ is in the lower range of typical values for diaminopyridines, but switching to linear acyl substituents has the potential to increase the binding strength[11] and allow for improved self-assembly of receptors.

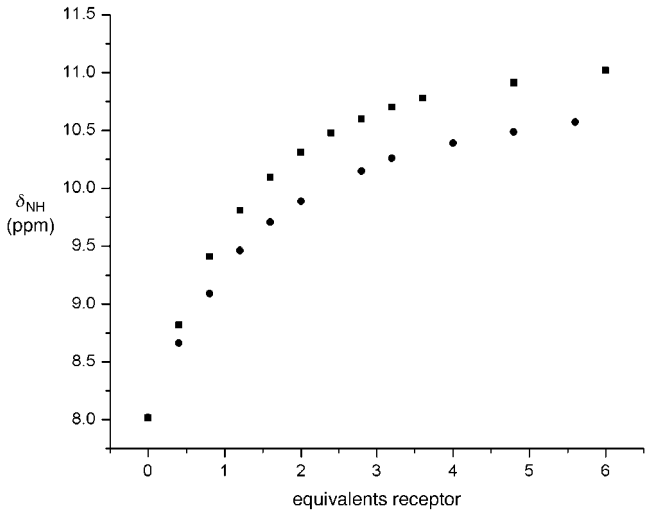

Figure 2. Chemical shifts of 1-butylthymine upon titration with monomer **13** and poly-**13** (60-mer). Equivalents for poly-**13** are based on monomer molecular weight.

Conclusion

To develop a methodology based on a "universal polymeric scaffold", we investigated the synthesis, polymerization, and self-assembly properties of diaminotriazine- and diaminopyridine-functionalized norbornenes. A strong effect of the alkyl spacer length on the reactivity of the monomers was observed, with monomers having long alkyl spacers and no functional group in the chain being exceptionally reactive. It is remarkable that the ring-opening metathesis polymerizations of these monomers, which are based on functional groups containing aromatic nitrogens, proceeds without decomposition of the catalyst. It is well known that nitrogen containing compounds deactivate ruthenium catalyst **17** in other olefin metathesis reactions such as ring-closing metathesis, thereby limiting their use. In self-assembly studies and polymerization experiments, we found that diaminopyridines are superior to diaminotriazines due to their high binding constants to receptors and their low self-association, eliminating the necessity to preform a monomer–receptor complex before polymerization.

The presented methodology of the synthesis of polymers containing hydrogen-bonding units and their functionalization based on self-assembly has a number of advantages over previously reported systems, including 1) high recognition motif density, 2) controllable polymerization behavior, and 3) low dimerization and high association constants of the recognition units towards hydrogen bonding based on a donor–acceptor–donor motif. With an optimized hydrogen-bonding polymer backbone in hand, research on the self-assembly of a suitable receptors for selected applications in materials science is in progress.

Experimental Section

General methods: All reactions were carried out under an argon atmosphere in oven-dried glassware. Anhydrous THF and dichloromethane were purchased from Aldrich and passed over columns of activated alumina under argon to remove traces of water. Deuterated chloroform used for polymerization experiments was distilled over calcium hydride and stored in the dark under argon. All other solvents and commercially available reagents were used without further purification. Ruthenium compounds were bought from Strem Chemicals, Inc. Flash-column chromatography was carried out on silica gel 60, 230–400 mesh (Whatman). Gel-permeation chromatography (GPC) was carried out on polymer solutions in THF at 30 °C (column combination: 2x American Polymer Standards 10 μ particle size, linear mixed bed packing, flow rate $1\,mL\,min^{-1}$) with a Waters 1525 binary pump coupled to a Waters 2414 refractive index detector. Calibrations are based on polystyrene standards. NMR spectra were recorded on a Varian Mercury 300 spectrometer (^{1}H: 300 MHz, ^{13}C: 75 MHz). Chemical shifts are reported in ppm on the δ scale relative to the solvent signal. Electrospray ionization (ESI) mass spectra were obtained on a Micromass Quattro LC spectrometer, and fast atom bombardment (FAB) mass spectra on a VG Instruments 70SE spectrometer. Elemental analyses were performed by Atlantic Microlabs, Norcross, GA. The following compounds were prepared according to literature procedures: 6-bromohexanitrile,[17] 6-bromohexanoic acid methyl ester,[18] 5-bromomethylnorbornene (**6**),[10] norbornene-2-carbonitrile (**1a**),[10] norbornene-2-yl-acetonitrile (**1b**),[19] norbornene-2-yl-acetic methyl ester (**4a**),[19] norbornene-2-carboxylic 11-bromoundecyl ester (**14**).[20] 4-Oxo-1,4-dihydropyridine-2,6-diethylcarboxylate[21] (**9**) was prepared by esterification of chelidamic acid.[22]

