Noncovalently Functionalized Block Copolymers Possessing Both Hydrogen Bonding and Metal Coordination Centers

Kamlesh P. Nair, Joel M. Pollino, and Marcus Weck*

School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400

Received October 13, 2005; Revised Manuscript Received November 27, 2005

ABSTRACT: Block copolymers containing both hydrogen bonding and metal coordination sites have been synthesized by ring-opening metathesis polymerization and subsequently functionalized using noncovalent interactions. The resulting block copolymers can be viewed as "universal polymer backbones", as a wide variety of polymers with varying functionalities can be prepared by altering the noncovalent functionalization strategy of the same polymer backbone. The effect of degree of polymerization, block copolymerization, block copolymer composition, and metal coordination on the hydrogen bonding interaction has been investigated. In general, none of these variables have a profound effect on the strength of the hydrogen bonding interactions along the polymer backbones, suggesting that the metal coordination and hydrogen bonding are orthogonal to each other in block copolymers. Finally, the effect of the noncovalent functionalization on the thermal properties of the polymers was investigated. We found that the noncovalent functionalization of all copolymers via hydrogen bonding and/or metal coordination reduced the glass-transition temperature and the thermal stability of all copolymers.

Introduction

The emerging area of functional materials for advanced applications will require both a high degree of functionalization and a high degree of control over the molecular architecture.[1] Examples include highly functionalized polymers for a wide variety of applications ranging from biomedical materials such as polymers for drug delivery to electrooptical materials.[2] Other polymeric materials with a high degree of control over their molecular architecture are used in applications such as thermoplastic elastomers and nanoscale lithography.[3] One major class of materials that has the potential to fulfill both of these characteristics, functionalization and architectural control, are block copolymers.[4] Block copolymers have the unique advantage that their properties can be easily tailored through several variables such as the choice of comonomers and the individual block lengths. Despite these advantages, the synthetic complexity of densely functionalized block copolymers that combine multifunctionalization and controlled block copolymer architecture makes them extremely rare. To efficiently synthesize such materials, one would need a polymerization route that is highly controlled and functional group tolerant, coupled with a fast and easy functionalization strategy. In this contribution we present such a system by combining block copolymer formation using ring-opening metathesis polymerization (ROMP) coupled with a noncovalent functionalization technique using self-assembly.

Ring-opening metathesis polymerization is well suited for this application, as it is a highly functional group tolerant polymerization technique that can synthesize polymers with controlled architectures.[5−7] Prior to this contribution, ROMP has been used to synthesize highly functionalized di- and triblock copolymers in a fast and efficient manner.[8−11] However, all of these examples are based on covalent functionalization strategies. Although highly successful, covalent polymer functionalization strategies are usually time-consuming and tedious. Furthermore, easy materials optimization, i.e., the modular exchange of functional groups along a polymeric material to optimize its properties that can be viewed as a rapid prototyping process, is not possible with current covalent chemistry strategies. Each covalent optimization step requires the synthesis of new monomers, and their polymerization kinetics and physical characteristics have to be studied in detail. A strategy that has been suggested in the literature to overcome this limitation is the use of noncovalent chemistry for the functionalization step, i.e., the use of supramolecular polymer chemistry.[12,13]

In supramolecular polymer science, a wide variety of recognition motifs have been employed, including metal coordination,[14−19] ionic interactions,[20] and hydrogen bonding.[21−24] In particular, the introduction of nucleic acid residues that are able to self-assemble via hydrogen bonding in polymeric systems has been studied extensively.[25,26] For example, polymers such as poly(norbornene)s,[27,28] poly(styrene)s,[29] and poly(acrylate)s[30] have been functionalized with thymine, and their self-assembly behavior with adenine or 2,6-diaminopyridine moieties has been studied in detail.[31,32] The resulting polymers have been used in the synthesis of cross-linked polymer spheres with functionalized surfaces,[33] nucleobase telechelic liquid-crystalline polymers,[34] and vesicles.[29] In this work, we utilize substituted 2,6-diaminopyridines and their complementary recognition units, substituted thymines, as hydrogen bonding moieties.

The second class of noncovalent interactions that have been employed extensively in the literature is metal coordination.[14,17] The main reasons for the use of metal coordination complexes in polymer science is their highly controlled synthesis, strong noncovalent bond strength, and the potential application of metal-containing polymers in areas such as supported catalysis,[35] light-emitting diodes,[36] and chemically responsive gels.[15]

While there have been extensive studies on the utilization of these noncovalent interactions in supramolecular polymer systems, reports that utilize more than one noncovalent interaction in polymers are scarce, with only a handful of contributions reported to date.[16,37−42] Furthermore, the combination of self-assembly with highly controlled polymerization techniques and complex polymeric architectures such as block copolymers has not been accomplished. Most literature reports employ random copolymers that have the advantage of being highly soluble and,

* Corresponding author. E-mail: marcus.weck@chemistry.gatech.edu.

10.1021/ma052222t CCC: $33.50
Published on Web 01/13/2006

in most cases, do not undergo phase separation. The employment of block copolymers in multistep self-assembly is significantly more challenging due to these solubility and phase separation issues. In this contribution, we report the first example of the synthesis and subsequent fast and facile noncovalent functionalization of block copolymers having well-defined architectures by using multiple noncovalent interactions, i.e., hydrogen bonding and metal coordination motifs, as noncovalent recognition sites. Our strategy demonstrates the straightforward synthesis of highly functionalized polymeric materials with a high degree of control over their molecular architecture by combining functional group tolerant polymerization technique, such as ROMP and noncovalent chemistry, using self-assembly.

Experimental Section

General. All reagents were purchased either from Acros Organics, Aldrich, or Strem Chemicals and used without further purification unless otherwise noted. Dimethylformamide (DMF) and deuterated chloroform ($CDCl_3$) were distilled over calcium hydride. Grubbs' first-generation catalyst was purified by filtration using purified benzene under an atmosphere of argon. *N*-(6-Propionylamino-pyridin-2-yl)-propionamide,[43] *N*-butylthymine,[44] isomerically pure *exo*-norbornene acid,[45] 12-hydroxydodecanitrile,[47] 5-octyloxyisophthalic acid dimethyl ester,[53] and monomers **2**,[45] **3**,[45] **4**,[46] and **5**[16] were synthesized according to published procedures. ^{1}H NMR and ^{13}C NMR spectra (300 MHz ^{1}H NMR, 75 MHz ^{13}C NMR) were taken using a Varian Mercury Vx 300 spectrometer. All spectra are referenced to residual proton solvent. Abbreviations used include singlet (s), broad singlet (bs), doublet (d), triplet (t), quartet (q), and unresolved multiplet (m). Mass spectral analyses were provided by the Georgia Tech Mass Spectrometry Facility on a VG-70se spectrometer using electron impact ionization (EI). Self-CI denotes self-chemical ionization. Elemental analyses were performed by Atlantic Microlabs, Norcross, GA. Gel-permeation chromatography (GPC) analyses were carried out using a Shimadzu pump, a Shimadzu UV detector with tetrahydrofuran (THF) or dichloromethane as the eluant, and a set of American Polymer Standards columns (100, 1000, 100 000 Å linear mixed bed). The flow rate used for all the measurements was 1 mL/min. All GPC measurements were calibrated using poly(styrene) standards and were carried out at room temperature. M_w, M_n, and PDI represent weight-average molecular weight, number-average molecular weight, and the polydispersity index, respectively. The glass-transition temperature of the polymers (T_g) was measured by differential scanning calorimetry (DSC). The DSC analyses were performed under an atmosphere of nitrogen using a Mettler Toledo DSC 822e that was calibrated using indium standards. The temperature program provided two heating and cooling cycles between −100 and 100 °C at 10 °C/min, with the sample size ranging from 5 to 9 mg. The onset of thermal degradation for the polymers (T_{deg}) was measured by thermal gravimetric analysis (TGA) using the intersection of the tangents to the baseline and the TGA curve. The TGA analyses were performed under an atmosphere of nitrogen using a Shimadzu TGA-50, and all samples were heated from 25 to 450 °C at a rate of 10 °C/min.

***exo*-Bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid 11-Cyanoundecyl Ester (1).** *exo*-Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (4.4 g, 0.021 mol) and 12-hydroxydodecanenitrile (**10**)[47] (4.16 g, 0.021 mol) were dissolved and stirred in anhydrous dichloromethane (100 mL). Dicyclohexyldicarbondiimide (DCC) (4.4 g, 0.021 mol) and a catalytic amount (20 mg) of 4-(dimethylamino)pyridine (DMAP) were added at room temperature. Immediately a white precipitate was formed. The mixture was refluxed for 12 h, after which it was cooled and filtered. The solution was then concentrated and purified by column chromatography (SiO_2, eluant: dichloromethane) and dried on high vacuum to yield **1** as a colorless liquid (5 g, 75%). ^{1}H NMR ($CDCl_3$): δ = 6.09 (m, 2H, −CH=CH−), 4.06 (t, 2H, J = 6.67 Hz, $-COOCH_2-$), 3.00 (s, 1H, norbornene signal), 2.88 (s, 1H, norbornene signal), 2.31 (2H, t, J = 7.08 Hz, $-CH_2-CN$), 2.17 (m, 1H, norbornene signal), 1.90 (m, 1H, norbornene signal), 1.67−1.55 (m, 4H, $-(CH_2)_2-$), 1.51−1.25 (m, 14H, $-(CH_2)_7-$). ^{13}C NMR ($CDCl_3$): δ = 176.1, 138.0, 135.8, 119.2, 64.6, 46.8, 46.5, 43.4, 41.8, 30.55, 29.6, 29.6, 29.5, 29.4, 29.0, 28.9, 28.9, 26.2, 25.6, 17.3. HRMS (self-CI) m/z (100%) = 318.2393 (M^+, calcd 318.2348). Anal. Calcd for $C_{20}H_{31}NO_2$: C, 75.67; H, 9.84. Found: C, 75.49; H, 9.93.

