Macromolecules **2004,** *37,* 9321−9330

Combining Ring-Opening Metathesis Polymerization (ROMP) with Sharpless-Type “Click” Reactions: An Easy Method for the Preparation of Side Chain Functionalized Poly(oxynorbornenes)

Wolfgang H. Binder* and Christian Kluger

Institute of Applied Synthetic Chemistry, Vienna University of Technology, Division of Macromolecular Chemistry, Getreidemarkt 9/163/MC, A-1060 Wien, Austria

Received September 27, 2004

ABSTRACT: Sharpless 1,3-dipolar cycloadditions (“click reactions”) between azides and acetylenes were used to prepare functional poly(oxynorbornenes) within their side chains. Two different strategies were applied to combine the preparation of ROMP polymers with the 1,3-dipolar cycloaddition approach: (a) the attachment of functional groups (i.e., hydrophobic and hydrogen bonding units) by 1,3-dipolar cycloaddition reactions to 7-oxynorbornenes bearing acetylenes and subsequent ROMP yielding the final polymers; (b) the ROMP polymerization furnishing first poly(oxynorbornenes) bearing acetylenic and azido moieties and subsequently attaching the functional units by use of the “click” reactions onto the modified polymers. Both strategies show efficient functionalization behavior with a high tolerance of functional groups with respect to the functional units attached as demonstrated by ^{1}H and ^{13}C NMR spectroscopy, opening the possibility to prepare a large variety of functionalized poly(oxynorbornenes) by use of only few starting materials.

Introduction

Ring-opening metathesis polymerization (ROMP) has become an extremely valuable tool for the preparation of functional homopolymers and block copolymers.[1] As reviewed recently,[2] the direct incorporation of functional groups bearing polar moieties (i.e., oligonucleotides,[3] carbohydrates,[4] nucleosides,[5] peptides[6]) as well as bulky side chains (i.e., dendrons,[7] polymeric side groups[8]) have been explored. Usually first- and second-generation Grubbs catalysts as well as Hoveyda-type catalysts are used for the polymerization, leading to polymers with often narrow polydispersities and defined molecular weights. An important concept in polymer chemistry aims at combining the ROMP-type polymerization with the concept of supramolecular polymers. The optimal realization of this concept employs the necessity to combine functional group tolerance (i.e., directed hydrogen bonds,[9] metal complexes,[10] $\pi-\pi$ stacking,[11] and ionic forces[12]) with the ROMP process under generation of highly functionalized homopolymers and block copolymers. Thus, ROMP-type polymerization reactions have been accomplished with metal complexes[13] as well as defined hydrogen bonding patterns in a direct polymerization reaction using the matching Grubbs- or Hoveyda-type catalysts: adenine[14] as well diaminotriazine moieties[15,16] and metal-binding complexes[16] can be introduced by direct polymerization of the appropriate monomers. In cases where this direct polymerization reaction does not proceed with satisfaction (due to catalyst inactivation, leading to broad polydispersity of the final polymers), concepts involving supramolecular protecting groups[17] as well as reactions after the ROMP polymerization have been developed. *N*-Hydroxysuccinimide esters[18] and alkyl bromides[19] have been used as scaffolds to allow the subsequent derivatization of the final ROMP polymers with a variety of polar reactants. Ideally, an optimal flexible synthetic procedure toward a variety of side chain-functionalized poly(norbornenes) involves reactions, where a clean, general polymerization reaction of ROMP (starting with a single monomer leading to narrow polydispersities as well as defined crossover reactions leading to block copolymers) can be combined with a generalized postmodification chemistry, allowing to introduce a variety of functional groups in high yields.

In the present publication we describe the combination of ROMP with a subsequent “click”-type derivatization chemistry as well as the direct incorporation of monomers bearing multiple hydrogen bonding sites (see Scheme 1). Thus, the concept of the Sharpless “click” reaction[20] (a 1,3-dipolar cycloaddition processe involving azides with terminal acetylenes under action of a copper(I) catalyst) is combined with the ROMP polymerization and the subsequent attachment of receptors bearing hydrogen bonding elements. The Sharpless “click” reaction has been demonstrated in the past[21] to lead to excellent coupling efficiencies with an extremely broad tolerance of functional groups and exceptionally high yields. Thus, reactions in combination with ATRP,[22] the formation of block copolymers[23] and dendrons,[24] and the efficient surface functionalization of gold[25] and silica surfaces[26] have been reported by use of this reaction. We here describe both approaches: the direct polymerization of functional monomers as well as the derivatization of polymers obtained by ROMP via the “click” reaction after the polymerization aiming at a controlled buildup of side chain-functionalized poly(norbornenes) complementing our concept of supramolecular polymers.[9c,9d,27]

Experimental Section

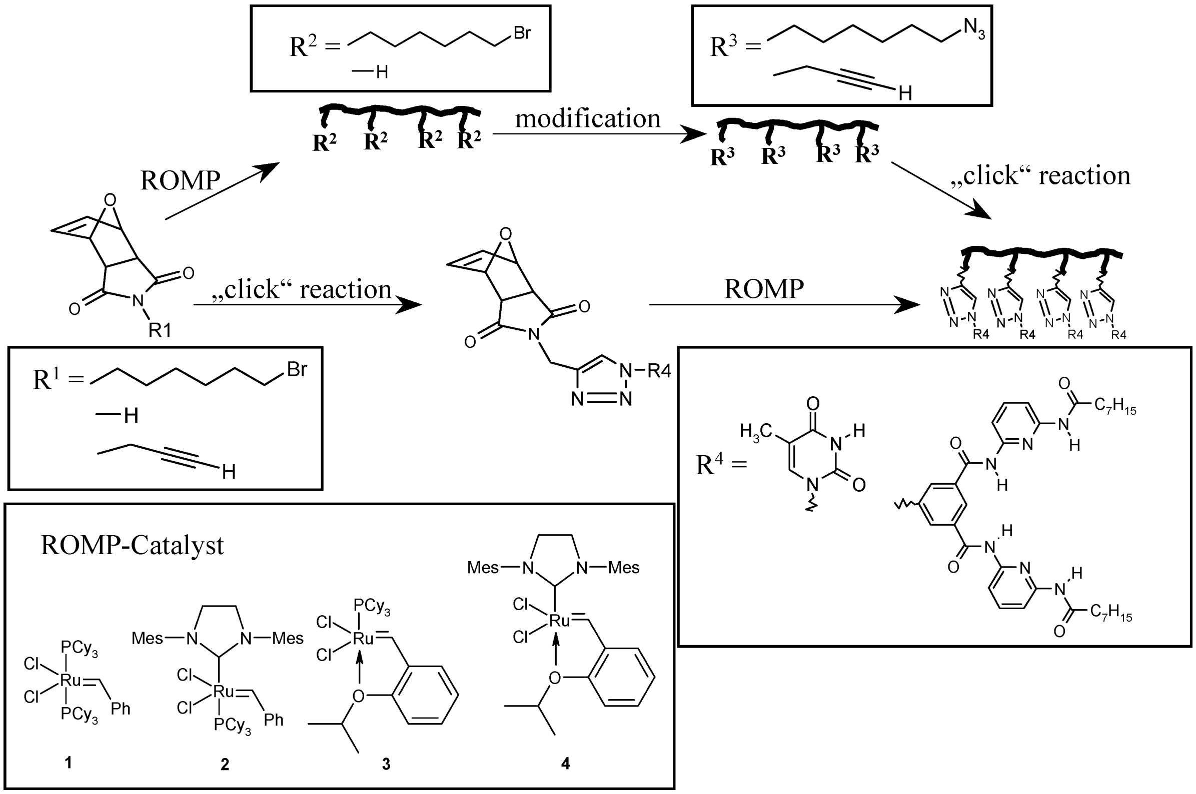
Instrumentation. NMR spectra were obtained from a 200 MHz Bruker AC200 spectrometer and a 400 MHz Bruker Avance DRX 400 MHz in $CDCl_3$, DMSO-d_6, and DMF-d_7. GPC analysis was performed on a Viscothek VE 2001 system using Styragel linear columns in THF at 40 °C. Polystyrene standards were used for conventional external calibration using a Waters RI 2410 refractive index detector.