***p*-Tolylbiguanide**: *p*-Toluidine hydrochloride (4.28 g, 0.030 mol) and dicyanodiamide (2.48 g, 0.029 mol) were heated under reflux in water (100 mL) for 12 h. On cooling, *p*-tolylbiguanidinium hydrochloride crystallized from the solution. The hydrochloride was heated under reflux with sodium hydroxide (4.0 g) in 50% aqueous ethanol (100 mL) for 1 h. The ethanol was evaporated and the precipitated product washed with water. Recrystallization from ethanol yielded white crystals (3.65 g, 66%). ^{1}H NMR ([D$_6$]DMSO): $\delta = 7.5-6.0$ (br, 4H, *NH*), 7.00 (d, $J = 7.7$ Hz, 2H), 6.70 (d, $J = 7.7$ Hz, 2H), 4.5 (brs, 2H, N*H*), 2.20 (s, 3H); ^{13}C NMR ([D$_6$]DMSO): $\delta = 160.2$, 158.6, 148.4, 130.2, 130.0, 123.4, 21.1; MS (ESI): *m*/*z*: calcd for: 191.2; found: 191.7 [M^+]; elemental analysis calcd (%) for $C_9H_{13}N_5$: C 56.53, H 6.85, N 36.62; found: C 56.46, H 6.73, N 36.38.

***N*-Butylthymine**: Thymine (10.0 g, 0.079 mol), bromobutane (3.62 g, 0.026 mol) and potassium carbonate (11.0 g, 0.08 mol) were stirred in DMSO (200 mL) at 50 °C for 8 h. The suspension was filtered, the filter cake washed with dichloromethane, and the filtrate concentrated in vacuo. The solid residue was treated with water (300 mL) and extracted with dichloromethane (3×200 mL). The organic phases were dried and the solvent removed. Purification of the remaining solid by column chroma-

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tography (hexanes/ethyl acetate 1:2) and recrystallization from chloroform/hexanes yielded the title compound as white crystals (2.70 g, 57%). ^{1}H NMR ($CDCl_3$): $\delta = 9.40$ (brs, 1H, N*H*), 6.96 (d, $J = 1$ Hz, 1H), 3.68 (t, $J = 7.1$ Hz, 2H), 1,90 (d, $J = 6.9$ Hz, 3H), 1.64 (m, 2H), 1.33 (m, 2H), 0.93 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR ($CDCl_3$): $\delta = 165.0$, 151.4, 140.7, 110.7, 48.4, 31.3, 19.9, 13.9, 12.5; MS (FAB): *m/z*: calcd for: 182.1; found: 182.1 [M^+]; elemental analysis calcd (%) for $C_9H_{14}N_2O_2$: C 59.32, H 7.74, N 15.37; found: C 59.04, H 7.77, N 15.19.

General procedure for the Grignard coupling reaction: 5-Bromomethylnorbornene (**6**; 8.84 g, 0.047 mol) was slowly added to magnesium turnings (1.30 g, 0.054 mol) in anhydrous THF (50 mL). After stirring for 24 h at ambient temperatures, the Grignard solution was isolated from residual magnesium (conversion: 90–95%) and slowly added at $-10\,^\circ$C to a solution of the ω-bromoalkane (0.040 mol) and Li_2CuCl_4 (0.1 M in THF, 5 mL) in anhydrous THF (30 mL). The reaction mixture was allowed to warm to ambient temperatures within 18 h. Diethyl ether (100 mL) was added and the solution washed with saturated aqueous NH_4Cl (50 mL). The aqueous phase was extracted with diethyl ether (100 mL) and the combined organic phases were washed with brine (100 mL) and dried over magnesium sulfate. The solvents were removed under vacuum and the residue purified by column chromatography or distillation.

7-Norbornenyl-heptanenitrile (1d): Prepared from **6** (8.84 g, 0.047 mol) and 6-bromohexanitrile (7.10 g, 0.040 mol). Purification by column chromatography on silica gel (dichloromethane/hexanes 1:1) gave **1d** as a light yellow oil (5.48 g, 71%). ^{1}H NMR ($CDCl_3$): $\delta = 6.12$ (dd, $J_1 = 5.5$, $J_2 = 2.7$ Hz, 1H$_{endo}$), 6.05 (m, 2H$_{exo}$), 5.95 (dd, 1H$_{endo}$), 2.72 (brs, 2H), 2.31 (t, $J = 7.1$ Hz, 2H), 2.00–0.40 (m, 15H); ^{13}C NMR ($CDCl_3$) (*endo* isomer): $\delta = 137.1$, 132.5, 120.1, 49.8, 45.6, 42.7, 38.9, 34.8, 32.6, 29.2, 28.8, 28.5, 25.6, 17.3; MS (ESI): *m/z*: calcd for: 203.2; found: 203.2 [M^+]; elemental analysis calcd (%) for $C_{14}H_{21}N$: C 82.70, H 10.41, N 6.89; found: C 82.54, H 10.61, N 6.79.