(3-Hydroxymethyl-5-octyloxyphenyl)methanol (12). 5-Octyloxyisophthalic acid dimethyl ester[53] (**11**) (7.1 g, 0.022 mol) was dissolved in anhydrous THF and added to a suspension of $LiAlH_4$ (1.66 g, 0.044 mol) in THF at 0 °C. The reaction was stirred at room temperature for 12 h, after which the THF was removed under reduced pressure. The residue was carefully acidified by adding 1 N HCl dropwise at 0 °C to dissolve the $LiAlH_4$. The solution was then extracted with dichloromethane (3 × 200 mL), the organic extracts were dried with $MgSO_4$, and the solvent was removed under reduced pressure to yield a white solid (6.00 g, 86%). ^{1}H NMR ($CDCl_3$): δ = 6.91 (s, 1H, ArH), 6.83 (s, 2H, ArH), 4.64 (s, 4H, $-CH_2OH$), 3.94 (t, 2H, J = 6.38 Hz, $-OCH_2-$), 1.93 (broad, 2H, −OH), 1.75 (m, 2H, $-OCH_2CH_2-$), 1.44−1.29 (m, 8H, $-(CH_2)_4-$), 0.87 (distorted t, 3H, J = 6.8 Hz, $-CH_3$). ^{13}C NMR ($CDCl_3$): δ = 159.3, 142.8, 117.6, 112.1, 68.3, 64.9, 64.8, 32.0, 29.7, 29.6, 26.4, 23.0, 14.5. MS (EI) m/z (100%) = 266.18 (M^+, calcd 266.19). Anal. Calcd for $C_{16}H_{26}O_3$: C, 72.14; H, 9.84. Found: C, 72.17; H, 9.86.

1,3-Bis(chloromethyl)-5-octyloxybenzene (13). Compound **12** (4.99 g, 0.019 mol) and triethylamine (5.68 g, 0.056 mol) were dissolved in 100 mL of anhydrous dichloromethane and cooled to 0 °C. Methane sulfonyl chloride (6.43 g, 0.056 mol) was added dropwise over a period of 1 h. After complete addition, the reaction mixture was gradually heated to 38 °C for 12 h. The reaction mixture was then washed with 1 N NaOH (50 mL), 1 N HCl (50 mL), and water (100 mL) and finally dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was purified by column chromatography (SiO_2, eluant: hexanes−dichloromethane 3/2, v/v) to yield a colorless liquid (3.94 g, 70%). ^{1}H NMR ($CDCl_3$): δ = 6.98 (s, 1H, ArH), 6.89 (s, 1H, ArH), 4.54 (s, 4H, $-CH_2Cl$), 3.94 (t, 2H, J = 6.50 Hz, $-OCH_2-$), 1.80 (p, 2H, J = 6.64 Hz, $-OCH_2CH_2-$), 1.48−1.34 (m, 10H, $-(CH_2)_5-$), 0.92 (distorted t, 3H, $-CH_3$). ^{13}C NMR ($CDCl_3$): δ = 159.7, 139.4, 120.8, 114.8, 68.4, 46.2, 32.2, 29.7, 29.6, 29.5, 26.4, 23.0, 14.5. MS (EI) m/z (100%) = 302.12 (M^+, calcd 302.12). Anal. Calcd for $C_{16}H_{24}Cl_2O$: C, 63.37; H, 7.98. Found: C, 63.72; H, 8.00.

1,3-Bis[(phenylsulfanyl)methyl]-5-octyloxybenzene (14). Sodium thiophenolate (7.10 g, 0.051 mol) was dissolved in anhydrous THF (100 mL), and dichloride **13** (3.94 g, 0.012 mol) was added dropwise to the reaction mixture at room temperature. The mixture was then heated at 50 °C for 12 h, after which the solvent was removed under reduced pressure, and the crude mixture was redissolved in dichloromethane (200 mL). The solution was then washed with brine (100 mL), 2 N NaOH (100 mL), and water (100 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude mixture was purified by column chromatography (SiO_2, eluant: hexanes−dichloromethane 7/3, v/v) to yield the product as a colorless liquid (3.94 g, 70%). ^{1}H NMR ($CDCl_3$): δ = 7.30−7.15 (m, 10H, $-SC_6H_5$), 6.85 (s, 1H, ArH), 6.70 (s, 2H, ArH), 4.03 (s, 4H, $-SCH_2-$), 3.84 (t, 2H, J = 6.57 Hz, $-OCH_2-$), 1.72 (m, 2H, $-OCH_2CH_2-$), 1.43−1.29 (m, 10H, $-(CH_2)_5-$), 0.89 (distorted t, 3H, J = 7.10 Hz, $-CH_3$). ^{13}C NMR ($CDCl_3$): δ = 159.8, 139.4, 137.2, 129.4, 127.7, 127.4, 120.8, 114.9, 68.5, 46.2, 32.2, 29.8, 29.7, 29.6, 26.4, 23.1, 14.6. MS (EI) m/z (100%) = 450.20 (M^+, calcd 450.21). Anal. Calcd for $C_{28}H_{34}OS_2$: C, 74.62; H, 7.60. Found: C, 74.64; H, 7.69.

Pd−Cl 1,3-Bis[(phenylsulfanyl)methyl]-5-octyloxybenzene (8). Compound **14** (400 mg, 0.89 mmol) was dissolved in a mixture of dichloromethane (5 mL) and acetonitrile (10 mL) and placed under an atmosphere of argon. $Pd[(C_6H_5CN)_2Cl_2]$ (340 mg, 0.89 mmol) was added to the stirred solution. The resulting orange solution was stirred for 30 min, after which $AgBF_4$ (425 mg, 2.19 mmol) was added in one portion. Immediately, the orange solution became

pale yellow due to the formation of silver chloride, and the solution was stirred for 30 min under argon. The reaction mixture was then diluted with dichloromethane (250 mL), and the solution was poured into a saturated aqueous solution of NaCl and stirred vigorously for 8 h. The organic layer was separated and dried over $MgSO_4$, and the solvent was removed under reduced pressure. Purification by column chromatography (SiO_2, eluant: dichloromethane−methanol 99/1, v/v) gave **8** as a yellow solid (400 mg, 77%). ^{1}H NMR (CD_2Cl_2): δ = 7.80 (m, 4H, $-SC_6H_5$), 7.43 (m, 6H, $-SC_6H_5$), 6.61 (s, 2H, ArH), 4.59 (bs, 4H, $-SCH_2-$), 3.85 (m, 2H, $-OCH_2-$), 1.74 (m, 2H, $-OCH_2CH_2-$), 1.45−1.30 (m, 10H, $-(CH_2)_5-$), 0.88 (m, 3H, $-CH_3$). ^{13}C NMR ($CDCl_3$): δ = 220.2, 157.2, 150.3, 132.6, 131.6, 129.9, 129.8, 109.0, 68.3, 51.9, 32.0, 29.5, 29.4, 29.4, 26.2, 22.8, 14.3. HRMS (EI) *m/z* (97.12%) = 590.06 (M^+, calcd 590.05). Anal. Calcd for $C_{28}H_{33}ClOPdS_2$: C, 57.96; H, 6.32. Found: C, 57.68; H, 5.75.

Polymerizations. The monomers were dissolved in an appropriate volume of dry distilled deuterated chloroform. The calculated amount of a stock solution of Grubbs' first generation catalyst in chloroform was added in one portion. The reaction mixture was stirred at room temperature and monitored by ^{1}H NMR spectroscopy. Upon complete polymerization, a drop of ethyl vinyl ether was added to terminate the polymerization.

Representative example of the synthesis of **Poly-1**: Monomer **1** (30 mg, 0.0944 mmol) was dissolved in 1 mL of dry distilled deuterated chloroform. A stock solution of Grubbs' first generation catalyst was prepared in dry distilled deuterated chloroform, and an amount of the stock solution equaling 3.09 mg (0.0037 mmol) of Grubbs' first generation catalyst was added to the monomer solution. The solution was stirred, and the reaction was monitored by observing the olefinic signals of the monomer by ^{1}H NMR spectroscopy. Upon complete conversion a drop of ethyl vinyl ether was added to terminate the polymerization.

Copolymers were synthesized by sequential polymerizations, in which the second monomer was added upon complete conversion of the first monomer. Representative example of the synthesis of **UPB-A**: Monomer **1** (30 mg, 0.0944 mmol) was dissolved in 0.5 mL of dry distilled deuterated chloroform. A stock solution of Grubbs' first generation catalyst was prepared in dry distilled deuterated chloroform, and an amount of the stock solution equaling 3.09 mg (0.0037 mmol) of Grubbs' first generation catalyst was added to the monomer solution. The solution was stirred, and the reaction was monitored by observing the olefinic signals of the monomer by ^{1}H NMR spectroscopy. Upon complete conversion of monomer **1**, a solution of monomer **2** (49.9 mg, 0.0944 mmol) in chloroform (1 mL) was added and the reaction mixture was stirred. Upon complete conversion of the second monomer a drop of ethyl vinyl ether was added to terminate the polymerization. Purification of all polymers was performed by precipitating the polymers from ice-cold methanol and repeated washings with ice-cold methanol and ice-cold hexanes, followed by prolonged drying at room temperature under high vacuum.