---

* Corresponding author: e-mail wbinder@mail.zserv.tuwien.ac.at.

10.1021/ma0480087 CCC: $27.50

Scheme 1



Materials. THF was dried by distillation from potassium and benzophenone; CH_2Cl_2 was freshly distilled from CaH_2. Furane and 1-hexyne were freshly distilled before us. The ROMP catalysts **2**, **3**, and **4** were purchased at Sigma-Aldrich while catalyst **1** was purchased at Fluka. Monomers **5**[28] and **8**[29] as well as both thymine derivatives **12a**[30] and **12b**[30] were synthesized according to the literature.

Synthesis of exo-*N*-[6-(5-Methyl-2,4-dioxo-3,4-dihydro-2*H*-pyrimidin-1-yl)-hexyl]-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (6). A mixture of 1-(6-bromohexyl)-5-methyl-1*H*-pyrimidine-2,4-dione[32] (0.086 g, 0.297 mmol), potassium carbonate (0.084 g, 0.605 mmol), and exo-oxabicyclo-[2.2.1]hept-5-ene-2,3-dicarboximide (**5**) (0.050 mg, 0.303 mmol) was stirred in deoxygenated and dry DMF (5 mL) at 50 °C for 4 h. The reaction mixture was evaporated to dryness, the crude product was purified by chromatography (SiO_2, ethyl acetate), and pure **6** was obtained as a white solid. Yield: 0.090 mg (0.241 mmol, 81%). ^1H NMR (DMSO-d_6): δ = 11.24 (s, 1H), 7.55 (s, 1H), 6.58 (s, 2H), 5.16 (s, 2H), 3.61 (t, 2H), 3.36 (t, 2H), 2.95 (s, 2H), 1.78 (s, 3H), 1.65−1.35 (m, 4H), 1.35−1.15 (m, 4H). ^{13}C NMR (DMSO-d_6): δ = 177.5, 165.2, 151.8, 142.4, 137.4, 109.3, 81.3, 48.0, 38.7, 29.2, 27.9, 26.5, 26.2, 12.9. Mp = 154−157 °C.

Synthesis of exo-*N*-Prop-2-ynyl-7-oxabicyclo[2.2.1]-hept-5-ene-2,3-dicarboximide (7). A mixture of propargyl bromide (0.288 g, 2.422 mmol), potassium carbonate (0.334 g, 2.417 mmol), and exo-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (**5**) (0.200 g, 1.211 mmol) was stirred in deoxygenated and dry DMF (5 mL) at 50 °C for 4 h. The reaction mixture was evaporated to dryness, the crude product was purified by chromatography (SiO_2, hexane/ethyl acetate = 1/1), and pure **7** was obtained as a white solid. Yield: 0.0227 g (1.117 mmol, 92%). ^1H NMR ($CDCl_3$): δ = 6.52 (s, 2H), 5.29 (s, 2H), 4.22 (d, 2H), 2.90 (s, 2H), 2.19 (t, 2H). ^{13}C NMR ($CDCl_3$): δ = 174.8, 136.5, 80.9, 71.5, 71.4, 47.5, 27.8. Mp = 136−139 °C.

Synthesis of exo-*N*-Hexyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (8). A mixture of 1-bromohexane (0.300 g, 1.8 mmol), potassium carbonate (0.248 g, 1.8 mmol), and exo-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (**5**) (0.200 g, 1.2 mmol) was stirred in deoxygenated and dry DMF (35 mL) at 50 °C for 4 h. The reaction mixture was evaporated to dryness, and the crude product was purified by chromatography (SiO_2, hexane/ethyl acetate = 1/1). Pure **8** was obtained as a colorless oil. Yield: 0.297 g (1.19 mmol, 98%). ^1H NMR ($CDCl_3$): δ = 6.45 (s, 2H), 5.19 (s, 2H), 3.39 (t, 2H), 2.77 (s, 2H), 1.47 (m, 2H), 1.20 (m, 6H), 0.80 (t, 3H). ^{13}C NMR ($CDCl_3$): δ = 176.1, 136.4, 80.7, 47.2, 38.8, 31.1, 27.4, 26.1, 22.3, 13.8.

Synthesis of exo-*N*-{1-[6-(5-Methyl-2,4-dioxo-3,4-dihydro-2*H*-pyrimidin-1-yl)-hexyl]-1*H*-[1,2,3]triazol-4-ylmethyl}-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (9). A solution of exo-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (**5**) (0.050 g, 0.246 mmol), 1-(6-bromo-hexyl)-5-methyl-1*H*-pyrimidine-2,4-dione (0.055 g, 0.2214 mmol), bromotris(triphenylphosphine)copper(I) (0.021 g, 0.022 mmol), and *N*,*N*-diisopropylethylamine (0.05 mL, 0.144 mmol) was stirred in deoxygenated DMF (5 mL) at 50 °C for 24 h. The crude mixture was evaporated to dryness and purified by chromatography (SiO_2, chloroform/methanol = 25/1). Yield: 0.088 g (0.174 mmol, 79%). ^1H NMR ($CDCl_3$): δ = 8.88 (s, 1H), 7.47 (s, 1H), 6.96 (s, 1H), 6.52 (s, 2H), 5.28 (s, 2H), 4.78 (s, 2H), 4.29 (t, 2H), 3.65 (t, 2H), 1.95−1.80 (m, 5H), 1.64 (m, 2H), 1.32 (m, 4H). ^{13}C NMR ($CDCl_3$): δ = 175.5, 164.1, 150.8, 142.1, 140.2, 136.5, 122.3, 110.7, 81.0, 50.1, 48.1, 47.5, 34.2, 29.9, 28.7, 25.8, 25.6, 12.3.

