# Supramolecular Graft Copolymers Based on 2,7-Diamido-1,8-naphthyridines

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ABSTRACT: Supramolecular graft copolymers containing a quadruple hydrogen bond motif in the main chain have been prepared by acyclic diene metathesis (ADMET) polymerization of an α,ω-diene monomer containing a 2,7-diamido-1,8-naphthyridine (Napy) unit. During the ADMET polymerization, a supramolecular protection strategy was applied in order to prevent naphthyridine coordination to the ruthenium catalyst. The 2-ureido-4[1*H*]-pyrimidinone (UPy) derivatives used as protecting groups also allowed for detection of the supramolecular graft copolymer with size exclusion chromatography. Deprotection by simple treatment with a polar solvent afforded free Napy binding sites on the main chain. Reversible grafting of UPy derivatives of various sizes onto the free poly-Napy was demonstrated by diffusion-ordered NMR experiments.

## Introduction

The reversibility and versatility of noncovalent architectures in nature have always inspired man to design and organize new soft and/or biocompatible materials. Especially the construction of supramolecular polymers and other dynamic architectures using noncovalent-based strategies has evolved tremendously over the past decade.[1−3] Such synthetic strategies make use of hydrogen bonding,[4,5] metal coordination,[6] and hydrophobic interactions.[7] Supramolecular polymers are typically divided into two categories: (i) side-chain and (ii) main-chain polymers. Pioneering work in the area of side-chain polymers was first reported for the synthesis of liquid crystalline materials.[8−13] A limitation of these early and still many current side-chain functionalized polymer systems based on hydrogen bonding is the lack of binding strength of the recognition motif or the lack of functional group density. Typically, the most ubiquitous examples employ single hydrogen bonds,[14,15] with fewer examples having double[16,17] or up to triple hydrogen bonding.[18−22] Although such weak side-chain self-assembly has been applied to materials design,[23,24] a methodology to increase both the degree of functionalization and the strength of the binding motif is desirable. In our attempt to expand the toolbox of noncovalent structures based on quadruple hydrogen bonding, we decided to develop a methodology to increase both the degree of functionalization and the strength of the binding motif for a supramolecular graft copolymer based on 2,7-diamido-1,8-naphthyridine[25] (Napy) monomers.

In the past, it was shown that supramolecular polymers with high degrees of polymerization in excess of several hundred can be formed by small monomers containing self-complementary 2-ureido-4[1*H*]-pyrimidinone (UPy) groups.[26−28] These molecules form extremely stable homodimers in chloroform solution (dimerization constant $K_{dim} = 6 \times 10^7$ $M^{-1}$ $CHCl_3$).[29] This last feature makes the UPy group very interesting for application in various polymeric systems. However, for use in side-chain functionalized systems, the self-complementary UPy units will result in a collapsed polymeric aggregate due to intramolecular binding within the chain. Furthermore, a statistical mixture of hetero- vs homodimers can be expected upon functionalization with a UPy pendent group. Although UPy heterodimers have been reported before,[30] the need for a strong complementary multiple hydrogen bond motif is evident. Fortunately, because of its ability to form an intramolecular hydrogen bond and prototropy on the pyrimidinone ring, the UPy unit is able to selectively form strong heterodimers in one of its tautomeric forms via a hydrogen bonding acceptor−donor−donor−acceptor (ADDA) array with the DAAD array of 2,7-diamido-1,8-naphthyridines[25,31] (Scheme 1a).

Recently, we reported that these dual complexation modes of UPy result in concentration-dependent selectivity, favoring UPy−Napy heterocomplexation over UPy dimerization by a factor of >20:1 above 0.1 M in 1:1 mixtures ($K_a$(UPy−Napy) > $10^6$ $M^{-1}$). In addition, UPy−Napy-based supramolecular copolymers were prepared.[32,33] The high selectivity for heterodimerization makes the UPy-Napy system eminently suitable to explore the possibilities of obtaining supramolecular graft copolymers with Napy units in the main-chain and UPy molecules as the side chains (Scheme 1b).

Among various polymerization techniques that can be used to obtain strictly linear polymers, acyclic diene metathesis (ADMET) polymerization has proven a valuable tool for the construction of new polymer architectures due to the high catalytic activity of the applied ruthenium catalysts and its high functional group tolerance.[34,35] In this report, we describe the ADMET polymerization of an α,ω-diene bearing a Napy unit to obtain a strictly linear polymer with a DAAD quadruply hydrogen bond motif in the main chain. Characterization of the grafted and ungrafted poly-Napy is done by $^1$H NMR analysis and size exclusion chromatography. Finally, the possibility of reversible grafting with different UPy derivatives is investigated with diffusion-ordered NMR spectroscopy.