7-Norbornenyl-heptanoic acid methyl ester (4b): Prepared from **6** (6.54 g, 0.035 mol) and 6-bromohexanoic acid methyl ester (4.81 g, 0.023 mol). Purification by column chromatography on silica gel (dichloromethane) gave **4b** as a light yellow oil (4.89 g, 89%). ^{1}H NMR ($CDCl_3$): $\delta = 6.12$ (dd, $J_1 = 5.5$, $J_2 = 2.7$ Hz, 1H$_{endo}$), 6.05 (m, 2H$_{exo}$), 5.95 (dd, 1H$_{endo}$), 3.63 (s, 3H), 2.70 (brs, 2H), 2.26 (t, $J = 7.7$ Hz, 2H), 2.00–0.40 (m, 15H); ^{13}C NMR ($CDCl_3$) (*endo* isomer): $\delta = 174.5$, 137.1, 132.6, 51.6, 49.7, 45.6, 42.7, 38.9, 34.9, 34.3, 32.6, 29.7, 29.4, 28.6, 25.1; MS (ESI): *m/z*: calcd for: 236.2; found: 237.0 [M^+]; elemental analysis calcd (%) for $C_{15}H_{24}O_2$: C 76.23, H 10.24; found: C 76.07, H 10.41.

5-(5-Bromopentyl)-norbornene (8): Prepared from 5-bromomethylnorbornene (8.84 g, 0.047 mol) and 1,4-dibromobutane (50 g, 0.24 mol). Distillation yielded **8** as a colorless liquid (b.p. 90—94 °C, 0.1 mbar) in 67% yield. The product is approx. 95% pure (GC) and was used without further purification. ^{1}H NMR ($CDCl_3$): $\delta = 6.12$ (dd, $J_1 = 5.5$, $J_2 = 2.7$ Hz, 1H$_{endo}$), 6.05 (m, 2H$_{exo}$), 5.95 (dd, 1H$_{endo}$), 3.40 (t, $J = 6.9$ Hz, 2H), 2.75 (brs, 2H), 2.00–0.50 (m, 13H); ^{13}C NMR ($CDCl_3$) (*endo* isomer): $\delta = 137.2$, 132.5, 45.6, 42.7, 38.9, 36.6, 34.8, 34.3, 33.1, 32.6, 28.6, 28.0.

7-Norbornenyl-hexanenenitrile (1c): Compound **8** (3.60 g, 0.014 mol) and finely powdered sodium cyanide (1.00 g, 0.020 mol) were stirred in DMSO (100 mL) at 80° C for 3 h. Water (100 mL) was added and the solution extracted with diethyl ether (2 × 200 mL). The extracts were washed with water and 5% hydrochloric acid (100 mL). The solvent was removed and the residue purified by column chromatography (hexanes/dichloromethane 1:1) to afford **1c** as a colorless oil (2.90 g, 90%). ^{1}H NMR ($CDCl_3$): $\delta = 6.12$ (dd, $J_1 = 5.5$, $J_2 = 2.7$ Hz, 1H$_{endo}$), 6.05 (m, 2H$_{exo}$), 5.95 (dd, 1H$_{endo}$), 2.72 (brs, 2H), 2.31 (t, $J = 7.1$ Hz, 2H), 2.00–0.40 (m, 13H); ^{13}C NMR ($CDCl_3$) (*endo* isomer): $\delta = 137.1$, 132.5, 120.1, 49.8, 45.6, 42.7, 38.8, 34.6, 32.6, 29.1, 28.0, 25.6, 17.3; MS (ESI): *m/z*: calcd for: 189.3; found: 189.9 [M^+]; elemental analysis calcd (%) for $C_{14}H_{21}N$: C 82.48, H 10.12, N 7.40; found: C 82.42, H 10.13, N 7.46.

General procedure for the preparation of diaminotriazines: Dicyanodiamide (4.20 g, 0.050 mol), potassium hydroxyde (1.0 g) and the norbornenylnitrile (0.035 mol) were stirred in anhydrous *n*-propanol (50 mL) at reflux for 12 h. The solvent was removed, the residue washed with hot water, dried, and recrystallized from ethanol.