Synthesis of 5-{4-[exo-7-Oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximidyl)-4-ylmethyl) [1,2,3]triazol-1-yl]benzoylamino}-*N*,*N′*-bis(6-octanoylaminopyridin-2-yl)isophthalamide (10). A solution of exo-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (**5**) (0.033 g, 0.162 mmol), 5-(4-azido-benzoylamino)-*N*,*N′*-bis(6-octanoylaminopyridin-2-yl)isophthalamide (0.131 g, 0.173 mmol), bromotris(triphenylphosphine)-copper(I) (0.017 g, 0.018 mmol), and *N*,*N*-diisopropylethylamine (0.03 mL, 0.173 mmol) was stirred in deoxygenated DMF (5 mL) at 50 °C for 24 h. The crude mixture was evaporated to dryness and purified by chromatography (SiO_2, hexane/ethyl acetate = 1/5), yielding a light yellow solid. Yield: 0.127 g (0.132 mmol, 81%); mp = 146−148 °C. ^1H NMR (DMSO-d_6): δ = 10.85 (s, 1H), 10.50 (s, 2H), 10.17 (s, 2H), 8.80 (s, 1H), 8.65 (s, 2H), 8.35 (s, 1H), 8.29 (d, 2H), 8.14 (d, 2H), 7.88 (m, 6H), 6.62 (s, 2H), 5.24 (s, 2H), 4.78 (s, 2H), 3.07 (s, 2H), 2.44 (t, 4H), 1.62 (t, 4H), 1.30 (m, 16H), 0.88 (t, 6H).

Table 1. Results (M_n, M_w/M_n) of the ROMP Polymerization of Monomers 5−11 and 20

entry	monomer	catalyst	polymer	$M_{n,th}$ [Da]	$M_{n,GPC}$ [Da]	PDI	solvent
1	**5**	**1**	**21**	3309	3840	1.1	THF
2	**5**	**1**	**21**	2477	*a*	*a*	CH_2Cl_2
3	**5**	**1**	**21**	2477	2930	1.1	THF
4	**5**	**1**	**21**	2477	2980	1.1	THF
5	**5**	**1**	**21**	1992	2990	1.1	THF
6	**5**	**1**	**21**	1652	2940	1.1	THF
7	**5**	**2**	**21**	2477	*a*	*a*	THF
8	**5**	**3**	**21**	3303	*a*	*a*	THF
9	**5**	**4**	**21**	3303	*a*	*a*	THF
10	**6**	**1**	**15**	1867	2190	1.2	CH_2Cl_2
11	**7**	**1**	**22**	2032	2380	1.5	CH_2Cl_2
12	**7**	**1**	**22**	5081	2539	1.8	CH_2Cl_2
13	**8**	**1**	**16**	3989	2881	1.2	CH_2Cl_2
14	**8**	**2**	**16**	3739	54130	1.3	CH_2Cl_2
15	**8**	**2**	**16**	3739	21020	2	THF
16	**8**	**4**	**16**	3739	33720	1.5	CH_2Cl_2
17	**8**	**4**	**16**	3739	21 850	1.9	THF
18	**9**	**1**	**17**	4545	1590[b]	1.1	CH_2Cl_2
19	**10**	**1**	**18**	8177	6180	1.3	THF
20	**11**	**1**	**19**	4987	5340	1.1	CH_2Cl_2
21	**20**	**1**	**23**	3282	2470	1.3	THF
22	**20**	**1**	**23**	2626	2975	1.1	CH_2Cl_2
23	**20**	**1**	**23**	3282	2980	1.1	CH_2Cl_2
24	**20**	**1**	**23**	3282	3170	1.1	CH_2Cl_2
25	**20**	**1**	**23**	3282	3070	1.1	CH_2Cl_2
26	**20**	**2**	**23**	3282	10455	1.8	THF
27	**20**	**3**	**23**	3282	10940	1.6	THF
28	**20**	**4**	**23**	3282	12990	1.7	THF

[a] Precipitation during polymerization. [b] Precipitation during polymerization; the soluble part was analyzed by GPC and NMR.

^{13}C NMR (DMSO-d_6): δ = 176.9, 173.2, 166.1, 165.6, 151.6, 151.1, 144.2, 141.1, 140.6, 139.7, 137.5, 135.7, 135.0, 130.6, 124.1, 122.6, 120.7, 111.2, 110.9, 81.4, 48.3, 37.1, 36.8, 32.2, 29.6, 29.5, 26.0, 23.1, 15.0.

Synthesis of exo-*N*-(1-Octadecyl-1*H*-[1,2,3]triazol-4-ylmethyl)-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (11). A solution of exo-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (**5**) (0.102 g, 0.504 mmol), 1-azidooctadecane (0.162 g, 0.547 mmol), bromotris(triphenylphosphine)copper(I) (0.051 g, 0.056 mmol), and *N*,*N*-diisopropylethylamine (0.1 mL, 0.574 mmol) was stirred in deoxygenated DMF (5 mL) at 50 °C for 24 h. The crude mixture was evaporated to dryness and purified by chromatography (SiO_2, hexane/ethyl acetate = 1/2), yielding a white solid. Yield: 0.240 g (0.481 mmol, 96%); mp = 116−118 °C. ^{1}H NMR (DMSO-d_6): δ = 7.90 (s, 1H), 6.59 (s, 2H), 5.18 (s, 2H), 4.62 (s, 2H), 4.32 (t, 2H), 3.01 (s, 2H), 1.78 (m, 2H), 1.27 (m, 30H), 0.89 (t, 3H).

Synthesis of 5-(4-Azidobenzoylamino)-*N*,*N*′-bis(6-octanoylaminopyridin-2-yl)isophthalamide (13a). A solution of 5-amino-*N*,*N*′-bis(6-octanoylaminopyridin-2-yl)isophthalamide[33] (0.300, 0.487 mmol) and *N*,*N*-diisopropylethylamine (0.09 mL, 0.536 mmol) in dry THF (10 mL) was cooled to 0 °C. A solution of 4-azidobenzoyl chloride[34] (0.097 g, 0.536 mmol) in dry THF (2 mL) was slowly added to the reaction mixture. The ice bath was removed and the solution stirred overnight. The mixture was evaporated to dryness, solubilized in ethyl acetate, extracted twice with water, dried over sodium sulfate, filtered, and evaporated to dryness again. The crude product was purified by chromatography (SiO_2, chloroform/ethyl acetate = 3/1), yielding **13a** as a brown solid. Yield: 0.253 g (0.333 mmol, 68%). ^{1}H NMR (DMSO-d_6): δ = 10.7 (s, 1H), 10.5 (s, 2H), 10.2 (s, 2H), 8.64 (s, 2H), 8.33 (s, 1H), 8.14 (d, 2H), 7.88 (m, 6H), 7.34 (d, 2H), 2.44 (t, 4H), 1.62 (m, 4H), 1.30 (m, 16H), 0.89 (t, 6H). ^{13}C NMR (DMSO-d_6): δ = 173.2, 166.1, 151.6, 151.0, 144.1, 141.1, 135.6, 131.6, 130.7, 124.1, 123.0, 120.1, 111.2, 111.0, 37.1, 32.1, 29.6, 29.5, 26.0, 23.1, 14.9.