## Results and Discussion

**Synthesis of Oligo-2,7-bis(9-decenoylamino)-1,8-naphthyridines.** 2,7-Bis(10-undecenoylamino)-1,8-naphthyridine (**1**) was chosen as the Napy monomer which can be prepared on multigram scale via Pd-catalyzed Buchwald−Hartwig amidation as reported recently by our group.[36]

ADMET polymerization of Napy diene **1** was performed in dry toluene at various temperatures using several ruthenium

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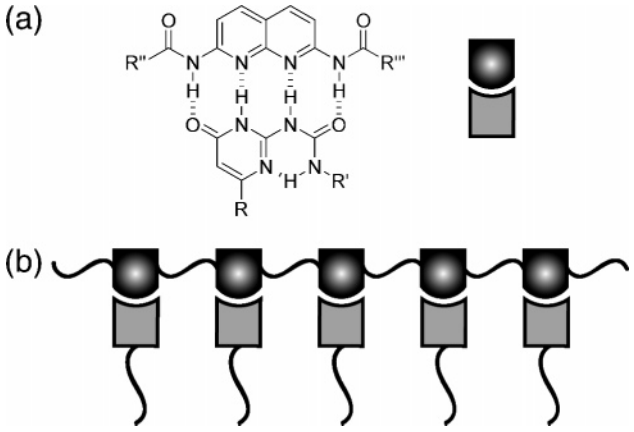
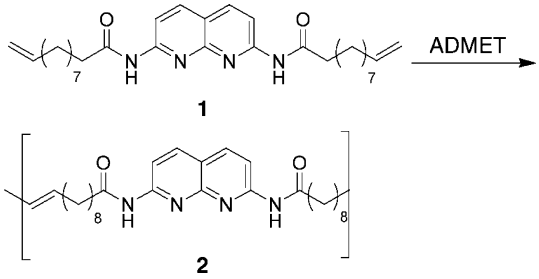
**Scheme 1. (a) Structure and Schematic Representation of the UPy−Napy Complex and (b) a Schematic Representation of a Napy-Based Graft-copolymer with UPy Pendent Groups**




**Scheme 2. ADMET of Acyclic Napy Diene 1**




catalysts. The reaction was monitored by $^1$H NMR, and conversion was determined by integration of the olefinic signals at 4.94 and 5.31 ppm for **1** and **2**, respectively. Unfortunately, initial attempts to polymerize **1** using the second-generation Grubbs' ruthenium catalyst (**A**) in toluene or dichloromethane did not yield any polymer (Table 1, entries 1 and 2). In order to facilitate the metathesis reaction, prolonging the lifetime of the active form of the ruthenium catalyst in which the phosphorus ligand is dissociated from the metal is a key issue as reported by Grubbs and co-workers.[37] For this purpose, two approaches have been used in the literature.

The first approach is to increase the rate of dissociation of the phosphine ligand from the catalyst. This can be achieved by replacing the ligand with one of lower basicity (catalysts **B**−**D**).[38−40] The second is to prevent reassociation of the dissociated ligand by using an acid as phosphine scavenger.[41,42] However, neither of these approaches was successful for efficient metathesis of Napy monomer **1**, as shown in Table 1 (entries 1−5).

According to MALDI-ToF mass spectroscopy, only dimer, trimer, and trace amounts of tetramer of ADMET polymer **2** were formed. Together with the fact that the color of the reaction mixture turned green upon addition of the ruthenium catalyst, these results suggest that the Napy deactivates the ruthenium catalyst by coordinating to the active ruthenium center. A similar observation was described by our group when main-chain supramolecular polymers were prepared by ring-opening metathesis polymerization (ROMP) using a bifunctional Napy chain transfer agent.[33] In order to circumvent coordination of the naphthyridine to the ruthenium catalyst and subsequent catalyst death, a supramolecular protective group strategy analogous to the use of protecting groups in traditional organic chemistry was considered. Such a strategy has been used before in the controlled ring-opening metathesis polymerization (ROMP) of norbornene monomers bearing triple hydrogen-bonding units.[19,43] In these polymerizations succinimide or butylthymine was added as a protecting group to prevent the self-association of adenine[43] and diamidopyridine[19] units, respectively. Here we propose the use of a supramolecular protective group to prevent coordination of the two nitrogen atoms on the naphthyridine ring to the catalyst (Scheme 3).