6-Norbornenyl-2,4-diamino-[1,3,5]-triazine (2a): Prepared from **1a** (4.16 g, 0.035 mol) to yield white crystals (4.68 g, 65%). ^{1}H NMR ([D$_6$]DMSO): $\delta = 6.80$ (brs, 4H, N*H*), 6.15 (m, 2H$_{endo}$), 6.05 (m, 1H$_{exo}$), 5.78 (m, 1H$_{exo}$), 3.50–1.00 (m, 7H); ^{13}C NMR ([D$_6$]DMSO) (*endo* + *exo*): $\delta = 180.8$, 179.7, 167.6, 167.4, 138.5, 137.4, 137.1, 133.8, 49.8, 48.1, 46.8, 46.5, 46.2, 42.7, 42.0, 30.8, 29.7; MS (ESI): *m/z*: calcd for: 203.2; found: 203.8 [M^+]; elemental analysis calcd (%) for $C_{10}H_{13}N_5$: C 59.10, H 6.45, N 34.46; found: C 58.78, H 6.48, N 34.64.

6-Norbornenyl-methyl-2,4-diamino-[1,3,5]-triazine (2b): Prepared from **1b** (4.66 g, 0.035 mol) to yield white crystals (5.31 g, 70%). ^{1}H NMR ([D$_6$]DMSO): $\delta = 6.55$ (brs, 4H, N*H*), 6.15 (dd, $J_1 = 5.5$, $J_2 = 2.7$ Hz, 1H$_{endo}$), 6.05 (m, 2H$_{exo}$), 5.95 (dd, 1H$_{endo}$), 3.50–0.50 (m, 9H); ^{13}C NMR ([D$_6$]DMSO) (*endo* isomer): $\delta = 177.9$, 167.7, 137.5, 133.4, 49.7, 45.9, 43.6, 42.7, 37.2, 31.9; MS (ESI): *m/z*: calcd for: 217.3; found: 217.9 [M^+]; elemental analysis calcd (%) for $C_{11}H_{15}N_5$: C 60.81, H 6.96, N 32.23; found: C 60.52, H 6.69, N 32.58.

6-(5-Norbornenyl-pentyl)-2,4-diamino-[1,3,5]-triazine (2c): Prepared from **1c** (3.20 g, 0.016 mol) to yield a white solid (2.94 g, 67%). ^{1}H NMR ([D$_6$]DMSO): $\delta = 6.52$ (brs, 4H, N*H*), 6.10 (dd, $J_1 = 5.5$, $J_2 = 2.7$ Hz, 1H$_{endo}$), 6.05 (m, 2H$_{exo}$), 5.90 (dd, 1H$_{endo}$), 2.70 (m, 2H), 2.45 (t, $J = 7.1$ Hz, 2H), 2.40–0.20 (m, 15H); ^{13}C NMR ([D$_6$]DMSO) (*endo* isomer): $\delta = 178.5$, 167.7, 137.4, 133.0, 49.8, 45.5, 42.6, 38.8, 38.7, 34.9, 32.7, 29.8, 28.6, 27.8; MS (FAB): *m/z*: calcd for: 273.4; found: 274.1 [M^++H]; elemental analysis calcd (%) for $C_{16}H_{25}N_5$: C 65.90, H 8.48, N 25.62; found: C 65.81, H 8.46, N 25.78.

6-(6-Norbornenyl-hexyl)-2,4-diamino-[1,3,5]-triazine (2d): Prepared from **1d** (7.09 g, 0.035 mol) to yield a white solid (5.75 g, 57%). ^{1}H NMR ([D$_6$]DMSO): $\delta = 6.55$ (brs, 4H, N*H*), 6.15 (dd, $J_1 = 5.5$, $J_2 = 2.7$ Hz, 1H$_{endo}$), 6.05 (m, 2H$_{exo}$), 5.95 (dd, 1H$_{endo}$), 2.70 (m, 2H), 2.25 (t, $J = 7.1$ Hz, 2H), 2.40–0.20 (m, 15H); ^{13}C NMR ([D$_6$]DMSO) (*endo* isomer): $\delta = 178.4$, 167.7, 137.4, 133.0, 49.8, 45.6, 42.6, 42.7, 39.1, 39.0, 34.9, 32.6, 29.8, 28.7, 27.2; MS (ESI): *m/z*: calcd for: 287.4; found: 288.1 [M^+]; elemental analysis calcd (%) for $C_{16}H_{25}N_5$: C 66.86, H 8.77, N 24.37; found: 66.76, H 9.03, N 23.77.