Synthesis of 5-(4-Ethynylbenzoylamino)-*N*,*N*′-bis(6-octanoylaminopyridin-2-yl)isophthalamide (13b). A solution of 5-amino-*N*,*N*′-bis(6-octanoylaminopyridin-2-yl)isophthalamide[33] (0.270, 0.438 mmol) and *N*,*N*-diisopropylethylamine (0.37 mL, 1.929 mmol) in dry THF (10 mL) was cooled to 0 °C. A solution of 4-ethynylbenzoyl chloride[ ] (0.316 g, 1.920 mmol) in dry THF (5 mL) was slowly added to the reaction mixture. The ice bath was removed and the solution stirred overnight. The mixture was evaporated to dryness, solubilized in ethyl acetate, extracted twice with water, dried over sodium sulfate, filtered, and evaporated to dryness again. The crude product was purified by chromatography (SiO_2, chloroform/ethyl acetate = 2/1), yielding a brown solid. Yield: 0.231 g (0.311 mmol, 71%). ^{1}H NMR (DMSO-d_6): δ = 10.8 (s, 1H), 10.5 (s, 2H), 10.2 (s, 2H), 8.64 (s, 2H), 8.33 (s, 1H), 8.09 (d, 2H), 7.87 (m, 6H), 7.72 (d, 2H), 4.50 (s, 1H), 2.44 (t, 4H), 1.62 (m, 4H), 1.31 (m, 16H), 0.89 (t, 6H). ^{13}C NMR (DMSO-d_6): δ = 173.2, 166.1, 151.6, 151.0, 144.1, 140.6, 135.7, 132.8, 129.0, 126.1, 124.1, 123.2, 111.2, 111.0, 83.8, 72.2, 37.1, 32.1, 29.5, 26.0, 23.0, 14.9.

Synthesis of exo-*N*-(6-Bromohexyl)-7-oxabicyclo[2.2.1]-hept-5-ene-2,3-dicarboximide (20). A mixture of 1,6-dibromohexane (3.69 g, 15 mmol), potassium carbonate (2.07 g, 15 mmol), and exo-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (**5**) (0.250 g, 1.5 mmol) was stirred in deoxygenated and dry DMF (35 mL) at 50 °C for 4 h. The reaction mixture was evaporated to dryness in vacuo, the residue was solubilized in ethyl acetate, washed twice with water, dried over sodium sulfate, filtrated, and evaporated to dryness again. The crude product was purified by chromatography (SiO_2, hexane/ethyl acetate = 2/1), and pure **20** was obtained as a colorless oil. Yield: 0.392 g (1.19 mmol, 80%). ^{1}H NMR ($CDCl_3$): δ = 6.49 (s, 2H), 5.24 (s, 2H), 3.45 (t, 2H), 3.36 (t, 2H), 2.82 (s, 2H), 1.81 (m, 2H), 1.55 (m, 2H), 1.42 (m, 2H), 1.26 (m, 2H). ^{13}C NMR ($CDCl_3$): δ = 176.2, 136.5, 80.9, 47.3, 38.7, 33.7, 32.4, 27.5, 27.3, 25.7.

General Polymerization Procedure for Homopolymers 15−19 and 21−23. This procedure describes the polymerization of monomers **5**−**11** and **20** for about 50−200 mg monomer conversion. For every monomer one procedure is described in depth, while all accounts are summarized in Table 1. The catalyst was dissolved in the least possible amount of solvent; in cases of poor solubility the catalyst solution was sonicated for 5 min. To a monomer solution of about 3−5 mL solvent, the solution of the catalyst was transferred quickly at room temperature, and the reaction mixture was stirred vigorously for about 15−20 min (monomer conversion was monitored by TLC). The polymer was quenched with 0.1 mL of ethyl vinyl ether (high excess) and purified by precipitation.

Preparation of Polymer 15. To a solution of exo-*N*-[6-(5-methyl-2,4-dioxo-3,4-dihydro-2*H*-pyrimidin-1-yl)hexyl]-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide **(6)** (33.5 mg, 0.090 mmol) in THF (3 mL) a solution of catalyst **1** (14.8 mg, 0.018 mmol) in THF (2 mL) was added quickly, and the reaction mixture was stirred vigorously for 15 min. The polymer was quenched with 0.1 mL of ethyl vinyl ether, the crude material was evaporated to dryness, and polymer **15** was precipitated twice from THF in methanol. Yield: 28 mg (85%). ^{1}H NMR ($CDCl_3$): $\delta = 9.72$ (s, 1H), 6.98 (s, 1H), 6.06 (s, 1.7H, trans), 5.78 (s, 0.3H, cis), 5.01 (s, 0.3H, cis), 4.46 (s, 1.7H, trans), 3.66 (s, 2H), 3.45 (s, 2H), 3.32 (s, 2H), 1.89 (s, 3H), 1.46 (m, 4H), 1.27 (m, 4H).^{13}C NMR ($CDCl_3$): $\delta = 175.7$, 164.6, 160.3, 156.8, 151.0, 140.5, 130.9, 128.6, 126.7, 110.6, 81.0, 52.3, 28.8, 27.6, 26.0, 25.6, 12.3. GPC (THF, polystyrene standards): $M_n = 2190$ Da (calculated $M_n = 1867$ Da), PDI = 1.2, cis/trans ratio = 85% trans (determined by ^{1}H NMR).

Preparation of Polymer 16. To a solution of exo-*N*-hexyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide **(8)** (50 mg, 0.201 mmol) in CH_2Cl_2 (3 mL) a solution of catalyst **1** (10.7 mg, 0.013 mmol) in CH_2Cl_2 (2 mL) was added quickly, and the reaction mixture was stirred vigorously for 15 min. The polymer was quenched with 0.1 mL of ethyl vinyl ether, the crude material was evaporated to dryness, and polymer **16** was precipitated twice from THF in methanol. Yield: 43 mg (87%). ^{1}H NMR ($CDCl_3$): $\delta = 6.04$ (s, 1.5H, trans), 5.76 (s, 0.5H, cis), 5.00 (s, 0.5H, cis), 4.43 (s, 1.5H, trans), 3.43 (t, 2H), 3.28 (s, 2H), 1.52 (m, 2H), 1.24 (m, 6H), 0.84 (t, 2H). ^{13}C NMR ($CDCl_3$): $\delta = 175.6$, 135.7, 131.8, 130.8, 128.5, 128.2, 126.7, 80.9, 53.3, 52.2, 38.8, 31.1, 27.5, 26.3, 22.3, 13.9. GPC (THF, polystyrene standards): $M_n = 2881$ Da (calculated $M_n = 3989$ Da), PDI = 1.2, cis/trans ratio = 75% trans (determined by ^{1}H NMR).