As a first attempt for a supramolecular protecting group for the naphthyridine moiety, *N*,*N*′-didodecylurea was added (entry 6). With 1.1 equiv of urea present, conversion of the terminal double bond of **1** improved from 20% to 40% (entry 7). Hydrogen bonding of the urea to the naphthyridine which was substantiated by a downfield shift in NH protons of the urea in the $^1$H NMR spectrum, however, was apparently not sufficient to completely prevent coordination of the naphthyridine to the ruthenium. In contrast, when UPy **3** was introduced as a protecting group, conversion was improved dramatically to 70% (entry 8). This strongly suggests efficient protection of the metathesis catalyst by selective formation of the UPy−Napy heterocomplex by complementary quadruple hydrogen bonding, as shown in Scheme 1. A further increase in conversion was obtained when more soluble UPy **4** was used (entry 9). A similar conversion of 80% was found when 1.2 equiv of the more polar triethylene glycol UPy derivative **5** was used (entry 10).

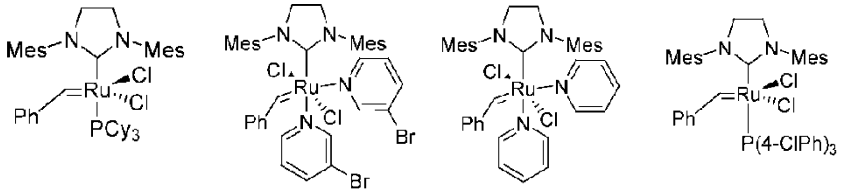
Purification of the crude reaction mixtures **2**−**3**$_n$ or **2**−**4**$_n$ proved to be difficult. More than 80% of UPy **4** could be removed from the supramolecular graft copolymer **2** by gel permeation chromatography using 10% v/v methanol in THF as an eluent. However, because of the poor solubility of **2** in highly polar solvents like methanol, this approach was not successful to obtain pure **2**. Furthermore, the Napy polymer chain itself seemed to aggregate, which renders it even more difficult to remove the protecting group from the polymer. Reaction mixture **2**−**5**$_n$ was substantially easier to purify. Because of the 3-heptyl group on the pyrimidinone ring and the polar triethylene glycol tail, UPy **5** displays a high solubility in a variety of solvents including THF and ethanol.[33] Removal of **5** after ADMET of monomer **1** was successfully performed by precipitation in warm ethanol. Unreacted monomer **1** was removed by trituration in hot ethanol, affording **2** in 59% yield.

**NMR Spectroscopy of ADMET Polymer 2**. The ADMET polymerization reaction of Napy diene **1** was monitored by $^1$H NMR, and conversion was determined by integration of the olefinic signals. Near-quantitative conversion of monomer to polymer is standard in these polymerizations, as few side reactions occur other than a small amount of cycle formation common in all polycondensation reactions.[44] However, olefin isomerization has been reported as a side-reaction with Grubbs' second-generation catalyst.[45]

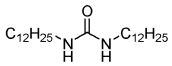
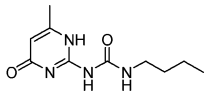
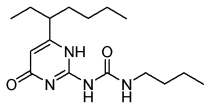
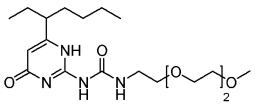
In the present reaction, $^1$H and $^{13}$C NMR analysis revealed the absence of significant amounts of isomerization products. Figure 1 shows a part of the spectrum of ADMET polymer **2** grafted with UPy **5** (left) and pure polymer **2** obtained after removal of **5** (right). The NH signals characteristic of UPy−Napy heterocomplex formation were observed in the downfield region at 13.89, 11.89, 11.36, and 9.90 ppm as well as the NH signals arising from UPy homodimers at 13.32, 11.96, and 10.24 ppm. In addition, a different resonance of the alkylidene proton of the UPy is found for its ADDA tautomer ($\delta$ = 6.01 ppm) compared to its AADD tautomer ($\delta$ = 5.87 ppm).

Unfortunately, polymer **2** is not very soluble in common organic solvents like chloroform, THF, and methanol. This is also evident from its NMR spectrum in chloroform in which considerable broadening of the naphthyridine signals at 8.00 and 8.50 ppm is observed, which indicates the formation of

**Table 1. ADMET of Napy Monomer 1 with Ru Catalysts A−D[a]**

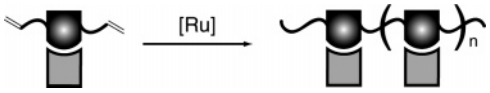


**A** **B** **C** **D**

| entry | catalyst | additive | T (°C) | conv.[b] (%) |
|---|---|---|---|---|
| 1 | **A** | - | 40[c] | <20 |
| 2 | **A** | - | 50 | <20 |
| 3 | **B** | - | 50 | <20 |
| 4 | **C** | - | 50 | <20 |
| 5 | **D** | - | 50 | <20 |
| 6 | **A** | $CH_3COOH$ 2.0 eq | 50 | <20 |
| 7 | **A** |  0.5 eq | 50 | 40 |
| 8 | **A** |  **3** 1.5 eq | 50 | 70 |
| 9 | **A** |  **4** 2.0 eq | 50 | 80 |
| 10 | **A** |  **5** 1.2eq | 50 | 80 |

[a] Reaction conditions: 10% [Ru], 0.2−0.5 M in dry toluene. [b] Conversion of **1** was determined by $^1$H NMR. [c] $CH_2Cl_2$ was used as solvent.