Poly-1. ^{1}H NMR ($CDCl_3$): δ = 5.34−5.18 (m, 2H, CH=CH), 4.01 (t, 2H, J = 6.18 Hz, $-COOCH_2-$), 2.68 (br m, 2H), 2.48 (br m, 2H), 2.31 (t, 2H, J = 7.08 Hz, $-CH_2-CN$), 2.02−1.91 (br m, 2H), 1.60 (br m, 5H), 1.41 (br m, 2H), 1.25 (br s, 14H). ^{13}C NMR ($CDCl_3$): δ = 176.1, 134−131, 120.0, 64.7, 50−49, 47.8, 43.2, 42.1, 41.3, 37.2, 36.4, 29.5, 28.9, 29.1, 25.5.

UPB-A. ^{1}H NMR ($CDCl_3$): δ = 8.19 (s, 2H, −NH−), 7.49 (s, 2H, Pyr_H), 5.32−5.17 (br m, 4H, −CH=CH−), 4.1 (br s, 4H, $-COOCH_2-$), 3.99 (br m, 2H, $-OCH_2-$), 2.64 (br m, 4H), 2.47 (br m, 4H, $-COOCH_2CH_3$), 2.34 (t, 2H, J = 7.1 Hz, $-CH_2-CN$), 2.16 (s, 2H), 2.01−1.9 (br m, 4H), 1.67−1.57 (br m, 8 H), 1.24−1.1 (br m, 16H, alkyl chains). ^{13}C NMR ($CDCl_3$): δ = 176.3, 172.9, 150.4, 133.9, 131.5, 120.1, 96.2, 69.7, 68.6, 64.7, 50.4, 49.7, 47.8, 42.1, 41.2, 37.1, 36.4, 35.0, 32.0, 30.8, 29.7, 29.5, 29.0, 28.8, 26.0, 25.5, 17.3, 9.5.

UPB-B. ^{1}H NMR (CD_2Cl_2): δ = 8.10 (s, 2H, −NH−), 7.80 (br m, 4H, $-SC_6H_5$), 7.49 (br s, 2H, Pyr_H), 7.33 (br m, 6H, $-SC_6H_5$), 6.54 (s, 2H, ArH), 5.32−5.16 (br m, 4H, CH=CH), 4.50 (br s, 4H, $-SCH_2-$), 4.00 (br m, 6H, $-COOCH_2-$), 3.82 (t, 4H, J = 6.22 Hz, $-OCH_2-$), 2.63 (br m, 4H), 2.44 (br m, 4H), 2.36 (br m, 4H, $-COOCH_2CH_3$), 2.16 (br s, 2H), 2.02−1.91 (br m, 4H), 1.69 (br m, 4H), 1.56 (br m, 4H), 1.24−1.16 (br m, 34H, alkyl chains). ^{13}C NMR ($CDCl_3$): δ = 176.5, 172.9, 169.2, 157.2, 151.6, 150.8, 150.3, 132.6, 131.5, 129.9, 109.0, 96.2, 69.7, 68.6, 64.7, 54.0, 51.0, 32.0, 30.8, 29.7, 29.4, 28.9, 26.0.

UPB-C. ^{1}H NMR (CD_2Cl_2): δ = 9.2 (s, 1H, −NH−), 6.14 (s, 1H, thymine proton), 5.03 (br s, 4H, −CH=CH−), 4.33 (br m, 4H, $-COOCH_2-$), 4.12 (br m, 2H, $-CH_2-N$), 2.92 (br m, 4H), 1.63−1.46 (br m, 11H), 1.27 (t, 2H, J = 7.00 Hz), 0.94−0.23 (br m, 16H, alkyl chains). ^{13}C NMR ($CDCl_3$): δ = 178.4, 167.6, 154.7, 144.0, 139.4, 137.36, 136.5−135.2, 131.9, 122.9, 112.9, 67.7, 53.2, 51.2, 48.6, 46.0, 45.4, 44.9, 40.0, 33.4, 32.8, 30.3, 29.8, 29.3, 20.0.

UPB-D. ^{1}H NMR (CD_2Cl_2): δ = 10.13 (s, 1H, −NH−), 7.83 (br m, 4H, $-SC_6H_5$), 7.39 (br m, 6H, $-SC_6H_5$), 7.04 (br m, 2H, ArH), 6.57 (br s, 1H, thymine proton), 5.37−5.2 (br m, 4H, −CH=CH−), 4.57 (br s, 4H, $-SCH_2-$), 4.01 (br m, 4H, $-COOCH_2-$), 3.85 (br m, 2H, $-OCH_2-$), 3.67 (t, 2H, J = 7.08 Hz, $-CH_2-N$), 2.67−2.48 (br m, 2H), 1.88 (br m, 4H), 1.63−1.57 (br m, 5H), 1.27 (br m, 20H, alkyl chains). ^{13}C NMR (CD_2Cl_2): δ = 177.7, 166.9, 159.1, 153.6, 152.2, 142.8, 134−131, 112.2, 110.9, 70.2, 66.4, 50.5, 44.2, 38.3, 31.7, 30.8, 28.5, 14.1.

Self-Assembly Experiments. *Hydrogen Bonding*. The polymers (100 mg) were dissolved in dry dichloromethane (5 mL) until a homogeneous solution was obtained. Then, the calculated amount of the hydrogen bonding recognition unit dissolved in dry dichloromethane (2−3 mL) was added in one portion, and the solution was stirred for 30 min, after which the solvent was removed under reduced pressure to yield the hydrogen-bonded polymer. Representative example of the synthesis of **Poly-2(SA)**: **Poly-2** (50 mg, 0.095 mmol of 2,6-diaminopyridine functional groups) was dissolved in 5 mL of dry distilled dichloromethane. Then 17.27 mg (0.095 mmol) of **7** was added, and the solution was stirred for 30 min. The solvent was then evaporated, and the self-assembled polymer was dried under high vacuum.

Metal Coordination. The polymers were dissolved in dry dichloromethane (5 mL) until a homogeneous solution was obtained. Then the calculated amount of **8**−**9**, dissolved in dry dichloromethane (2−3 mL), was added. The reaction mixture was stirred and $AgBF_4$(aq) was added, whereas for the pincer-based polymers, an equivolume solution (0.02 mL) of nitromethane and acetonitrile was used to dissolve the $AgBF_4$. After 1 min, the solution turned green and AgCl precipitated. The solution was then allowed to stir for 1 h. The reaction mixture was filtered through Celite, and then the solvent was removed under reduced pressure to yield the metal coordinated polymers as light green solids. Representative example of the synthesis of **Poly-1(SA)**: **Poly-1** (22.5 mg, 0.071 mmol of nitrile functional groups) was dissolved in 5 mL of dry distilled dichloromethane. Then, 41.92 mg (0.071 mmol) of **8** was added, and the reaction mixture was stirred. An aqueous stock solution of $AgBF_4$ was prepared, and a calculated amount of $AgBF_4$ (27.46 mg, 0.14 mmol) was added to the solution. The mixture was stirred for 1 h, during which silver chloride precipitated and the solution turned pale green. The solution was then filtered through a short plug of Celite to remove the precipitated silver salts. The solution was then dried under high vacuum to yield the self-assembled polymer.

Titration Experiments. Association constants were measured by ^{1}H NMR titration at room temperature of a 0.005 M solution of the polymer (based on the hydrogen bonding moieties) in $CDCl_3$ with a 0.01 M solution of the corresponding receptor moiety. The chemical shifts of the amide protons for the 2,6-diaminopyridines and the imide protons of the substituted thymines were monitored. The ^{1}H NMR data were evaluated by ChemEquili software to calculate the association constants.[48] The errors ranged from 10 to 15%.

Research Design. Multifunctional diblock copolymers having both hydrogen bonding and metal coordination sites are the basis of our research design. These polymers can be viewed as the development of the "universal polymer backbones" concept since a family of different functionalized polymeric materials can be

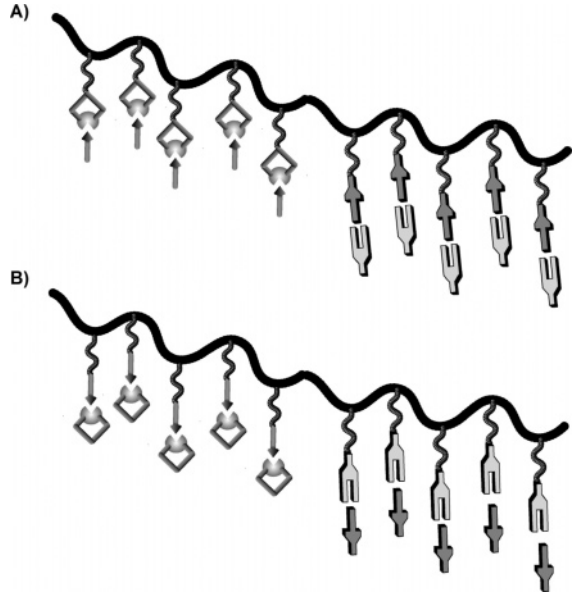


Figure 1. A depiction of block copolymers functionalized by complementary sets of recognition units based on hydrogen bonding and metal coordination: (A) block copolymer containing "polymeric" metal complexes; (B) block copolymer containing "polymeric" ligands.