Preparation of Polymer 17. To a solution of exo-*N*-{1-[6-(5-methyl-2,4-dioxo-3,4-dihydro-2*H*-pyrimidin-1-yl)hexyl]-1*H*-[1,2,3]triazol-4-ylmethyl}-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide **(9)** (50 mg, 0.110 mmol) in CH_2Cl_2 (3 mL) a solution of catalyst **1** (9.0 mg, 0.011 mmol) in CH_2Cl_2 (2 mL) was added quickly, and the reaction mixture was stirred vigorously for 15 min. The polymer was quenched with 0.1 mL of ethyl vinyl ether, the crude material was evaporated to dryness, and polymer **17** was precipitated twice from THF in hexane. Yield: 39 mg (78%). ^{1}H NMR (DMSO-d_6): $\delta = 11.2$ (s, 1H), 7.92 (s, 1H), 7.54 (s, 1H), 5.98 (s, 1.5H, trans), 5.77 (s, 0.5H, cis), 5.00 (s, 0.5H, cis), 4.62 (s, 2H), 4.48 (s, 1.5H, trans), 4.33 (t, 2H), 3.61 (t, 2H), 1.77 (m, 5H), 1.56 (m, 2H), 1.26 (m, 4H). ^{13}C NMR (DMSO-d_6): $\delta = 176.2$, 165.3, 151.8, 142.4, 132.1, 124.1, 109.0, 81.4, 50.2, 48.2, 34.5, 30.5, 29.2, 26.4, 12.9. GPC (THF, polystyrene standards): $M_n = 1590$ Da (calculated $M_n = 4545$ Da), PDI = 1.1, cis/trans ratio = 65% trans (determined by ^{1}H NMR).

Preparation of Polymer 18. To a solution of 5-{4-[exo-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximidyl)-4-ylmethyl) [1,2,3]triazol-1-yl]benzoylamino}-*N,N'*-bis(6-octanoylamino-pyridin-2-yl)isophthalamide **10** (80 mg, 0.083 mmol) in THF (4 mL) a solution of catalyst **1** (7.3 mg, 0.009 mmol) in THF (2 mL) was added quickly, and the reaction mixture was stirred vigorously for 15 min. The polymer was quenched with 0.1 mL of ethyl vinyl ether, the crude material was evaporated to dryness, and polymer **18** was precipitated twice from CH_2Cl_2 in hexane. Yield: 39 mg (49%). ^{1}H NMR (DMSO-d_6): $\delta =$ 10.81 (s, 1H), 10.43 (s, 2H), 10.10 (s, 2H), 8.81 (s, 1H), 8.63 (s, 2H), 8.40−8.00 (m, 5H), 7.86 (m, 6H), 6.06 (s, 1.5H, trans), 5.84 (s, 0.5H, cis), 5.01 (s, 0.5H, cis), 4.78 (s, 2H), 4.59 (s, 1.5H, trans), 3.53 (s, 2H), 2.43 (t, 4H), 1.61 (m, 4H), 1.29 (m, 16H), 0.88 (t, 6H). ^{13}C NMR (DMSO-d_6): $\delta = 176.1$, 173.1, 166.0, 151.5, 151.0, 141.0, 140.6, 137.50, 135.6, 130.4, 124.1, 120.6, 111.1, 110.9, 81.4, 52.6, 37.1, 32.1, 29.5, 25.9, 23.0, 14.9. GPC (THF, polystyrene standards): $M_n = 6180$ Da (calculated $M_n = 8677$ Da), PDI = 1.3, cis/trans ratio = 75% trans (determined by ^{1}H NMR).

Preparation of Polymer 19. To a solution of exo-*N*-(1-octadecyl-1*H*-[1,2,3]triazol-4-ylmethyl)-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide **(11)** (81 mg, 0.162 mmol) in CH_2Cl_2 (3 mL) a solution of catalyst **1** (15.3 mg, 0.019 mmol) in CH_2Cl_2 (2 mL) was added quickly, and the reaction mixture was stirred vigorously for 15 min. The polymer was quenched with 0.1 mL of ethyl vinyl ether, the crude material was evaporated to dryness, and polymer **19** was precipitated twice from CH_2Cl_2 in methanol. Yield: 75 mg (92%). ^{1}H NMR ($CDCl_3$): $\delta = 7.50$ (s, 1H), 5.96 (s, 1.5H, trans), 5.70 (s, 0.5H, cis), 4.93 (s, 0.5H, cis), 4.67 (s 2H), 4.44 (s, 1.5H, trans), 4.22 (t, 2H), 3.31 (s, 2H), 1.80 (m, 2H), 1.18 (m, 30H), 0.80 (t, 3H). ^{13}C NMR ($CDCl_3$): $\delta = 175.0$, 141.3, 130.8, 122.5, 80.6, 52.2, 50.3, 33.9, 31.8, 30.1, 29.6, 29.3, 29.2, 28.9, 26,4, 22.5, 14.0. GPC (THF, polystyrene standards): $M_n = 5340$ Da (calculated $M_n = 4987$ Da), PDI = 1.1, cis/trans ratio = 77% trans (determined by ^{1}H NMR).

Preparation of Polymer 21. To a solution of exo-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide **(5)** (150 mg, 0.908 mmol) in THF (3 mL) a solution of catalyst **1** (50 mg, 0.061 mmol) in THF (2 mL) was added quickly, and the reaction mixture was stirred vigorously for 15 min. The polymer was quenched with 0.1 mL of ethyl vinyl ether, the crude material was evaporated to dryness, and polymer **21** was precipitated twice from THF in methanol. Yield: 120 mg (80%). ^{1}H NMR (DMSO-d_6): $\delta = 11.28$ (s, 1H), 5.95 (s, 1.6H, trans), 5.74 (s, 0.3H, cis), 4.91 (s, 0.3H, cis), 4.50 (s, 1.6H, trans), 3.37 (s, 2H). ^{13}C NMR (DMSO-d_6): $\delta = 178.4$, 132.1, 80.8, 55.3, 54.3. GPC (THF, polystyrene standards): $M_n = 2980$ Da (calculated $M_n = 2477$ Da), PDI = 1.1, cis/trans ratio = 85% trans (determined by ^{1}H NMR).

Preparation of Polymer 22. To a solution of exo-*N*-prop-2-ynyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide **(7)** (100 mg, 0.492 mmol) in CH_2Cl_2 (3 mL) a solution of catalyst **1** (41 mg, 0.049 mmol) in CH_2Cl_2 (2 mL) was added quickly, and the reaction mixture was stirred vigorously for 5 min. The polymer was quenched with 0.1 mL of ethyl vinyl ether, the crude material was evaporated to dryness, and polymer **22** was precipitated twice from THF in methanol. Yield: 82 mg (82%). ^{1}H NMR (DMSO-d_6): $\delta = 6.06$ (s, 1.6H, trans), 5.83 (s, 0.3H, cis), 4.93 (s, 0.3H, cis), 4.52 (s, 1.6H, trans), 4.18 (s, 2H), 3.52 (s, 2H), 2.00−1.60 (m, 1H). ^{13}C NMR (DMSO-d_6): $\delta = 175.6$, 131.9, 80.5, 78.5, 74.8, 52.9, 28.3. GPC (THF, polystyrene standards): $M_n = 2380$ Da (calculated $M_n = 2032$ Da), PDI = 1.5, cis/trans ratio = 85% trans (determined by ^{1}H NMR).