**Scheme 3. Schematic Representation of ADMET Polymerization of a Supramolecularly Protected Monomer**




aggregates. Additionally, the broad signal around 10 ppm attributed to the NH protons is shifted downfield, which probably indicates weak hydrogen bond formation to other naphthyridine units. However, using the terminal $CH_2$ peak at 4.94 ppm and the internal CH signal at 5.31 ppm, an average DP of 12.4 was determined by conventional end-group analysis. Although polymer **2** should be easy to protonate due to the basic nitrogen atoms in the central naphthyridine ring, analysis by MALDI-ToF-MS only showed small oligomers.

**Size Exclusion Chromatography.** Size exclusion chromatography (SEC) has previously been demonstrated to be an effective tool to study the size of supramolecular structures.[46−48] However, important factors for the outcome of the SEC experiments are the dynamics of the assemblies.[49] Although the UPy−Napy heterodimer has a high $K_a$ value and displays slow exchange on the NMR time scale, their exchange is fast on the SEC time scale. This implies that the observed behavior of each dimer (UPy−Napy and $UPy_2$) on the SEC column represents a time average. Furthermore, continuous dissociation and exchange due to dilution during the elution will result in a broadened and tailed retention profile for graft polymer **2**−**4**$_n$. As expected, reliable elution curves could not be obtained by simple injection of supramolecular graft copolymer **2**−**4**$_n$ and ungrafted poly-Napy **2**. This can be explained by the poor solubility of **2** and the fast dynamics of the system.

An alternative methodology similar to gel filtration chromatography was therefore applied to detect the supramolecular graft copolymer by SEC analysis in the presence of UPy in the eluent. This technique has been used to determine association constants of protein−ligand,[50,51] protein−protein,[52] and metal−ligand complexes[53] on Sephadex columns. As in gel filtration chromatography, the SEC column (mixed-D Polymer Labs) was equilibrated with a 0.80 mM UPy **4** solution in chloroform. UV/vis detection was performed at 350 and 270 nm, corresponding to the absorption maximum of Napy in the heterodimer and UPy, respectively. The baseline of the UV/vis detector was adjusted to a 0.8 mM UPy **4** solution. As shown in Figure 2a,