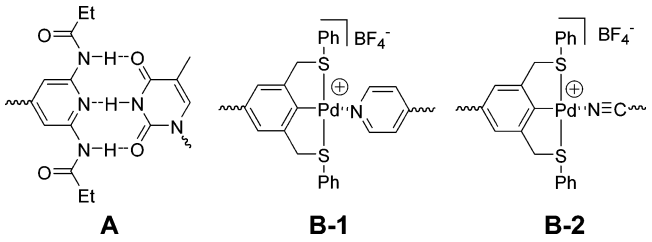


Figure 2. Self-assembly motifs employed in this study: (**A**) three-point hydrogen bonded complex between 2,6-diaminopyridine and thymine; (**B**) metal coordination complexes of palladated SCS pincer system with pyridines (**B-1**) and nitriles (**B-2**).

obtained from a single polymer backbone by varying the self-assembled functional groups.[12] These polymer backbones are based on monomers that are comprised of three basic structural elements: a norbornene monomer that can be polymerized using ROMP, a long C-11 alkyl spacer to improve solubility, and finally the recognition unit itself. During the course of this study, 100% isomerically pure *exo*-norbornene acid derivatives were used as precursor for the synthesis of all monomers. Isomerically pure *exo*-norbornenes have been shown to polymerize in a highly controlled fashion using the first generation Grubbs' catalyst, making *exo*-norbornenes the monomers of choice.[45] Four recognition units have been covalently linked to the monomers that are based either on DAD−ADA three hydrogen bonding arrays or on palladium-based metal coordination motifs.

Three-point hydrogen bonding DAD−ADA arrays are the most studied hydrogen bonding receptor systems to date.[43,49] In this work the DAD−ADA arrays are composed of functionalized 2,6-diaminopyridines (DAD) and thymines (ADA) by using two sets of complementary units, as shown in Figure 2A. The first set involves anchoring the 2,6-diaminopyridine recognition unit as the side-chain functionality onto the monomer with *N*-butylthymine being the complementary recognition unit while the second set utilizes a thymine recognition unit covalently linked to the monomer with 2,6-diaminopyridine being used as the complementary recognition unit.

Palladated sulfur−carbon−sulfur (SCS) pincer complexes are an important class in coordination chemistry and are widely used in catalysis[35,50] and functional materials.[51] These complexes consist of the tridentate pincer ligand and have a square-planar coordination sphere with only one chemically accessible coordination site for self-assembly with a monodentate ligand such as a nitrile or a pyridine (Figure 2B).[52] In this study, the coordination of palladated SCS pincer systems with either nitriles or pyridines using again two sets of complementary units is utilized. The first set involves anchoring the palladated SCS pincer ligand as side-chain functionality onto the monomer with pyridine or functional nitriles as complementary ligands. The second set is based on a nitrile-functionalized monomer that can be viewed, after polymerization, as a "polymeric" ligand. This polymeric ligand can then be functionalized by coordination of a palladated pincer center as the complementary coordination system. Figure 3 outlines the monomers and recognition units employed in this study.

Results and Discussion

Synthesis of Monomers and Recognition Units. Monomer **1** was synthesized as outlined in Scheme 1 by converting 11-bromoundecan-1-ol to its corresponding nitrile derivative, **10**,[47] followed by esterification of **10** with the *exo*-norbornene acid.

The ether-functionalized Pd−pincer compound **8** was synthesized as outlined in Scheme 2. The starting compound, 5-octyloxyisophthalic acid dimethyl ester, was synthesized

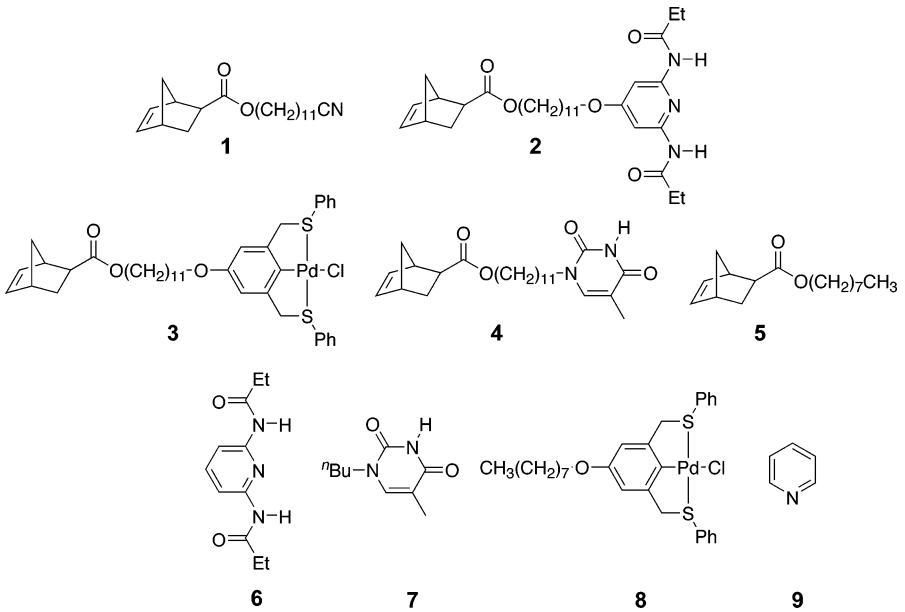
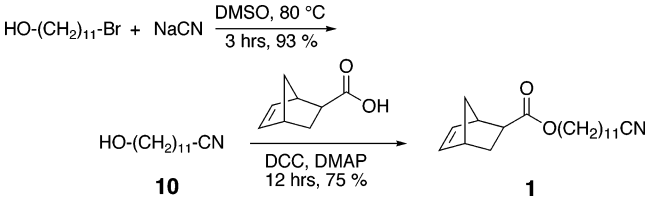


Figure 3. Monomers **1**−**5** and recognition units **6**−**9** utilized in this study.

Scheme 1. Synthesis of Monomer 1



according to literature procedures[53] and was reduced with lithium aluminum hydride to yield the corresponding diol (**12**). The diol was then converted to the dichloride using methanesulfonyl chloride, and the dichloride was coupled with an excess of sodium thiophenolate resulting in the formation of **14**, which on cyclopalladation with $Pd[PhCN]_2Cl_2$ and further workup yielded the ether-functionalized palladated pincer recognition unit, **8**.

Homopolymerization Studies. All polymerizations were carried out using Grubbs' first generation catalyst in chloroform at room temperature.[37,45,54] The polymerizations were monitored by ^{1}H NMR spectroscopy. Upon complete conversion, a drop of ethyl vinyl ether was added to terminate the polymerization. While the living polymerization of monomers **2**−**4** has been proven before,[45] **1** is a new monomer, and its living character, a prerequisite for the formation of block copolymers, had to be established.

Complete monomer conversion of **1** occurred in less than 3 h depending upon the monomer-to-initiator ratios. This clearly indicates that Grubbs' first generation catalyst is compatible with the terminal nitrile group. This result was surprising since nitriles act as ligands for the ruthenium metal center of the catalyst, thereby preventing polymerization of nitrile-containing monomers.[55−58] However, monomers containing nitrile groups have been polymerized by ROMP before using tungsten initiators giving some precedent to our observation.[57] The favorable polymerization behavior of **1** using Grubbs' first generation catalyst might be related to the fact that 100% isomerically pure *exo*-monomer was used since *exo*-norbornene monomers have faster polymerization kinetics than their *endo* isomers.[45] To investigate the living nature of the polymerization, a series of polymerizations with variable monomer to initiator (M/I) ratios were carried out, and the resulting molecular weights were plotted against the M/I ratios. Figure 4A shows a linear relationship between the M/I ratio and the molecular weights, indicating a controlled polymerization. Furthermore, the PDI depended upon the molecular weight of the polymers: at lower molecular weights the PDIs were higher with values being around 1.7, whereas the PDI decreased from 1.7 to 1.5 for the high molecular weight polymers, suggesting a slower rate of initiation compared to the rate of propagation. Nevertheless, full initiation was observed within 120 s indicated by a complete shift of the carbene signal of the catalyst in the ^{1}H NMR spectrum from 19.1 ppm before addition of the monomer to 18.0 ppm after complete initiation. No signal corresponding to the uninitiated catalyst was observed.

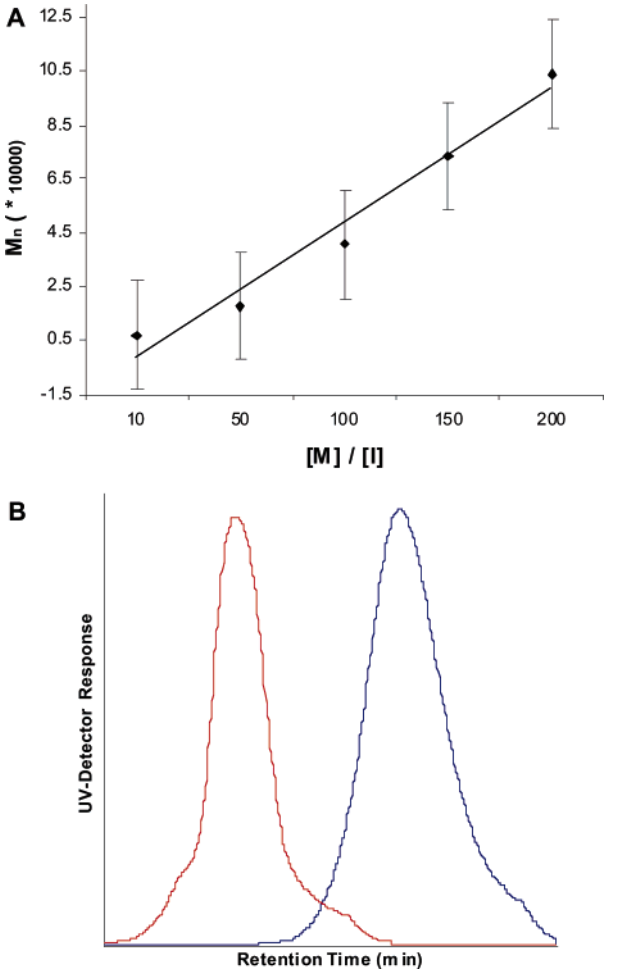
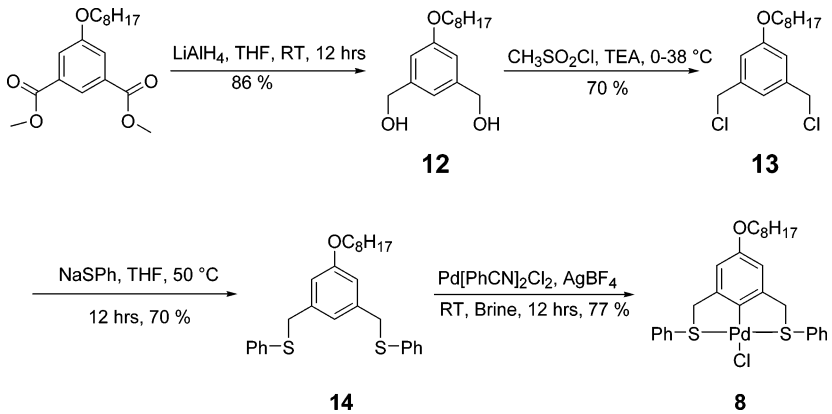