6-Norbornenyl-2,4-bis(acetylamino)-[1,3,5]-triazine (3a): Compound **2a** (2.95 g, 0.0145 mol) was heated with acetic anhydride (12.50 g, 0.12 mol) to 140 °C until the solution became clear. Upon cooling, **3a** precipitated and was purified by column chromatography (ethyl acetate) to give off-white crystals (2.71 g, 65%). ^{1}H NMR ($CDCl_3$): $\delta = 9.96$ (brs, 1H, N*H*), 9.92 (brs, 1H, N*H*), 6.15 (m, 2H$_{endo}$), 6.05 (dd, $J_1 = 5.5$, $J_2 = 2.7$ Hz, 1H$_{endo}$), 5.78 (dd, 1H$_{exo}$), 2.58 (s, 6H, C*H*$_3$), 3.50–1.20 (m, 7H); ^{13}C NMR ($CDCl_3$) (*endo* + *exo* isomers): $\delta = 184.9$, 183.6, 173.5, 173.2, 163.9, 163.7, 138.6, 137.9, 136.7, 132.6, 50.2, 48.5, 48.4, 47.9, 47.7, 46.1, 43.1, 42.4, 31.9, 30.2, 26.5; MS (ESI): *m/z*: calcd for: 288.1; found: 288.1 [M^++H]; elemental analysis calcd (%) for $C_{14}H_{17}N_5O_2$: C 58.52, H 5.96, N 24.38; found: C 58.15, H 5.84, N 24.38.

6-Norbornenyl-methyl-2,4-bis(acetylamino)-[1,3,5]-triazine (3b): Compound **3b** was prepared in analogy to above using **2b** (3.25 g, 0.015 mol) and acetic anhydride (12.50 g, 0.12 mol). Purification by column chromatography (ethyl acetate) yielded a white solid (1.96 g, 45%). ^{1}H NMR ($CDCl_3$): $\delta = 9.50$ (brs, 2H, N*H*), 6.15 (dd, $J_1 = 5.5$, $J_2 = 2.7$ Hz, 1H$_{endo}$), 6.05 (m, 2H$_{exo}$), 6.02 (dd, 1H$_{endo}$), 2.47 (s, 6H, C*H*$_3$), 2.80–0.60 (m, 9H); ^{13}C NMR ($CDCl_3$) (*endo* isomer): $\delta = 181.7$, 173.1, 164.0, 137.8, 132.6, 49.6, 45.9, 44.1, 42.8, 37.2, 32.3, 26.4; MS (ESI): *m/z*: calcd for: 302.1; found: 302.1 [M^++H]; elemental analysis calcd (%) for $C_{15}H_{19}N_5O_2$: C 59.79, H 6.36, N 23.24; found: C 59.32, H 6.36, N 22.73.

6-(6-Norbornenyl-hexyl)-2,4-bis(isobutyrylamino)-[1,3,5]-triazine (3c): Isobutyryl chloride (1.2 mL) was added to a solution of **2c** (1.26 g, 4.6 mmol) in pyridine (30 mL) and the reaction mixture stirred at 90 °C for 2 h. Evaporation of volatiles and chromatographic purification of the residue (ethyl acetate/hexanes 1:1) yielded **3c** as a slightly yellow sticky solid (1.34 g, 70%). ^{1}H NMR ($CDCl_3$): $\delta = 9.10$ (brs, 2H, N*H*), 6.15 (dd, $J_1 = 5.5$, $J_2 = 2.7$ Hz, 1H$_{endo}$), 6.05 (m, 2H$_{exo}$), 5.95 (dd, 1H$_{endo}$), 2.70 (m, 2H), 2.57 (s, 6H, C*H*$_3$), 2.40–0.20 (m, 15H); ^{13}C NMR ($CDCl_3$) (*endo* isomer): $\delta = 182.2$, 173.1, 164.0, 137.1, 132.6, 49.7, 45.6, 42.7, 39.1, 39.0, 34.9, 32.6, 29.8, 29.4, 28.7, 27.2, 26.4; MS (ESI): *m/z*: calcd for: 413.6; found: 414.1 [M^+]; elemental analysis calcd (%) for $C_{23}H_{35}N_5O_2$: C 66.80, H 8.53, N 16.93; found: C 65.61, H 8.69, N 15.51.

6-(6-Norbornenyl-hexyl)-2,4-bis(acetylamino)-[1,3,5]-triazine (3d): Acetic anhydride (6 mL) was added to a solution of **2d** (0.94 g, 3.1 mmol) in pyridine (25 mL) and the reaction mixture stirred at 120 °C for 12 h. Evaporation of volatiles and chromatographic purification of the residue (ethyl acetate) yielded **3d** as a white solid (0.31 g, 27%). ^{1}H NMR ($CDCl_3$): $\delta = 9.10$ (brs, 2H, NH), 6.15 (dd, $J_1 = 5.5$, $J_2 = 2.7$ Hz, 1H$_{endo}$), 6.05 (m,

2 H_{exo}), 5.95 (dd, 1 H_{endo}), 2.70 (m, 2H), 2.57 (s, 6H, CH_3), 2.40 – 0.20 (m, 15H); ^{13}C NMR ($CDCl_3$) (*endo* isomer): δ = 182.2, 173.1, 164.0, 137.1, 132.6, 49.7, 45.6, 42.7, 39.1, 39.0, 34.9, 32.6, 29.8, 29.4, 28.7, 27.2, 26.4; MS (ESI): *m*/*z*: calcd for: 371.5; found: 372.0 [M^+]; elemental analysis calcd (%) for $C_{20}H_{29}N_5O_2$: C 64.66, H 7.87, N 18.85; found: 64.68, H 8.02, N 18.62.