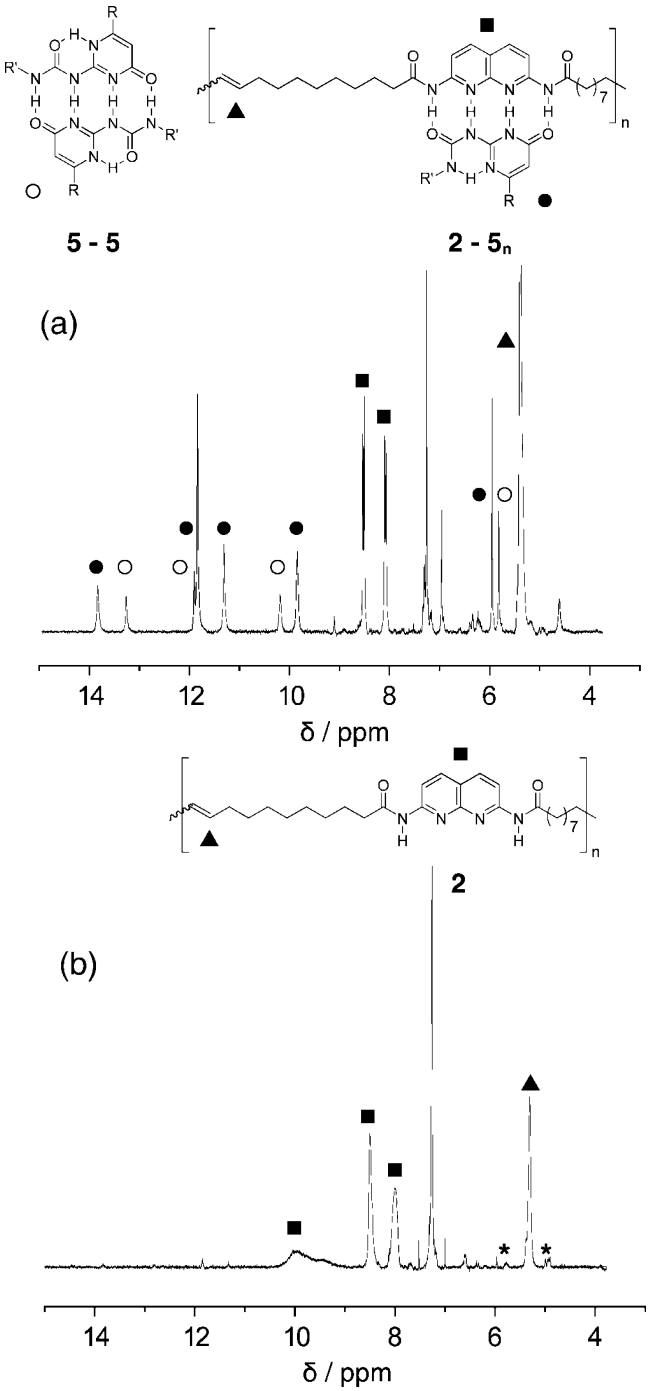



**Figure 1.** (a) $^1$H NMR spectrum in $CDCl_3$ of **2** grafted with UPy **5**. (b) $^1$H NMR spectrum in $CDCl_3$ of pure **2**. Symbols indicate signals from UPy in UPy dimer (Ō), UPy in UPy−Napy heterodimer (●), Napy (■), and the internal olefin (▲). Terminal olefin end groups are indicated with asterisks.

when a chloroform solution of UPy **4** was injected, the dimer was detected as a positive peak at 9.0 min. However, when a solution of toluene in chloroform was injected as a blank sample, a negative peak was observed at 9.0 min due to dilution of UPy in the eluent. The positive peak at higher retention times was attributed to toluene. A good elution curve was obtained for graft copolymer **2**−**4**$_n$ by detection at 350 nm which is selective for 2,7-diamido-1,8-naphthyridines in the complexed form (Figure 2b). When completely deprotected poly-Napy **2** was injected, one positive peak of **2** and one negative peak of UPy were detected at 270 nm (Figure 2c). In this case, a portion of the UPy in solution in which poly-Napy **2** was dissolved became

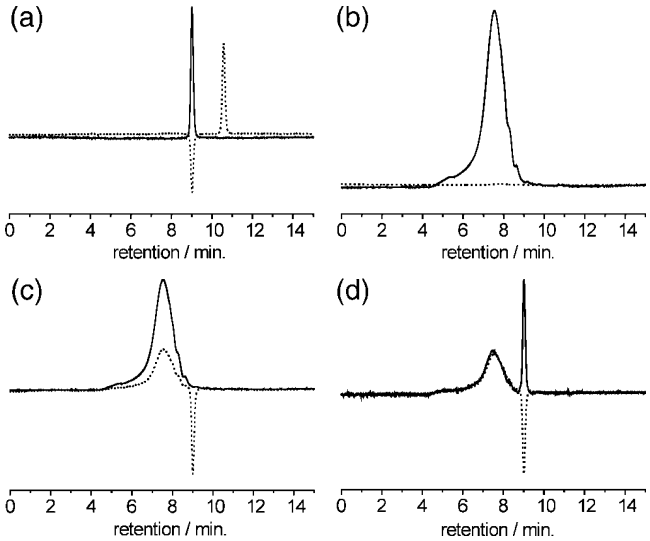
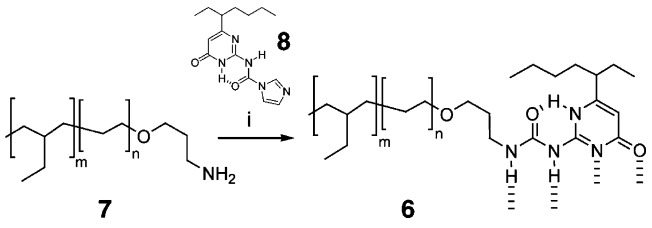



**Figure 2.** SEC elution curves: (a) full line: UPy **4**; dotted line: toluene, detection at 270 nm; (b) full line: poly-Napy·UPy **2**−**4**$_n$; dotted line; UPy **4**, detection at 350 nm; (c) full line: poly-Napy·UPy **2**−**4**$_n$, detection at 350 nm; dotted line; poly-Napy·UPy **2**−**4**$_n$, detection at 270 nm; (d) full line: poly-Napy·UPy **2**−**4**$_n$; dotted line; poly-Napy **2**, detection at 270 nm.