Figure 4. Controlled polymerization of **1**. (A) Plot of M_n vs the monomer-to-catalyst ([M]:[I]) ratios. The error bars represent a 5% standard error in the measurements. (B) GPC chromatographs of the block copolymer test of **1**: (blue —) homopolymer after complete conversion ([M]:[I] = 20:1, M_w = 20 800, M_n = 11 700, PDI = 1.8), (red —) the same polymer after the addition of 350 equiv of monomer **5** ([M_2]:[M_1] = 350:1, [M];[I] = 20, M_w = 346 000, M_n = 254 100, PDI = 1.4).

The living nature of the polymerization was unequivocally confirmed by a block copolymerization test. First, 20 equiv of

Scheme 2. Synthesis of the Ether-Functionalized Pd Pincer Recognition Unit 8



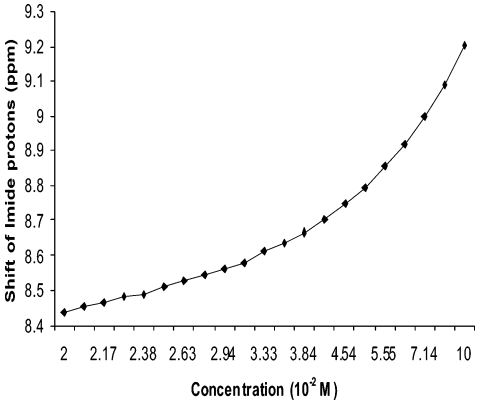


Figure 5. Chemical shift in ppm of the imide proton (N−H) of the thymine monomer (**4**, Figure 3) as a function of concentration in chloroform at room temperature.

monomer **1** were polymerized. Upon complete conversion as monitored by ^{1}H NMR spectroscopy, 350 equiv of monomer **5** were added. Complete conversion occurred within 3 h. The homopolymer and the copolymer were characterized by GPC, and the results are shown in Figure 4B. The GPC trace of the block copolymer is unimodal and shows a complete and dramatic shift to high molecular weight without traces of terminated low molecular weight polymer. This result in combination with the linear relationship between the M/I ratios and the molecular weight clearly proves the living nature of **1**.

Thymine Monomer Studies. Monomer **4** could be polymerized homogeneously in chloroform only at low concentrations and low degrees of polymerization. At concentrations above 100 mg/mL and at degrees of polymerization above 25, phase separation occurred. Phase separation was also observed in dichloromethane and at elevated temperatures. These results clearly indicate that high molecular weight thymine homopolymers are not completely soluble in these solvents. However, these polymers are soluble in polar solvents like THF. We rationalize that this phenomenon might be due to self-association of the functionalized thymines which can dimerize.[30] Hence, we carried out dimerization experiments and established the self-association constant of **4** in chloroform using ^{1}H NMR dilution experiments (Figure 5). The self-association constant of **4** was found to be 21 M^{-1}, which is close to the published literature value.[25]

Table 1. GPC (Number (M_n) and Weight (M_w) Average Molecular Weights and Polydispersities Indices (PDI)), DSC (Glass-Transition Temperatures (T_g)), and TGA (Onset of Decomposition Temperatures (T_{dec})) Analyses of All Homo- and Copolymers[a]

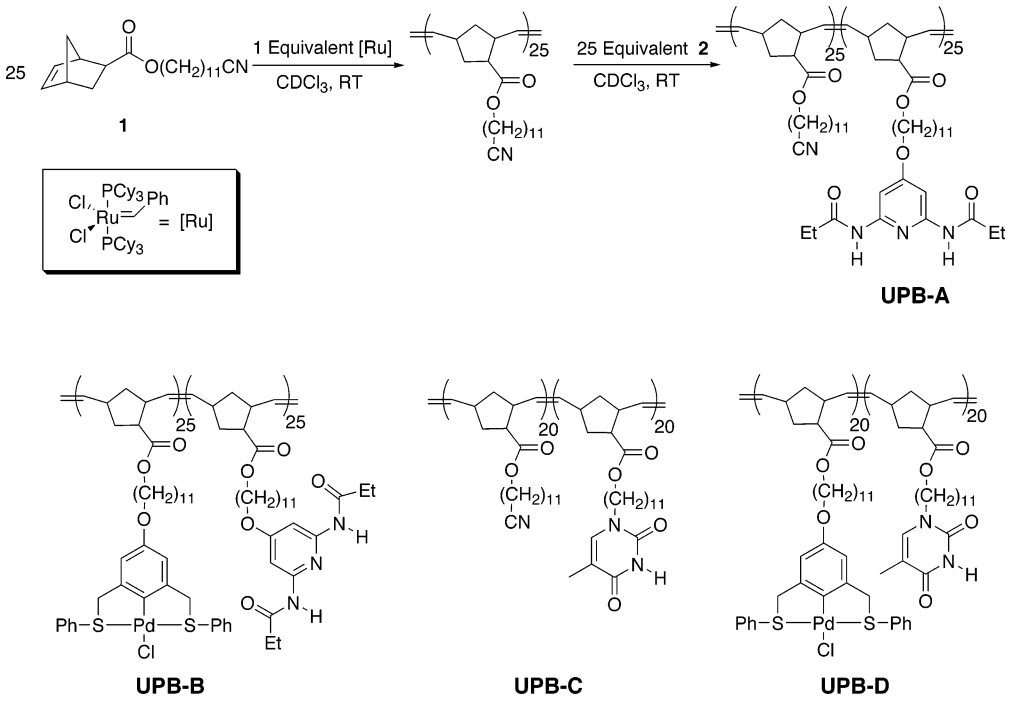
polymer	M/I	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	PDI	T_g (°C)	T_{deg} (°C)
Poly-1	50	17.9	34.0	1.89	91	400
Poly-2	50	8.4	6.8	1.23	54	383
Poly-3[b]	50	30.6	36.1	1.17	79	299
Poly-4	20	3.9	4.4	1.12	69	387
UPB-A[c]	25	30.0	49.0	1.63	21	370
UPB-B[b,c]	25	11.4	15.8	1.30	48	255
UPB-C[c]	20	7.0	12.5	1.77	24	380
UPB-D[c]	20	21.6	29.4	1.36	44	376

[a] GPC measurements were carried out at room temperature using THF as the eluant unless otherwise noted. [b] Eluant: Dichloromethane. [c] M/I ratios for each block. Polymer abbreviations are based on Scheme 3.

On the basis of these results, we limited the M/I ratios to 20 for all copolymers containing **4** to ensure homogeneous reaction conditions. Complete conversion of **4** by ROMP occurred in about 30 min as monitored by ^{1}H NMR analysis, and the GPC trace of the resulting homopolymer showed a unimodal signal with a narrow PDI of 1.12. We have previously reported that the ROMP of monomers **2** and **3** are living yielding polymers of narrow PDIs.[45]

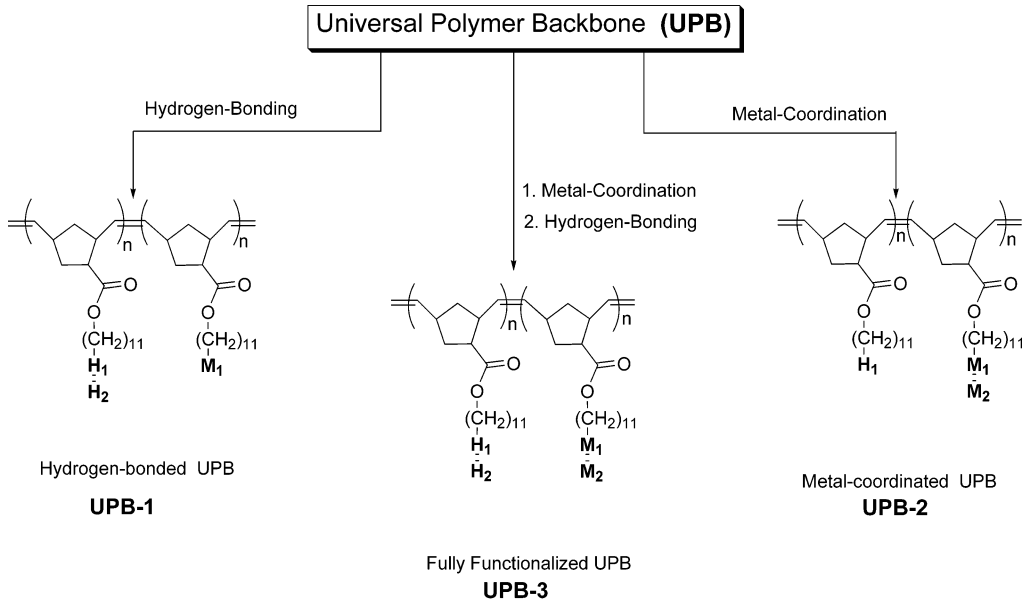
Copolymerization Studies. As monomer **1** could be polymerized in a living fashion, it was possible to synthesize block copolymers starting with any monomer. Four classes of diblock copolymers were synthesized containing one hydrogen bonding block and one metal coordination block (**UPB-A**−**D**). All block copolymerizations were carried out by the sequential monomer addition after the first monomer was completely polymerized, as determined by ^{1}H NMR analysis. The resulting block

Scheme 3. Block Copolymer Formation Using the Synthesis of UPB-A as an Example and the Depiction of All Synthesized Di Block Copolymers[a]

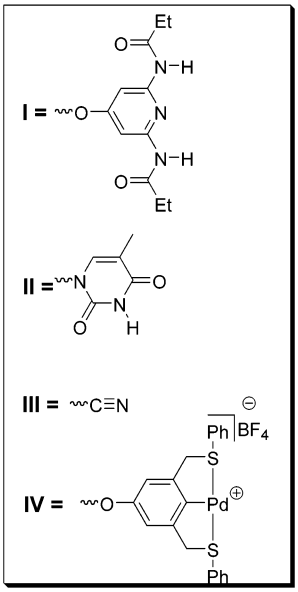


[a] Polymer end groups have been omitted for clarity.