6-Norbornenyl-methyl-2-(*N*-(p-tolyl))-amino-4-amino-[1,3,5]-triazine (5a): In a pressure bottle, **4a** (1.65 g, 0.010 mol), *p*-tolylbiguanide (1.92 g, 0.010 mol), and sodium methoxide (0.2 g) were stirred at 90 °C in anhydrous methanol (40 mL) for 96 h. Evaporation of the solvent and purification of the residue by column chromatography (hexanes/ethyl acetate 1:1) gave the title compound as a white solid (1.38 g, 45 %). ^{1}H NMR ([D$_6$]DMSO): δ = 9.22 (br s, 1H, NH), 7.62 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.82 (br s, 2H, NH_2), 6.15 (dd, J_1 = 5.5, J_2 = 2.7 Hz, 1 H_{endo}), 6.05 (m, 2 H_{exo}), 5.95 (dd, 1 H_{endo}), 2.21 (s, 3H), 2.70 – 0.50 (m, 9H); ^{13}C NMR ([D$_6$]DMSO) (*endo*): δ = 178.0, 167.4, 164.9, 138.1, 137.5, 133.3, 131.2, 129.5, 120.4, 49.8, 45.9, 43.7, 42.7, 37.3, 32.0, 21.0; MS (ESI): *m*/*z*: calcd for: 307.4; found: 308.1 [M^+]; elemental analysis calcd (%) for $C_{18}H_{21}N_5$: C 70.33, H 6.89, N 22.78; found: 69.79, H 6.90, N 22.79.

6-(6-Norbornenyl-hexyl)-2-(*N*-(*p*-tolyl))-amino-4-amino-[1,3,5]-triazine (5b): The title compound was prepared in analogy to above using **4b** (2.36 g, 0.010 mol), *p*-tolylbiguanide (2.06 g, 0.011 mol), and sodium methoxide (0.2 g). Purification by column chromatography (hexanes/ethyl acetate 1:1) gave **5b** as a white solid (1.54 g, 41 %). ^{1}H NMR ([D$_6$]DMSO): δ = 9.30 (br s, 1H, N*H*), 7.40 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 6.80 (br s, 2H, NH_2), 6.05 (dd, J_1 = 5.5, J_2 = 2.7 Hz, 1 H_{endo}), 6.05 (m, 2 H_{exo}), 5.90 (dd, 1 H_{endo}), 2.31 (s, 3H), 2.70 – 0.50 (m, 18H); ^{13}C NMR ([D$_6$]DMSO) (*endo*): δ = 178.4, 167.4, 164.9, 138.1, 137.3, 133.0, 131.2, 129.4, 120.4, 49.8, 45.5, 42.6, 38.9, 38.7, 35.0, 32.7, 29.9, 29.5, 28.7, 21.1; MS (FAB): *m*/*z*: calcd for: 377.5; found: 378.3 [M^++H]; elemental analysis calcd (%) for $C_{23}H_{31}N_5$: C 73.17, H 8.28, N 18.55; found: C 72.82, H 8.24, N 18.49.

4-Benzyloxy-pyridine-2,6-diethylcarboxylate: 4-Oxo-1,4-dihydropyridine-2,6-diethylcarboxylate **9** (3.67 g, 0.0153 mol), potassium carbonate (2.3 g, 0.017 mol), and benzyl bromide (1.9 mL, 0.016 mol) were stirred at 85 °C in dry DMF (30 mL) for 4 h. Water (200 mL) was added and the mixture extracted with dichloromethane (2 × 150 mL). The extracts were washed with brine, dried, the solvents removed in vacuo, and the residue recrystallized from ethanol (4.56 g, 77 %). ^{1}H NMR ($CDCl_3$): δ = 7.84 (s, 2H), 7.45 – 7.30 (m, 5H), 5.20 (s, 2H), 4.44 (q, *J* = 7.1 Hz, 4H), 1.42 (t, 6H); ^{13}C NMR ($CDCl_3$): δ = 166.7, 164.7, 150.3, 134.9, 129.0, 128.8, 127.9, 114.8, 70.9, 62.5, 14.3; MS (ESI): *m*/*z*: calcd for: 329.1; found: 329.9 [M^+]; elemental analysis calcd (%) for $C_{18}H_{19}NO_5$: C 65.64, H 5.81, N 4.25; found: C 65.55, H 5.83, N 4.24.