bound to **2**. This portion of UPy, being associated with **2**, moved faster down the column than the UPy that remained unbound. This resulted in the depletion of UPy in the elution profile corresponding to the injected solution. The higher negative peak than the blank experiment, which corresponds to the decrease in UPy concentration, is the summation of the effects of dilution and the capture of UPy **4** from the eluent by the ungrafted poly-Napy **2**. Additionally, the elution curve obtained when poly-Napy **2** was injected together with an excess of UPy **4** to yield the fully substituted supramolecular graft copolymer showed two positive peaks at 7.5 and 9.0 min, attributed to **2**−**4**$_n$ and **4**$_2$, respectively (Figure 2d). The latter peak is due to the increase of the UPy concentration in the injected sample. The retention time of grafted poly-Napy was identical to the ungrafted poly-Napy. This is direct evidence that **2** selectively captures UPy molecules from the eluent and can therefore be detected as a supramolecular graft copolymer. Consequently, the molecular weight of **2**−**4**$_n$ could be determined as $M_n = 7000$, $M_w = 11\,690$, and $M_w/M_n = 1.67$, which corresponds to a number-average DP of 11.1. This value is in fair agreement with the values obtained by $^1$H NMR end-group analysis and complexation analysis described in the previous section.

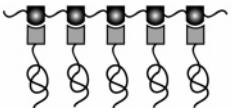
**Supramolecular Grafting.** The dynamic nature of the noncovalent bond is an interesting feature which can be addressed by external stimuli such as polarity of a solvent, temperature, and pH. To demonstrate reversible grafting of UPy derivatives of different size on the poly-Napy main chain of **2**, diffusion-ordered $^1$H NMR spectroscopy (DOSY) measurements were performed on chloroform solutions of various aggregates, using heptakis(2,3,6-tri-*O*-methyl)-*β*-cyclodextrin (CD) as an internal standard. 2D-DOSY NMR measurements have been applied for the characterization of supramolecular aggregates and have provided useful information about the size of these aggregates.[54,55] In order to obtain measurable differences in diffusion behavior compared to UPy derivatives **3, 4**, and **5** PEB−UPy (PEB = poly(ethylenebutylene)) **6** ($M_w \sim 3900$) was used. PEB−UPy **6** was synthesized by UPy end-group modification of amino-functionalized PEB **7** by reaction with an activated imidazolide (Scheme 4). Imidazolide **8** was obtained according to a literature procedure and is used in situ.[56] Amino-

**Scheme 4. Synthesis of PEB−UPy 6**[a]




[a] i: UPy−imidazolide **8**, $CHCl_3$, 16 h, RT, 84%.

**Table 2. Normalized Diffusion Constants of Supramolecular Graft Copolymers with UPy Derivatives 4 or 6**

| Compound | | Normalized diffusion coefficient |
|---|---|---|
| **1** |  | 1.16 |
| **4** |  | 1.38 |
| **6** |  | 0.31 |
| **2** |  | 0.36 |
| **2 – 4$_n$** |  | 0.28 |
| **2 – 6$_n$** |  | 0.17 |

functionalized PEB **7** was prepared via Michael addition of α-hydroxy-PEB to acrylonitrile to the PEB-nitrile and subsequent reduction with 1.0 M $BH_3$ in THF.[57]

As can be seen in Table 2, significant differences in diffusion coefficients could be determined. As expected for small molecules, **1** and **4** displayed high diffusion constants compared to the internal standard (1.16 and 1.38, respectively) while PEB−UPy **6** displays a low diffusion constant of 0.31. In contrast to ungrafted Napy polymer **2** which had a diffusion coefficient of 0.36, graft copolymer **2**−**4**$_n$ had a smaller diffusion coefficient of 0.28. This implies that the hydrodynamic radius is larger for the grafted polymer as expected. Interestingly, when **2** is grafted with polymeric UPy **6**, an even smaller diffusion constant of 0.17 is obtained, indicating efficient grafting of the parent Napy−polymer with large dangling polyethylene−butylene side chains. In this way, reversible immobilization of different UPy derivatives is demonstrated on a supramolecular polymer containing 2,7-diamido-1,8-naphthyridine moieties in the main chain.