Preparation of Polymer 23. To a solution of exo-*N*-(6-bromohexyl)-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide **(20)** (150 mg, 0.457 mmol) in CH_2Cl_2 (3 mL) a solution of catalyst **1** (47 mg, 0.057 mmol) in CH_2Cl_2 (2 mL) was added quickly, and the reaction mixture was stirred vigorously for 15 min. The polymer was quenched with 0.1 mL of ethyl vinyl ether, the crude material was evaporated to dryness, and polymer **23** was precipitated twice from CH_2Cl_2 in methanol. Yield: 130 mg (87%). ^{1}H NMR ($CDCl_3$): $\delta = 6.07$ (s, 1.4H, trans), 5.79 (s, 0.6H, cis), 5.02 (s, 0.6H, cis), 4.45 (s, 1.4H, trans), 3.60−3.20 (m, 6H), 1.84 (m, 2H), 1.70−1.20 (m, 6H). ^{13}C NMR ($CDCl_3$): $\delta = 175.7$, 130.8, 81.0, 53.4, 52.3, 38.7, 33.6, 32.5, 27.6, 27.5, 25.9. IR (KBr): 2935, 2961, 1778, 1702, 1443, 1399, 1356, 1258, 1173, 1140, 1032, 968. GPC (THF, polystyrene standards): $M_n = 2980$ Da (calculated $M_n = 2477$ Da), PDI = 1.1, cis/trans ratio = 85% trans (determined by ^{1}H NMR).

Synthesis of Polymer 24. A solution of polymer **21** (32 mg, ∼0.011 mmol), propargyl bromide (0.15 mL, 1.94 mmol), and potassium carbonate (0.276 g, 1.94 mmol) was stirred at 50 °C in deaerated DMF (10 mL) for 8 h. The reaction mixture was evaporated to dryness, dispersed in chloroform, filtrated, and concentrated. Polymer **24** was purified by precipitation in methanol. Yield: 38 mg (∼96%). ^{1}H NMR (DMSO-d_6): $\delta =$ 6.01 (s, 1.6H, trans), 5.81 (s, 0.4H, cis), 4.90 (s, 0.4H, cis), 4.48 (s, 1.6H, trans), 4.19 (s, 2H), 3.52 (s, 2H), 2.00−1.70 (m, 1H). ^{13}C NMR ($CDCl_3$): $\delta = 175.6$, 131.9, 80.5, 78.5, 74.8, 52.9, 28.3. IR (KBr): 2937, 2964, 2098, 1783, 1708, 1440, 1400, 1356, 1239, 1160, 1142, 1035, 973, 922. GPC (THF, polystyrene standards): $M_n = 3535$ Da, PDI = 1.1, cis/trans ratio = 80% trans (determined by ^{1}H NMR).

Synthesis of Polymer 25. A solution of polymer **23** (0.130 g, ∼0.044 mmol) and sodium azide (0.163 g, 2.51 mmol) was stirred at 50 °C in deaerated DMF (10 mL) for 8 h. The reaction mixture was evaporated to dryness, dispersed in chloroform, filtrated, and concentrated. Polymer **25** was purified by precipitation in methanol. Yield: 0.099 g (∼76%). ^{1}H NMR ($CDCl_3$): δ = 6.03 (s, 1.5H, trans), 5.76 (s, 0.5H, cis), 5.00 (s, 0.5H, cis), 4.43 (s, 1.5H, trans), 3.44 (s, 2H), 3.23 (m, 4H), 1.56 (m, 4H), 1.32 (m, 4H). ^{13}C NMR ($CDCl_3$): δ = 175.5, 130.8, 82.2, 80.9, 53.3, 52.2, 51.1, 38.7, 28.6, 27.4, 26.2, 26.1. GPC (THF, polystyrene standards): M_n = 2624 Da, PDI = 1.2, cis/trans ratio = 85% trans (determined by ^{1}H NMR).

Synthesis of Polymer 26. A solution of polymer **24** (30 mg, ∼0.009 mmol), 1-(6-azidohexyl)-5-methyl-1*H*-pyrimidine-2,4-dione (**12a**) (0.081 g, 0.322 mmol), bromotris(triphenylphosphine)copper(I) (0.007 g, 0.007 mmol), and *N*,*N*-diisopropylethylamine (0.05 mL, 0.287 mmol) was stirred at 50 °C in deaerated DMF (5 mL) for 48 h. The crude polymer **26** was evaporated to dryness and precipitated twice from DMF in methanol. Yield: 61 mg (∼91%). ^{1}H NMR (DMSO-d_6): δ = 11.2 (s, 1H). 8.04 (s, 1H), 7.53 (s, 1H), 6.03 (s, 1.6H, trans), 5.80 (s, 0.4H, cis), 4.93 (s, 0.4H, cis), 4.67 (s, 2H), 4.50 (s, 1.6H, trans), 4.34 (t, 2H), 3.62 (t, 2H), 3.51 (s, 2H), 1.78 (m, 5H), 1.58 (m, 2H), 1.29 (m, 4H). ^{13}C NMR ($CDCl_3$): δ = 176.1, 165.1, 151.7, 142.2, 131.8, 123.8, 109.3, 80.6, 53.0, 50.1, 47.9, 30.4, 29.1, 26.3, 26.0, 12.8.

Synthesis of Polymer 27. A solution of polymer **24** (20 mg, ∼0.006 mmol), 5-(4-azidobenzoylamino)-*N*,*N*′-bis(6-octanoylaminopyridin-2-yl)isophthalamide (**13a**) (0.110 g, 0.145 mmol), bromotris(triphenylphosphine)copper(I) (0.014 g, 0.015 mmol), and *N*,*N*-diisopropylethylamine (0.025 mL, 0.144 mmol) was stirred at 50 °C in deaerated DMF (5 mL) for 48 h. The crude polymer **27** was evaporated to dryness and precipitated twice from THF in methanol. Yield: 84 mg (∼87%). ^{1}H NMR (DMSO-d_6): δ = 10.76 (s, 1H), 10.38 (s, 2H), 10.05 (s, 2H), 8.82 (s, 1H), 8.63 (s, 2H), 8.40−7.50 (m, 11H), 6.20−5.70 (m, 2H), 5.10−4.40 (m, 4H). 3.41 (s, 2H), 2.42 (t, 4H), 1.60 (m, 4H), 1.23 (m, 16H), 0.87 (t, 6H). ^{13}C NMR ($CDCl_3$): δ = 175.1, 173. 4, 172.1, 165.0, 150.5, 150.0, 140.0, 139.6, 138.6, 134.6, 133.9, 131.0, 129.5, 123.1, 121.4, 119.6, 110.1, 109.9, 79.7, 52.2, 48.5, 36.1, 31.1, 28.5, 24.9, 22.0, 13.8. GPC (THF, polystyrene standards): M_n = 10 930 Da, PDI = 1.5.

Synthesis of Polymer 28. A solution of polymer **24** (40 mg, ∼0.011 mmol), 1-azidooctadecane (**14a**) (0.116 g, 0.392 mmol), bromotris(triphenylphosphine)copper(I) (0.018 g, 0.020 mmol), and *N*,*N*-diisopropylethylamine (0.1 mL, 0.576 mmol) was stirred at 50 °C in deaerated DMF (5 mL) for 48 h. The crude polymer **28** was evaporated to dryness and precipitated twice from THF in methanol. Yield: 85 mg (∼87%). ^{1}H NMR ($CDCl_3$): δ = 7.56 (s, 1H), 6.20−5.60 (m, 2H), 5.10−4.00 (m, 6H), 3.35 (s, 2H), 1.85 (m, 2H), 1.23 (m, 30H), 0.86 (t, 3H). ^{13}C NMR ($CDCl_3$): δ = 175.0, 141.4, 130.9, 122.7, 80.6, 52.2, 50.4, 31.8, 30.2, 29.6, 29.4, 29.3, 29.0, 26.5, 22.6, 14.0. GPC (THF, polystyrene standards): M_n = 7615 Da, PDI = 1.2.