4-Benzyloxy-pyridine-2,6-dicarboxylic dihydrazide (10): 4-Benzyloxy-pyridine-2,6-diethylcarboxylate (4.50 g, 0.0136 mol) was heated under reflux with hydrazine hydrate (5 mL) in ethanol (50 mL) for 12 h. The crystalline precipitate was filtered, washed with diethyl ether and dried to yield white needles (3.70 g, 92 %). ^{1}H NMR ($CDCl_3$): δ = 10.64 (s, 2H, *NH*), 7.66 (s, 2H), 7.50 – 7.30 (m, 5H), 5.32 (s, 2H), 4.50 (s, 6H, *NH*); ^{13}C NMR ($CDCl_3$): δ = 167.4, 162.4, 151.2, 136.4, 129.2, 128.9, 128.5, 110.7, 70.6; MS (FAB): *m*/*z*: calcd for: 302.1; found: 302.1 [M^+H]; elemental analysis calcd (%) for $C_{14}H_{15}N_5O_3$: C 55.81, H 5.02, N 23.24; found: C 54.65, H 5.04, N 23.75.

4-Benzyloxypyridine-2,6-diamine (11): Hydrazide **10** (2.66 g, 0.083 mol) was suspended in 10 % hydrochloric acid (150 mL) at 0 °C and treated dropwise with a saturated solution of sodium nitrite until the azide floated on top as a sticky solid. The azide was isolated by filtration, washed with water and air-dried. The solid was dissolved in ethanol (100 mL), and heated under reflux for 12 h to generate the carbamate. The solution was then reduced to 50 mL, 10 % aqueous potassium hydroxide (1:1, 50 mL) were added, and the mixture heated under reflux for 8 h. The ethanol was distilled off and the residue extracted with chloroform (3 × 100 mL). The extracts were washed with brine, dried, and evaporated to yield the amine **11** as a fluffy white solid (0.87 g, 49 %). ^{1}H NMR ([D$_6$]DMSO): δ = 7.40 – 7.30 (m, 5H), 5.30 (s, 2H), 5.28 (s, 4H, NH), 4.94 (s, 2H); ^{13}C NMR, ([D$_6$]DMSO): δ = 167.6, 160.7, 137.8, 129.1, 128.4, 128.1, 82.9, 68.8; MS (ESI): *m*/*z*: calcd for: 215.1; found: 215.8 [M^+].

4-Benzyloxy-2,6-bis(isobutyrylamino)pyridine: Isobutyryl chloride (1.50 g 14.1 mmol) was slowly added at 0 °C to a suspension of **11** (1.468 g, 6.82 mmol) and triethylamine (3 mL) in dichloromethane (40 mL). The reaction mixture was allowed to warm to ambient temperatures and purified by column chromatography (hexanes/ethyl acetate 1:1) to yield the title compound as a white solid (2.087 g, 86 %). ^{1}H NMR ($CDCl_3$): δ = 7.70 (br s, 2H, N*H*), 7.68 (s, 2H, H_{py}), 7.45 – 7.25 (m, 5H), 5.13 (s, 2H, CH_2), 2.51 (septet, *J* = 6.9 Hz, 2H), 1,24 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR ($CDCl_3$): δ = 175.7, 168.9, 150.8, 136.0, 128.8, 128.4, 127.8, 96.7, 70.3, 37.1, 19.6; MS (ESI): *m*/*z*: calcd for: 355.2; found: 356.0 [M^+]; elemental analysis calcd (%) for $C_{20}H_{25}N_3O_3$: C 67.58, H 7.09, N 11.82; found: C 66.98, H 7.12, N 11.36.

4-Hydroxy-2,6-bis(isobutyrylamino)pyridine (12): In a pressure bottle, 4-benzyloxy-2,6-bis(*N*-isobutyryl)pyridine (0.940 g, 2.64 mmol) was dissolved in absolute ethanol (100 mL), 5 % palladium on charcoal (300 mg) was added, and the reaction mixture shaken under hydrogen (3 bar) for 1 h. The suspension was filtered over Celite and the solvent removed to yield **12** as a white solid (0.700 g, 100 %). ^{1}H NMR ([D$_6$]DMSO): δ = 9.70 (br s, 2H, N*H*), 7.24 (s, 2H, H_{py}), 2.70 (septet, *J* = 6.9 Hz, 2H), 1.05 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR ([D$_6$]DMSO): δ = 175.7, 169.9, 150.8, 96.7, 70.3, 37.1, 19.6; MS (ESI): *m*/*z*: calcd for: 265.1; found: 265.9 [M^+].