Scheme 4. Functionalization Strategies of All Block Copolymers, "Universal Polymer Backbones (UPBs)"[a]



UPB	H_1	H_2	M_1	M_2
UPB-A-1	**I**	**7**	**III**	**-**
UPB-A-2	**I**	**-**	**III**	**8**
UPB-A-3	**I**	**7**	**III**	**8**
UPB-B-1	**I**	**7**	**IV**	**-**
UPB-B-2	**I**	**-**	**IV**	**9**
UPB-B-3	**I**	**7**	**IV**	**9**
UPB-C-1	**II**	**6**	**III**	**-**
UPB-C-2	**II**	**-**	**III**	**8**
UPB-C-3	**II**	**6**	**III**	**8**
UPB-D-1	**II**	**6**	**IV**	**-**
UPB-D-2	**II**	**-**	**IV**	**9**
UPB-D-3	**II**	**6**	**IV**	**9**



[a] Polymer end groups have been omitted for clarity. Polymer abbreviations are based on Scheme 3.

copolymers were characterized by GPC analysis, which showed unimodal distributions for all copolymers. In general, block copolymers containing **1** displayed higher PDIs around 1.7 while all other block copolymers (**UPB-B**, **UPB-D**) showed lower PDIs around 1.3 (Table 1). Scheme 3 outlines all block copolymers that have been synthesized for this study.

Noncovalent Functionalizations. Functionalization of the resulting block copolymers using noncovalent interactions as well as the investigation into the orthogonal character of all functionalization steps is key to our study. Therefore, after establishing the living nature of the polymerization of all monomers, the homopolymerization characteristics, and the synthesis of all block copolymers, we investigated the noncovalent functionalizations of all homopolymers and block copolymers via hydrogen bonding and/or metal coordination. First, we carried out the self-assembly of a single block by using either hydrogen bonding or metal coordination as well as the stepwise multifunctionalization beginning with the metal coordination followed by hydrogen bonding, as depicted in Scheme 4.

Hydrogen Bonding. All homopolymers and copolymers were easily self-assembled via hydrogen bonding by simply stirring the polymer solution in dichloromethane with the appropriate complementary recognition unit, followed by removal of the solvent under reduced pressure. Association constants (K_a values) of the monomers, homopolymers, and block copolymers were determined by ^{1}H NMR titration experiments in chloroform at room temperature (Table 2). We first investigated the K_a values of monomers **2** and **4**. The K_a value of the hydrogen-bonded complex between **2** and **7** was 1080 M^{-1}, whereas the K_a value between **4** and **6** was determined to be 920 M^{-1}. Both of these values are comparable to published literature values.[43,59] Upon polymerization, the K_a values of the homopolymers of both monomers (**Poly-2** and **Poly-4**) showed a significant decrease from 1080 to around 540 M^{-1} and from 920 to 460

Table 2. Association Constants (K_a Values) for the Self-Assembly via Hydrogen Bonding of Monomers 2 and 4, All Homopolymers, and All Block Copolymers before and after Metal Coordination[a]

entry	K_a value[a] (M^{-1})	entry	K_a value[a] (M^{-1})
2	1080	**UPB-A**	410
3	920	**UPB-A-2**	460
Poly-2 (50-mer)	540	**UPB-B**	510
Poly-2 (100-mer)	540	**UPB−C**	370
Poly-4 (20-mer)	460	**UPB-C-2**	310
		UPB-D	340

[a] Errors for all K_a measurements ranged from 10 to 15%. Polymer abbreviations are based on Schemes 3 and 4.

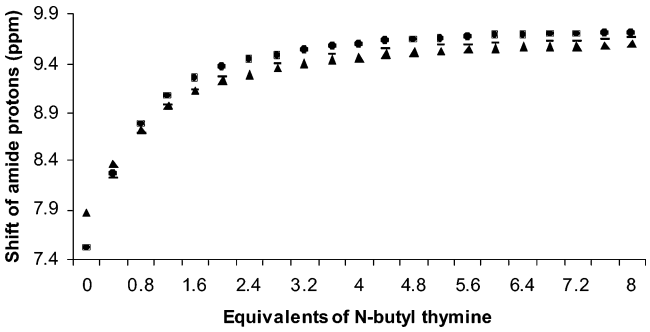


Figure 6. ^{1}H NMR titration curves for monomer **2** (●), a 50-mer of **2** (—), and a 100-mer (▲) of **2** with *N*-butylthymine. The polymer solutions (0.005 M, based on the hydrogen bonding moieties) were titrated against *N*-butylthymine (0.01 M) at room temperature using chloroform as solvent.

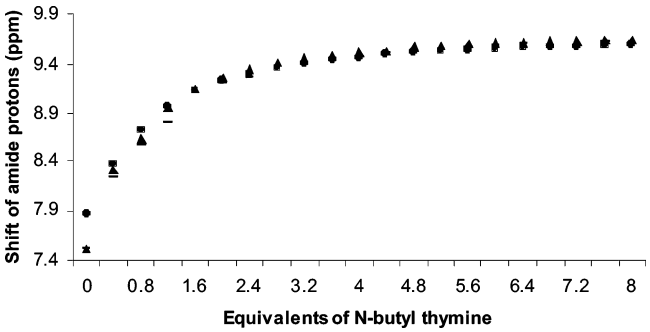


Figure 7. ^{1}H NMR titration curves for **Poly-2 (**100-mer**)** (●), **UPB-A** (—), and **UPB-B** (▲) with *N*-butylthymine. The polymer solutions (0.005 M, based on the hydrogen bonding moieties) were titrated against *N*-butylthymine (0.01 M) at room temperature using chloroform as solvent.

M^{-1} for **Poly-2** and **Poly-4**, respectively. We have previously reported similar decreases in the K_a values of hydrogen bonding monomers based on 2,6-diaminopyridines upon polymerization.[44]

Next we studied the effect of molecular weight on the association constant by measuring the K_a values of a 100-mer and a 50-mer of **2** (Figure 6). For both polymers, we measured the K_a values to be similar (540 M^{-1}) (Table 2), indicating the independence of the association constant from the polymer molecular weight. Similar results were obtained for monomer **4**.

After establishing the K_a values of the homopolymers, we investigated the K_a values of all block copolymers and compared them to the corresponding monomers and homopolymers to study the effect of block copolymerization on the hydrogen bonding interaction (Figures 7−9). In general, we found that the K_a values of all block copolymers were comparable to their homopolymer analogues. Block copolymers containing **2** had K_a values of 500 ± 50 M^{-1} while block copolymers based on

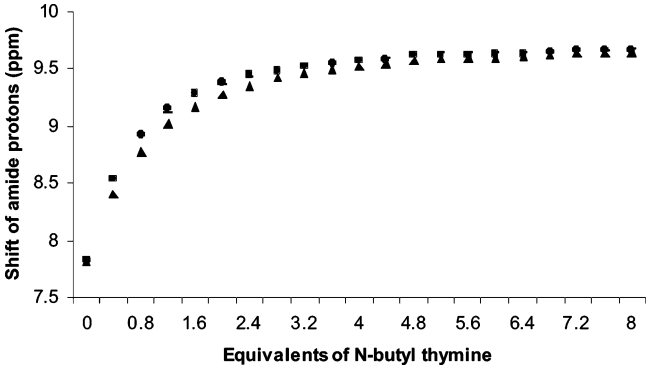


Figure 8. ^{1}H NMR titration curves for **UPB-A** (25/75) (●), **UPB-A** (50/50) (—), and **UPB-A** (75/25) (▲) with *N*-butylthymine. The polymer solutions (0.005 M, based on the hydrogen bonding moieties) were titrated against *N*-butylthymine (0.01 M) at room temperature using chloroform as solvent.

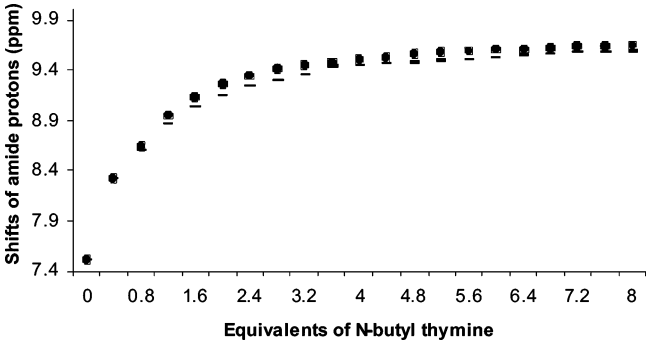


Figure 9. ^{1}H NMR titration curves for **UPB-A** (●) and **UPB-A-2** (—) with *N*-butylthymine. The polymer solutions (0.005 M, based on the hydrogen bonding moieties) were titrated against *N*-butylthymine (0.01 M) at room temperature using chloroform as solvent.