Synthesis of Polymer 29. A solution of polymer **25** (55 mg, ∼0.016 mmol), 5-methyl-1-prop-2-ynyl-1*H*-pyrimidine-2,4-dione (**12b**) (0.069 g, 0.420 mmol), bromotris(triphenylphosphine)copper(I) (0.019 g, 0.020 mmol), and *N*,*N*-diisopropylethylamine (0.1 mL, 0.576 mmol) was stirred at 50 °C in deaerated DMF (5 mL) for 48 h. The crude polymer **29** was evaporated to dryness and precipitated twice from DMF in methanol. Yield: 80 mg (∼93%). ^{1}H NMR (DMSO-d_6): δ = 11.3 (s, 1H), 8.08 (s, 1H), 7.62 (s, 1H), 6.01 (s, 1.6H, trans), 5.78 (s, 0.4H, cis), 4.91 (m, 2H + 0.4H, cis), 4.44 (s, 1.6H), 4.34 (t, 2H), 3.41 (m, 4H), 1.78 (m, 5H), 1.49 (m, 2H), 1.26 (m, 4H). ^{13}C NMR (DMSO-*d6*): δ = 176.7, 165.2, 151.6, 142.0, 132.0, 124.3, 109.8, 80.7, 52.9, 50.2, 43.1, 30.4, 27.8, 26.4, 12.8. IR (KBr): 3466, 3139, 3062, 2937, 2863, 1774, 1701, 1465, 1436, 1398, 1351, 1218, 1141, 1048, 914.

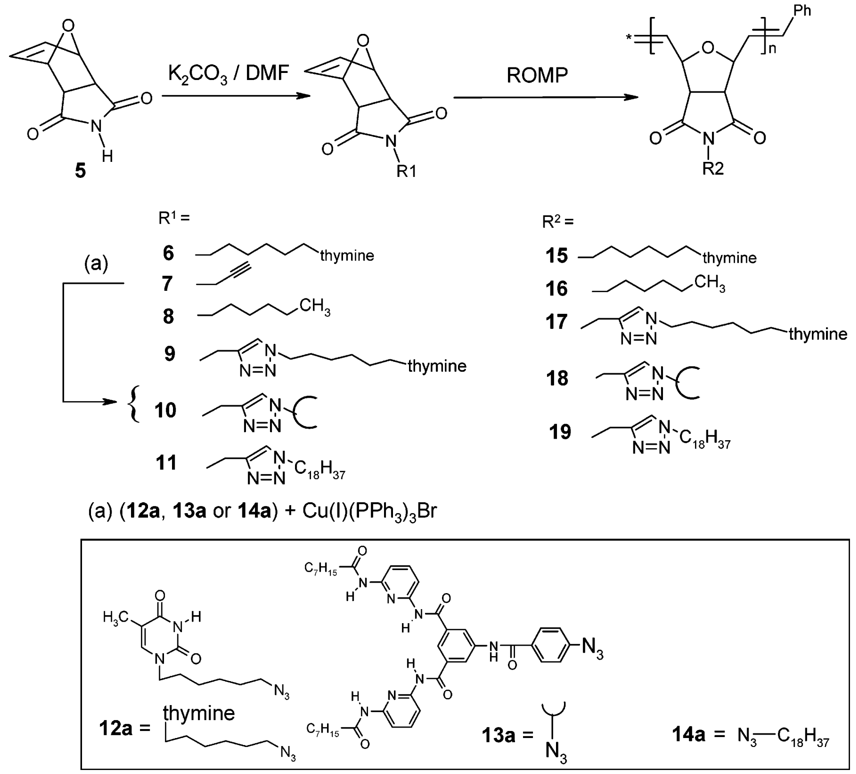
Synthesis of Polymer 30. A solution of polymer **25** (20 mg, ∼0.006 mmol), 5-(4-ethynylbenzoylamino)-*N*,*N*′-bis(6-octanoylaminopyridin-2-yl)isophthalamide (**13b**) (0.076 g, 0.102 mmol), bromotris(triphenylphosphine)copper(I) (0.006 g, 0.007 mmol), and *N*,*N*-diisopropylethylamine (0.01 mL, 0.058 mmol) was stirred at 50 °C in deaerated DMF (5 mL) for 48 h. The crude polymer **30** was evaporated to dryness and precipitated twice from THF in methanol. Yield: 59 mg (∼83%). ^{1}H NMR (DMSO-d_6): δ = 10.69 (s, 1H), 10.42 (s, 2H), 10.12 (s, 2H), 9.00−7.50 (m, 14H), 6.20−5.60 (m, 2H), 5.20−4.10 (m, 4H), 3.90−3.10 (m, 4H), 2.60−0.70 (m, 38H). ^{13}C NMR ($CDCl_3$): δ = 176.7, 173.1, 166.0, 151.5, 151.0, 146.3, 140.9, 135.5, 135.0, 134.0, 132.1, 129.4, 125.8, 124.0, 123.1, 111.1, 80.8, 53.0, 50.4, 37.0, 32.0, 30.3, 29.5, 29.4, 26.4, 25.9, 22.9, 14.8. IR (KBr): 3288, 2924, 2854, 1775, 1702, 1584, 1515, 1446, 1291, 1240, 1153, 1052, 799. GPC (THF, polystyrene standards): M_n = 8080 Da, PDI = 3.8.

Synthesis of Polymer 31. A solution of polymer **25** (50 mg, ∼0.014 mmol), 1-hexyne (**14b**) (0.028 g, 0.344 mmol), bromotris(triphenylphosphine)copper(I) (0.016 g, 0.017 mmol), and *N*,*N*-diisopropylethylamine (0.01 mL, 0.576 mmol) was stirred at 50 °C in deaerated DMF (5 mL) for 48 h. The crude polymer **31** was evaporated to dryness and precipitated twice from THF in diethyl ether. Yield: 58 mg (∼92%). ^{1}H NMR (DMSO-d_6): δ = 7.85 (s, 1H), 6.00 (s, 1.6H, trans), 5.77 (s, 0.4H, cis), 4.91 (s, 0.4H, cis), 4.45 (s, 1.6H, trans), 4.30 (t, 2H), 3.41 (m, 4H), 2.59 (t, 2H), 1.80 (m, 2H), 1.51 (m, 4H), 1.27 (m, 6H), 0.90 (t, 3H). ^{13}C NMR (DMSO-d_6): δ = 175.8, 131.3, 128.6, 126.6, 79.9, 52.0, 49.0, 31.0, 29.5, 26.8, 25.4, 24.6, 21.6, 13.6. IR (KBr): 2936, 2860, 1776, 1704, 1437, 1398, 1351, 1150, 1045, 968, 916. GPC (THF, polystyrene standards): M_n = 4770 Da, PDI = 1.5.