## Discussion and Conclusions

In summary, the first supramolecular graft copolymers based on the UPy−Napy heterodimer were successfully synthesized and characterized. The use of a supramolecular protecting group for the α,ω-Napy diene monomer turned out to be a prerequisite for efficient ADMET polymerization and ensures conversions up to 80% of the Napy monomer. In contrast to UPy derivatives with alkyl substituents, the introduction of a triethylene glycol tail on the ureido position ensures increased solubility in polar solvents like ethanol and THF. Therefore, purification of the poly-Napy could be simplified to precipitation and trituration with ethanol. We believe this UPy protecting group approach is a powerful strategy toward constructing macromolecular architectures containing 2,7-diamido-1,8-naphthyridine moieties by a wide range of metathesis reactions. The Napy polymer could be identified using size exclusion chromatography using a UPy solution as the mobile phase. It was shown that functionalization at low concentration of the ungrafted polymer can be achieved in the SEC run. The degree of polymerization determined from SEC measurements was in good agreement with the DP calculated from NMR analysis. This new method based on complementary affinity will open the way for detailed characterization studies of a variety of supramolecular architectures containing either Napy or UPy moieties. Finally, diffusion-ordered NMR experiments revealed a significant decrease in relative diffusion coefficient upon grafting of the Napy polymer with UPy derivatives which indicates a larger hydrodynamic volume of the supramolecular graft copolymers. In conclusion, we believe these results may not only open the way toward new supramolecular polymers bearing quadruple hydrogen bond arrays but also toward the synthesis of materials for reversible immobilization in solution-phase combinatorial chemistry in which Napy-functionalized polymers are used to bind substrates equipped with a UPy group to a solid phase.

## Experimental Section

**General.** All synthetic procedures were performed under an inert atmosphere of dry argon unless stated otherwise. Commercial solvents and reagents were used without purification unless stated otherwise. Toluene was distilled over sodium prior to use. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Varian Gemini 300, Varian Mercury 400, or Varian Inova 500 spectrometer. Chemical shifts are reported in ppm relative to tetramethylsilane (TMS) and multiplicities as singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). Diffusion-ordered 2D NMR measurements were performed using the bipolar pulse pair (BPPSTE) pulse sequence and were evaluated by the Varian DOSY software incorporated in VNMR.[58] Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer with a Universal ATR sampling Accessory. Melting points were determined on a Büchi Melting Point B-540 apparatus.

**Size Exclusion Chromatography.** Analytical SEC analyses were performed on a Shimadzu SEC system including a SPD-10AV UV−vis detector, using a Polymer Laboratories gel 5 μm mixed-D SEC column. A solution of 0.8 mM UPy **4** in $CHCl_3$ was used as eluent at a flow rate of 1.0 mL/min. 270 nm was selected to detect both Napy and UPy derivatives, while 350 nm was selected for the specific detection of the Napy chromophore. Usual sample concentration was 1 mg/mL for single injection of ungrafted polymer **2**, while for the grafted polymer **2**−**4**$_n$ injection, a total concentration of 3 mg/mL with a 1:2 w/w ratio of **2** and **4** was applied. Analysis was based on polystyrene standards.

**Diffusion Ordered 2D NMR** (Table 2). Sample preparation using heptakis(2,3,6-tri-*O*-methyl)-β-cyclodextrin (CD) as internal standard was as follows: Entry 1: 8 mg **1**, 1 mg CD/mL $CDCl_3$; entry 2: 8 mg **4**, 1 mg CD/mL $CDCl_3$; entry 3: 3 mg **2**, 1 mg CD/mL $CDCl_3$ (not dissolved completely); entry 4: 5 mg **2**, 2.36 mg **4**, 1 mg CD/mL $CDCl_3$ (heated at 40 °C to yield a clear solution); entry 5: 8 mg **6**, 1 mg CD/mL $CDCl_3$; entry 6: 5.01 mg **2**, 29.9 mg **6**, 1 mg CD/mL $CDCl_3$ (heated at 40 °C to yield a clear solution).

The diffusion coefficient of the internal standard (CD) was much lower than in previous samples. To minimize the influence of the viscosity to diffusion coefficient (although the diffusion coefficients were normalized), the sample solution was diluted 20 times by $CDCl_3$ in order to make the reference diffusion coefficient similar to the previous samples.

**Synthesis.** 2,7-Bis(10-undecenoylamino)-1,8-naphthyridine (**1**) was synthesized as reported by Ligthart et al.;[36] 2-*n*-butylureido-6-methyl-4[1*H*]-pyrimidinone (**3**) was prepared as reported by Beijer et al.;[59] butylureido-6-(3-hexyl)-4[1*H*]-pyrimidinone (**4**) and UPy−imidazolide (**8**) were prepared according to Keizer et al.;[56] (2-(2-(2-methoxyethoxy)ethoxy)ethyl)-2-ureido-6-(3-heptyl)-4[1*H*]-pyrimidinone (**5**) was synthesized as reported by Scherman et al.;[33] PEB-$NH_2$ (**7**) was synthesized as reported by Hirschberg et al.[57]

**General Procedure of ADMET Polymerization of 2,7-Bis/(10-undecenoylamino)-1,8-naphthyridine** (Table 1). To a 20 mL Schlenk flask charged with 2,7-bis(10-undecenoylamino)-1,8-naphthyridine (**1**) (100 mg, 0.202 mmol) and the additive, 1.00 mL of distilled toluene was added and deoxygenated by a freeze−pump−thaw cycle. After backfilling with argon, the resulting dispersion was stirred at 50 °C until the monomer was completely dissolved. Ruthenium catalyst (**A**−**D**) (25 $\mu$mol) was added to this solution and stirred for 20 h while maintaining the temperature at 50 °C. The solvent was removed by evaporation, and a $^1$H NMR spectrum of the crude mixture was taken.