4 showed K_a values of 360 ± 50 M^{-1} (Figure 7). These results clearly prove that the block copolymerization had no significant effect on the stability of the hydrogen bonding complex. Furthermore, the association constants are also independent of the comonomer used (either **1** or **3**), proving that the comonomer does not interfere with the hydrogen bonding: i.e., the hydrogen bonding step is orthogonal to the metal coordination sites in block copolymers.

To further study the effect of block copolymer composition on the K_a values, **UPB-A** was synthesized with three different ratios of block A to block B (ratios of 25:75, 50:50 and 75:25 of **1**:**2**), and the K_a values of each block copolymer were determined (Figure 8). The K_a values of these different block copolymer compositions were identical within the experimental error, indicating that the block copolymer composition had little effect on the K_a values.

Effect of the Dimerization of the Thymine Functional Groups. The block copolymers **UPB-A** and **UPB-B** are identical to **UPB-C** and **UPB-D** but for the terminal hydrogen-bonding units (**UPBs A** and **B** are based on 2,6-diaminopyridine while **UPBs C** and **D** are based on thymine). Nevertheless, both terminal hydrogen bonding units are complementary to each other consisting of identical ADA−DAD units: hence, it is expected that the K_a values for all polymers be similar. However, the K_a values of all block copolymers containing **4** are significantly lower (about 10−30%) than those containing **2**. These lower association constants can be attributed to the dimerization of the thymine groups attached to the polymer backbone, thereby lowering the association constant. In contrast, block copolymers based on **2** have a low propensity to dimerize, resulting in higher association constants.[44]

Metal Coordination. The terminal nitrile-functionalized monomers and polymers as well as the palladated pincer complex-functionalized monomers and polymers represent a complementary set of a metal coordination system. Functionalization of the pincer moieties in both cases began with the abstraction of the chlorine atom from the palladated center using $AgBF_4$ followed by coordination by the appropriate ligand to the palladium atom.[17]

The nitrile-functionalized polymers in essence act as a "polymeric ligand" that can coordinate with the Pd pincer center **8** whereas the covalent functionalization of the pincer complex onto the polymer can be seen as a "polymeric metal center" which needs to be activated prior functionalization. The functionalization of the nitrile-based polymers was significantly easier and could be carried out in analogy to literature procedures in a variety of solvents including chloroform and dichloromethane.[60] However, every attempt to coordinate the pincer block copolymers in chloroform resulted in immediate precipitation. Furthermore, polar solvents such as DMF and DMSO could not be employed because of the severe disruption of the hydrogen bonding complex formation of the block containing the hydrogen bonding recognition units. Therefore, the metal coordination of the pincer-based block copolymers (**UPBs B** and **D**) was successful only in anhydrous dichloromethane using a saturated solution of $AgBF_4$ in an equivolume mixture of nitromethane and acetonitrile. This important difference can be ascribed to the fact that during the metal-coordination step the pincer-functionalized block copolymer gets converted into a "polyelectrolyte species", thus decreasing the solubility of the system in a nonpolar environment, whereas in the case of the nitrile-functionalized block copolymers the Pd pincer center **8** become positively charged on activation, thereby circumventing the formation of a "polyelectrolyte species". Nevertheless, when using an appropriate solvent, quantitative metal coordination took place, and no interferences of the hydrogen bonding moieties during the metal coordination steps were observed.

Multifunctionalizations. After establishing that (a) the metal coordination steps on all homopolymers and block copolymers can be carried out quantitatively within seconds without interference of the hydrogen bonding recognition motifs and (b) the strength of the hydrogen bonding interaction is independent of the copolymers used, we carried out multifunctionalization experiments. In particular, we investigated the hydrogen bonding strength via ^{1}H NMR titration experiments of block copolymers that were first functionalized via metal coordination. As can be seen in Figure 9 and Table 2, similar K_a values for the hydrogen bonding titration experiments for all metal coordinated block copolymers were observed as described above for all single hydrogen bonding functionalization studies on homopolymers and block copolymers (the K_a values range from 460 M^{-1} for block copolymers containing **2** to 360 M^{-1} for block copolymers containing **4**). These results clearly demonstrate that metal coordination does not interfere with the hydrogen bonding functionalization; i.e., both recognition motifs are orthogonal to each other in all block copolymers. However, because of poor solubility in chloroform, we were not able to measure the association constants for **UPB-B-2** and **UPB-D-2**.

Thermal Characterization. To study the effect of the noncovalent functionalization on the thermal properties of all polymers, we measured the glass-transitions temperatures (T_g) and onset temperatures of degradation (T_{deg}) of all homopolymers and block copolymers. The results are tabulated in Tables 1 and 3. **Poly-1** displayed the highest T_g as well as T_{deg} values, which can be explained by the strong intermolecular as well as intramolecular dipole−dipole interactions between the nitrile groups, as reported for other nitrile-based polymers such as poly(acrylonitrile).[61] **Poly-1**, upon metal coordination with **8**, gave the self-assembled **Poly-1(SA)** which exhibited a large decrease in the T_g due to the disruption of these intermolecular interactions. **Poly-1(SA)** also showed a large decrease in the thermal stability, which can be explained by the introduction of metallic species into the system. Similarly, **Poly-3**, a metalated polymer, showed the lowest thermal stability as compared to the other non-metal-containing polymers. This can be explained by the fact that metal residues catalyze the thermal degradation of polymers.[62,63] **Poly-3**, upon functionalization by either pyridine or functionalized nitriles, gave the self-assembled **Poly-3(SA)** which did not exhibit significant changes in the T_g but, upon metal coordination with **9**, a large decrease in the thermal stability. **Poly-4**, which is able to undergo a high degree of intermolecular interactions via hydrogen bonding, exhibited a large decrease in the T_g after functionalization with **6** to give self-assembled **Poly-4(SA**). However, the thermal stability of **Poly-4** was not affected by the functionalization. **Poly-2**, on self-assembly with **7**, gave the self-assembled **Poly-2(SA)** which showed a large decrease in both the T_g and T_{deg}.

Table 3. Thermal Characterization Data of All Self-Assembled Homopolymers and Block Copolymers[a]

polymer	T_g (°C)	T_{deg} (°C)	polymer	T_g (°C)	T_{deg} (°C)
Poly-1(SA)	72	185	**UPB-B-2**	31	190
Poly-2(SA)	10	278	**UPB-B-3**	33	222
Poly-3(SA)	64	194	**UPB-C-1**	13	320
Poly-4(SA)	36	383	**UPB-C-2**	5	284
UPB-A-1	6	265	**UPB-C-3**	2	284
UPB-A-2	6	240	**UPB-D-1**	29	312
UPB-A-3	10	232	**UPB-D-2**	42	205
UPB-B-1	32	227	**UPB-D-3**	30	230

[a] Polymer abbreviations are based on Schemes 3 and 4.

All block copolymers displayed lower glass-transition temperatures than their homopolymer counterparts although their T_{deg} are similar. To understand the individual effects of hydrogen bonding and metal coordination interactions on the thermal properties of the copolymers, we measured the glass-transition temperature and onset of thermal degradation after each functionalization step. Both functionalizations, hydrogen bonding and metal coordination, decreased the T_g of the copolymers, by similar extents, although the fully functionalized copolymers had lower T_g due to the combined effects of both functionalizations. The decrease in the T_g values upon functionalization can be explained by the plasticization of the polymers. Similarly, the polymers, upon metal coordination, had lower onsets of degradation temperatures. It can be seen in every case that the thermal stability decreases to a higher extent upon metal coordination as compared to their corresponding hydrogen-bonded counterparts.

Summary and Conclusions

In this contribution, we have synthesized diblock copolymers possessing both hydrogen bonding and metal coordination recognition units via ROMP. The hydrogen bonding recognition system consisted of substituted thymines and substituted 2,6-diaminopyridines, whereas the metal coordination system consisted of palladated SCS pincer complexes and functionalized nitriles and pyridine. The effect of degree of polymerization, block copolymer composition, and most importantly metal coordination on the noncovalent functionalization via hydrogen bonding was studied in detail. None of these variables had any

substantial impact on the stability of the hydrogen bonded complexes. These results suggest that the investigated noncovalent interactions are orthogonal in block copolymers, a prerequisite to employ this strategy in material science. Finally, the effect of these noncovalent functionalizations on the thermal properties of the polymers was studied. We found that both functionalization by hydrogen bonding and metal coordination decrease the glass-transition temperatures of all polymers due to disruption of the intermolecular forces, and similarly the functionalized polymers had lower thermal stability than their corresponding unfunctionalized counterparts.

In summary, by combining a highly functional group tolerant polymerization route with noncovalent functionalization techniques, we have demonstrated that such a strategy allows for the fast synthesis of highly functionalized materials having a high degree of control over their molecular structure. Using noncovalent interactions such as hydrogen bonding and metal coordination, we can synthesize from a single polymer backbone ("universal polymer backbone") a large variety of functionally varied polymers, which widely differ in their physical and chemical properties, simply by altering the functionalization strategy.

Acknowledgment. Financial support has been provided by the National Science Foundation (CHE-0239385) and the Office of Naval Research (MURI, Award N00014-03-1-0793). The GPC instrument was purchased through a DURIP grant from the Office of Naval Research (N00014-04-1-0488). M.W. gratefully acknowledges a 3M Untenured Faculty Award, a DuPont Young Professor Award, an Alfred P. Sloan Fellowship, a Camille Dreyfus Teacher-Scholar Award, and a Blanchard Assistant Professorship.