4-(5-Norbornenylpentyloxy)-2,6-bis(isobutyrylamino)pyridine (13): Compound **12** (196 mg , 0.74 mmol), bromoalkyl-norbornene **8** (190 mg, 0.78 mmol), potassium carbonate (200 mg, 1.44 mmol), and 18-crown-6 (10 mg, 0.04 mmol) were stirred in DMSO (10 mL) at 90 °C for 3 h. Water (50 mL) was added and the mixture extracted with diethyl ether. Purification by column chromatography (hexanes/ethyl acetate 1:1) gave **13** (260 mg, 81 %) as a colorless viscous oil that crystallized upon standing. ^{1}H NMR ($CDCl_3$): δ = 7.54 (s, 4H, H_{py} + NH), 6.12 (dd, J_1 = 5.5, J_2 = 2.7 Hz, 1 H_{endo}), 6.05 (m, 2 H_{exo}), 5.95 (dd, 1 H_{endo}), 4.00 (t, *J* = 6.2 Hz, 2H), 2.74 (br s, 2H), 2.49 (septet, *J* = 6.9 Hz, 2H), 2.0 – 1.7 (m, 4H), 1.5 – 1.0 (m, 8H), 1.23 (d, *J* = 6.9 Hz, 12H), 0.52 – 0.44 (m, 1H); ^{13}C NMR ($CDCl_3$) (*endo* isomer): δ = 175.5, 169.1, 150.6, 137.1, 132.6, 96.4, 68.7, 49.9, 45.7, 45.5, 42.8, 38.9, 37.2, 35.0, 32.7, 29.3, 28.6, 26.4, 19.8; MS (ESI): *m*/*z*: calcd for: 427.3; found: 428.2 [M^+]; elemental analysis calcd (%) for $C_{25}H_{37}N_3O_3$: C 70.22, H 8.72, N 9.83; found: C 68.85, H 8.83, N 9.62.

Norbornene-2-carboxylic 11-(2,6-bisisobutyrylamino-pyridin-4-yloxy) undecyl ester (16): Compound **12** (210 mg, 0.79 mmol), bromo-ester **15** (300 mg, 0.80 mmol), and potassium carbonate (400 mg, 2.88 mmol) were stirred in DMSO (10 mL) at 95 °C for 5 h. Water (50 mL) was added and the mixture extracted with diethyl ether. The extracts were washed with brine, dried, and the solvent removed. Purification by column chromatography (hexanes/ethyl acetate 1:1) yielded **15** as a white solid (284 mg, 65 %). ^{1}H NMR ($CDCl_3$): δ = 8.02 (s, 2H, *NH*), 7.47 (s, 2H), 6.08 (dd, J_1 = 5.5, J_2 = 2.7 Hz, 1 H_{endo}), 6.02 (m, 2 H_{exo}), 5.83 (dd, 1 H_{endo}), 3.95 (m, 4H), 3.10 (br s, 1H), 2.86 (m, 1H), 2.79 (br s, 1H), 2.40 (septet, *J* = 6.9 Hz, 2H), 1.80 – 1.05 (m, 35H); ^{13}C NMR ($CDCl_3$) (*endo* isomer): δ = 176.0, 175.2, 169.1, 150.9, 137.8, 132.5, 96.4, 68.5, 49.8, 45.9, 43.5, 42.8, 36.8, 29.6, 29.4, 29.3, 29.0, 28.8, 26.1, 26.0, 19.6; MS (ESI): *m*/*z*: calcd for: 555.4; found: 556.4 [M^+].

Self-assembly experiments: Dimerization constants of the monomers and polymers were determined from ^{1}H NMR experiments by monitoring the chemical shift of the amide protons at various concentrations (0.0020 – 0.1000 M) in deuterated chloroform. Association constants were measured by titration of a 0.005 M solution of *N*-butylthymine with 0.010 M solutions of the monomer or polymer, and monitoring the chemical shift of the butylthymine imide proton. The molarity of the polymer solution is based on the number of recognition units. The computer program ChemEquili was used for evaluation of the data.[16]

Polymerizations: A typical polymerization experiment was conducted as following: To a stirred solution of the monomer (0.3 mmol in 1.0 mL $CDCl_3$), a solution of the ruthenium initiator (0.006 mmol in 0.5 mL $CDCl_3$) was added. For diaminotriazine monomers, *N*-butylthymine (0.3 – 0.9 mmol) was added before addition of the initiator. The mixture was stirred at ambient temperatures and the reaction progress was monitored by ^{1}H NMR. After complete conversion, ethyl vinyl ether (0.1 mL) was added to terminate the reaction. The polymers were precipitated in hexanes and dried in high vacuum for 24 h.

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