**Oligo-2,7-bis(9-decenoylamino)-1,8-naphthyridines/ADMET Polymer 2** (Table 1, entry 10). To a 20 mL Schlenk flask charged with 2,7-bis(10-undecenoylamino)-1,8-naphthyridine (**1**) (100 mg, 0.202 mmol) and UPy **5** (120.0 mg, 302 $\mu$mol), 670 $\mu$L of distilled toluene was added and deoxygenated by a freeze−pump−thaw cycle. After backfilling with argon, the resulting dispersion was stirred at 50 °C until the monomer was completely dissolved. Second generation Grubbs' ruthenium catalyst (20.8 mg, 24.5 $\mu$mol) was added to this solution and stirred for 24 h under an inert atmosphere while maintaining the temperature at 50 °C. The solvent was removed by evaporation. The residue was dissolved in a minimum amount of chloroform and precipitated in hot ethanol. The pale-brownish precipitate was collected by filtration. According to the NMR spectrum, conversion of the double bond was 76% and 80% removal of UPy was observed. The precipitate was dispersed in ethanol and heated to reflux temperature for 1 h, followed by filtration. The precipitate was collected on a glass filter and dried in vacuo to yield 56 mg (59%) of the Napy polymer with >95% removal of the UPy as a pale-brownish powder. $^1$H NMR ($CDCl_3$): $\delta$ = 10.0 (br, 2H, NH), 8.50 (2H, Napy), 8.00 (2H, Napy), 5.31 (m, 2H, C═C*H*CH$_2$), 3.70 (m, 4H, NHC*H*$_2$), 2.45 (m, 4H, C═CHC*H*$_2$), 1.93 (m, 4H), 1.66 (m, 4H), 1.55 (m, 4H), 1.26−1.19 (m, 12H) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 172.7, 154.5, 153.6, 139.1, 130.6, 130.1, 125.1, 118.4, 113.8, 37.9, 33.9, 29.5−29.0 (multiple peaks), 25.4 ppm; FT−IR (ATR): $\nu$ = 3321, 3008, 2920, 2850, 1672, 1611, 1579, 1544, 1506, 1468, 1385, 1312, 1287, 1175, 1136, 1118, 968, 851, 802 cm$^{-1}$.

**UPy-Functionalized Poly(ethylenebutylene) (PEB−UPy) 6.** To a solution of PEB-NH$_2$ **7** (6.50 g, 1.67 mmol) in 100 mL of chloroform in a 300 mL round-bottom flask, UPy−imidazolide **8** (1.00 g, 3.30 mmol) was added and stirred for 48 h at 40 °C under a nitrogen atmosphere. The solution was washed twice with 1 N HCl aqueous solution and then brine. After drying over $MgSO_4$, the organic layer was filtered, concentrated by evaporation, and precipitated in methanol twice. After drying in vacuo, the title compound was obtained as a pale-yellowish, highly viscous oil (5.75 g, 84%). $^1$H NMR ($CDCl_3$): $\delta$ = 13.26 (br, 1H, NH), 11.94 (br, 1H, NH), 10.22 (br, 1H, NH), 5.80 (s, 1H, C*H*CO), 3.49 (t, 2H, NHCC*H*$_2$O), 3.43 (t, 2H, C*H*$_2$O), 3.37 (m, 2H, NHC*H*$_2$CH$_2$), 2.29 (m, 1H, CC*H*), 1.91 (m, 2H, NHCH$_2$C*H*$_2$), 1.65−1.00 (m, 510 H, C*H*$_2$), 0.95−0.75 (m, 110 H, C*H*$_3$) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ = 173.1, 156.8, 155.4, 154.9, 106.2, 69.5, 68.3, 45.4, 38.9, 38.4, 37.9, 37.4, 36.7, 36.1, 34.4, 33.5, 33.4, 33.2, 32.9, 30.6, 30.2, 30.0, 29.7, 29.5, 29.3, 27.1, 26.8, 26.6, 26.4, 26.3, 26.1, 26.0 (2), 25.9, 22.5, 19.5, 19.2, 13.9, 11.7, 11.4, 10.9, 10.7, 10.6 (2), 10.4, 10.2 ppm. FT-IR (ATR): $\nu$ = 3148, 3051, 2960, 2912, 2853, 1698, 1648, 1590, 1528, 1461, 1411, 1379, 1255, 1117, 850 cm$^{-1}$.

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