References and Notes

(1) Ikkala, O.; ten Brinke, G. *Science* **2002**, *295*, 2407−2409.
(2) Yoda, N. *Polym. Adv. Technol.* **1997**, *8*, 215−226.
(3) de Boer, B.; Stalmach, U.; Melzer, C.; Hadziioannu, G. *Synth. Met.* **2001**, *121*, 1541−1542.
(4) Stupp, S. I.; Keser, M.; Tew, G. N. *Polymer* **1998**, *39*, 4505−4509.
(5) Abd-El-Aziz, A. S.; May, L. J.; Hurd, J. A.; Okasha, R. M. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2716−2722.
(6) Kanaoka, S.; Grubbs, R. H. *Macromolecules* **1995**, *28*, 4707−4713.
(7) Carlise, J. R.; Weck, M. W. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 2973−2984.
(8) Weck, M.; Schwab, P.; Grubbs, R. H. *Macromolecules* **1996**, *29*, 1789−1793.
(9) Bazzi, H. S.; Bouffard, J.; Sleiman, H. F. *Macromolecules* **2003**, *36*, 7899−7902.
(10) Bullock, S. E.; Kofinas, P. *Macromolecules* **2004**, *37*, 1783−1786.
(11) Riegler, S.; Slugovc, C.; Trimmel, G.; Stelzer, F. *Macromol. Symp.* **2004**, *217*, 231−246.
(12) Pollino, J. M.; Weck, M. *Chem. Soc. Rev.* **2005**, *34*, 193−207.
(13) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071−4097.
(14) Schubert, U. S.; Eschbaumer, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 2892−2926.
(15) Beck, J. B.; Rowan, S. J. *J. Am. Chem. Soc.* **2003**, *125*, 13922−13923.
(16) Pollino, J. M.; Nair, K. P.; Stubbs, L. P.; Adams, J.; Weck, M. *Tetrahedron* **2004**, *60*, 7205−7215.
(17) Pollino, J. M.; Weck, M. *Synthesis* **2002**, 1277−1285.
(18) Johnson, R. M.; Fraser, C. L. *Macromolecules* **2004**, *37*, 2718−2727.
(19) Calzia, K. J.; Tew, G. N. *Macromolecules* **2002**, *35*, 6090−6093.
(20) Percec, V.; Johansson, G.; Rodenhouse, R. *Macromolecules* **1992**, *25*, 2563−2565.
(21) Prins, L. J.; Reinhoudt, D. N.; Timmerman, P. *Angew. Chem., Int. Ed.* **2001**, *40*, 2382−2426.
(22) Berl, V.; Schmutz, M.; Krische, M. J.; Khoury, R. G.; Lehn, J.-M. *Chem.—Eur. J.* **2002**, *8*, 1227−1244.
(23) Kumar, U.; Kato, T.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1992**, *114*, 4, 6630−6639.
(24) Xu, H.; Rudkevich, D. M. *J. Org. Chem.* **2004**, *69*, 8609−8617.
(25) Farnik, D.; Kluger, C.; Kunz, M. J.; Machl, D.; Petraru, L.; Binder, W. H. *Macromol. Symp.* **2004**, *217*, 247−266.
(26) Sivakova, S.; Rowan, S. J. *Chem. Soc. Rev.* **2005**, *34*, 9−21.
(27) Gareth Davies, R.; Gibson, V. C.; Hursthouse, M. B.; Light, M. E.; Marshall, E. L.; North, M.; Robson, D. A.; Thompson, I.; White, A. J. P.; Williams, D. J.; Williams, P. J. *J. Chem. Soc., Perkin Trans. 1* **2001**, 3365−3381.
(28) Gibson, V. C.; Marshall, E. L.; North, M.; Robson, D. A.; Williams, P. J. *Chem. Commun.* **1997**, 1095−1096.
(29) Carroll, J. B.; Waddon, A. J.; Nakade, H.; Rotello, V. M. *Macromolecules* **2003**, *36*, 6289−6291.
(30) Kita, Y.; Uno, T.; Inaki, Y.; Takemoto, K. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 477−485.
(31) Drechsler, U.; Thibault, R. J.; Rotello, V. M. *Macromolecules* **2002**, *35*, 9621−9623.
(32) Ilhan, F.; Gray, M.; Rotello, V. M. *Macromolecules* **2001**, *34*, 2597−2601.
(33) Thibault, R. J.; Hotchkiss, P. J.; Gray, M.; Rotello, V. M. *J. Am. Chem. Soc.* **2003**, *125*, 11249−11252.
(34) Sivakova, S.; Rowan, S. J. *Chem. Commun.* **2003**, 2428−2429.
(35) Yu, K.; Sommer, W.; Weck, M.; Jones, C. W. *J. Catal.* **2004**, *226*, 101−110.
(36) El-Ghayoury, A.; Schenning, A. P. H. J.; van Hal, P. A.; Weidl, C. H.; van Dongen, J. L. J.; Janssen, R. A. J.; Schubert, U. S.; Meijer, E. W. *Thin Solid Films* **2002**, *403−404*, 97−101.
(37) Pollino, J. M.; Stubbs, L. P.; Weck, M. *J. Am. Chem. Soc.* **2004**, *126*, 563−567.
(38) Huck, W. T. S.; Hulst, R.; Timmerman, P.; van Veggel, F. C. J. M.; Reinhoudt, D. N. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1006−1008.
(39) Hofmeier, H.; El-ghayoury, A.; Schenning, A. P. H. J.; Schubert, U. S. *Chem. Commun.* **2004**, 318−319.
(40) Ruokolainen, J.; Mäkinen, R.; Torkkeli, M.; Mäkelä, T.; Serimaa, R.; Ten Brinke, G.; Ikkala, O. *Science* **1998**, *280*, 557−560.
(41) Bazuin, C. G.; Brodin, C. *Macromolecules* **2004**, *37*, 9366−9372.
(42) Valkama, S.; Lehtonen, O.; Lappalainen, K.; Kosonen, H.; Castro, P.; Repo, T.; Torkkeli, M.; Serimaa, R.; ten Brinke, G.; Leskelä, M.; Ikkala, O. *Macrol. Rapid Commun.* **2003**, *24*, 556−560.
(43) Beijer, F. H.; Sijbesma, R. P.; Vekemans, J. A. J. M.; Meijer, E. W.; Kooijman, H.; Spek, A. L. *J. Org. Chem.* **1996**, *61*, 6371−6380.
(44) Stubbs, L. P.; Weck, M. *Chem.—Eur. J.* **2003**, *9*, 992−999.
(45) Pollino, J. M.; Stubbs, L. P.; Weck, M. *Macromolecules* **2003**, *36*, 2230−2234.
(46) Burd, C.; Weck, M. *Macromolecules* **2005**, *38*, 7225−7230.
(47) Sayre, C. N.; Collard, D. M. *Langmuir* **1997**, *13*, 714−722.
(48) Solov'ev, V. ChemEquili 6.1., 1996−1998.
(49) Zimmerman, S. C.; Corbin, P. S. *Struct. Bonding (Berlin)* **2000**, *96*, 63−94.
(50) Pollino, J. M.; Weck, M. *Org. Lett.* **2002**, *4*, 753−756.
(51) Friggeri, A.; van Manen, H.; Auletta, T.; Li, X.; Zapotoczny, S.; Schönherr, H.; Vancso, G. J.; Huskens, J.; van Veggel, F. C. J. M.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **2001**, *123*, 6388−6395.
(52) van Manen, H.; Nakashima, K.; Shinkai, S.; Kooijman, H.; Spek, A. L.; van Veggel, F. C. J. M.; Reinhoudt, D. N. *Eur. J. Inorg. Chem.* **2000**, 2533−2540.
(53) Danprasert, K.; Kumar, R.; H-Cheng, M.; Gupta, P.; Shakil, N. A.; Prasad, A. K.; Parmar, V. S.; Kumar, J.; Samuelson, L. A.; Watterson, A. C. *Eur. Polym. J.* **2003**, *39*, 1983−1990.
(54) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100−110.
(55) Demel, S.; Riegler, S.; Wewerka, K.; Schoefberger, W.; Slugovc, C.; Stelzer, F. *Inorg. Chim. Acta* **2003**, *345*, 363−366.
(56) Gangadhara; Campistron, I.; Thomas, M.; Reyx, D. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 2807−2821.
(57) Yoshida, Y.; Goto, K.; Komiya, Z. *J. Appl. Polym. Sci.* **1997**, *66*, 367−375.
(58) Slugovc, C.; Riegler, S.; Hayn, G.; Saf, R.; Stelzer, F. *Macromol. Rapid Commun.* **2003**, *24*, 435−439.
(59) Yu, L.; Schneider, H.-J. *Eur. J. Org. Chem.* **1999**, 1619−1625.
(60) Huck, W. T. S.; van Veggel, F. C. J. M.; Kropman, B. L.; Blank, D. H. A.; Keim, E. G.; Smithers, M. M.; A.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 8293−8294.
(61) Gupta, A. K.; Singhal, R. P.; Bajaj, P.; Agarwal, V. K. *J. Appl. Polym. Sci.* **1983**, *28*, 1167−77.
(62) Day, M.; Cooney, J. D.; MacKinnon, M. *Polym. Degrad. Stab.* **1995**, *48*, 341−349.
(63) Gorghiu, L. M.; Jipa, S.; Zaharescu, T.; Setnescu, R.; Mihalcea, I. *Polym. Degrad. Stab.* **2004**, *84*, 7−11.

MA052222T