Synthesis of Block Copolymer 32. To a solution of exo-*N*-hexyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide **(8)** (84 mg, 0.337 mmol) in CH_2Cl_2 (3 mL) a solution of catalyst **1** (18 mg, 0.022 mmol) in CH_2Cl_2 (2 mL) was added quickly, and the reaction mixture was stirred vigorously for 15 min. After complete conversion of monomer **8** (as monitored by TLC) the reaction mixture was divided and one part was quenched with ethyl vinyl ether. A solution of exo-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide (**5**) (0.025 g, 0.151 mmol) in CH_2Cl_2 (2 mL) was transferred to the second part, the reaction mixture was stirred for another 15 min, and after complete conversion of the second monomer (**5**) the block copolymer was quenched with 0.1 mL of ethyl vinyl ether. The crude polymers were evaporated to dryness and precipitated twice from THF in methanol. Yield (block copolymer): 54 mg (∼81%). ^{1}H NMR (block copolymer) ($CDCl_3$): δ = 7.31 (s, N*H*), 6.08 (s, $CH_2{=}CH_2$, trans), 5.79 (s, $CH_2{=}CH_2$, cis), 5.03 (s, C*H*−O−C*H*, cis), 4.46 (s, C*H*−O−C*H*, trans), 3.45 (s, C*H*−C=O), 3.31 (t, N−CH_2), 1.54 (m, alkyl), 1.28 (m, alkyl), 0.87 (t, CH_3). ^{13}C NMR (block copolymer) (δ): δ = 175.8, 130.8, 81.0, 52.2, 38.9, 31.2, 27.6, 26.4, 22.4, 14.0. GPC (THF, polystyrene standards): $M_{n,\mathrm{homopoly}}$ = 2880 Da (calculated M_n = 2989 Da), $\mathrm{PDI}_{\mathrm{homopoly}}$ = 1.2, $M_{n,\mathrm{block-copoly}}$ = 4350 Da (calculated M_n = 6301 Da), $\mathrm{PDI}_{\mathrm{block-copoly}}$ = 1.2. cis/trans ratio = 80% trans (determined by ^{1}H NMR).

Synthesis of Block Copolymer 33. To a solution of exo-*N*-[6-(5-methyl-2,4-dioxo-3,4-dihydro-2*H*-pyrimidin-1-yl)hexyl]-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide **(6)** (34 mg, 0.090 mmol) in THF (3 mL) a solution of catalyst **1** (15 mg, 0.018 mmol) in THF (2 mL) was added quickly, and the reaction mixture was stirred vigorously for 15 min. After complete conversion of monomer **6** (as monitored by TLC) the reaction mixture was divided, and one part was quenched with ethyl vinyl ether. A solution of exo-*N*-hexyl-7-oxabicyclo[2.2.1]-hept-5-ene-2,3-dicarboximide **(8)** (0.034 g, 0.134 mmol) in THF (2 mL) was transferred to the second part, the reaction mixture was stirred for another 15 min, and after complete conversion of the second monomer (**8**) the block copolymer was quenched with 0.1 mL of ethyl vinyl ether. The crude polymers were evaporated to dryness and precipitated twice from THF in hexane. Yield (block copolymer): 41 mg (∼82%). ^{1}H NMR (block copolymer) ($CDCl_3$): δ = 9.70 (s, N*H*), 6.98 (s, C*H*=C− thymine), 6.06 (s, $CH_2{=}CH_2$, trans), 5.78 (s, $CH_2{=}CH_2$, cis), 5.01 (s, C*H*−O−C*H*, cis), 4.45 (s, C*H*−O−C*H*, trans), 3.66 (t, CH_2−N− thymine) 3.45 (s, C*H*−C=O), 3.32 (t, N−CH_2), 1.89 (m, CH_2−CH_2−N− thymine), 1.55 (m, alkyl), 1.27 (m, alkyl), 0.86 (t, CH_3). ^{13}C NMR (block copolymer) ($CDCl_3$): δ = 175.7, 164.6, 151.0, 140.5, 130.9, 110.6, 81.0, 52.3, 48.2, 39.0, 31.2, 28.8, 27.6, 26.4, 25.6, 22.4, 14.0, 12.3. GPC (THF, polystyrene standards): $M_{n,\mathrm{homopoly}}$ = 2190 Da (calculated M_n = 1867 Da), $\mathrm{PDI}_{\mathrm{homopoly}}$ = 1.2, $M_{n,\mathrm{block-copoly}}$ = 4700 Da (calculated M_n = 5607 Da), $\mathrm{PDI}_{\mathrm{block-copoly}}$ = 1.2, cis/trans ratio = 85% trans (determined by ^{1}H NMR).

Scheme 2



Synthesis of Block Copolymer 34. To a solution of exo-*N*-(6-bromohexyl)-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide **(20)** (0.210 g, 0.638 mmol) in CH_2Cl_2 (4 mL) a solution of catalyst **1** (0.050 g, 0.061 mmol) in CH_2Cl_2 (3 mL) was added quickly, and the reaction mixture was stirred vigorously for 15 min. After complete conversion of monomer **20** (as monitored by TLC) the reaction mixture was divided, and one part was quenched with ethyl vinyl ether. A solution of exo-*N*-hexyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide **(8)** (0.080 g, 0.322 mmol) in CH_2Cl_2 (2 mL) was transferred to the second part, the reaction mixture was stirred for another 15 min, and after complete conversion of the second monomer **8** the block copolymer was quenched with 0.2 mL of ethyl vinyl ether. The crude polymers were evaporated to dryness and precipitated twice from THF in methanol. Yield (block copolymer): 160 mg (~86%). ^{1}H NMR (block copolymer) ($CDCl_3$): δ = 6.04 (s, CH_2=CH_2, trans), 5.76 (s, CH_2=CH_2, cis), 4.99 (s, CH–O–CH, cis), 4.43 (s, CH–O–CH, trans), 3.66 (t, CH_2–N– thymine) 3.45 (s, CH–C=O), 3.37 (t, CH_2–Br), 3.28 (t, N–CH_2), 1.82 (m, CH_2–CH$_2$–Br), 1.51 (m, alkyl), 1.24 (m, alkyl), 0.84 (t, CH$_3$). ^{13}C NMR (block copolymer) ($CDCl_3$): δ = 175.7, 131.8, 80.9, 53.3, 52.2, 38.9, 33.6, 32.3, 31.1, 27.5, 26.3, 25.8, 22.3, 13.9. GPC (THF, polystyrene standards): $M_{\mathrm{n,homopoly}}$ = 2990 Da (calculated M_{n} = 3282 Da), PDI$_{\mathrm{homopoly}}$ = 1.1, $M_{\mathrm{n,block-copoly}}$ = 4580 Da (calculated M_{n} = 4986 Da), PDI$_{\mathrm{block-copoly}}$ = 1.1, cis/trans ratio = 75% trans (determined by ^{1}H NMR).

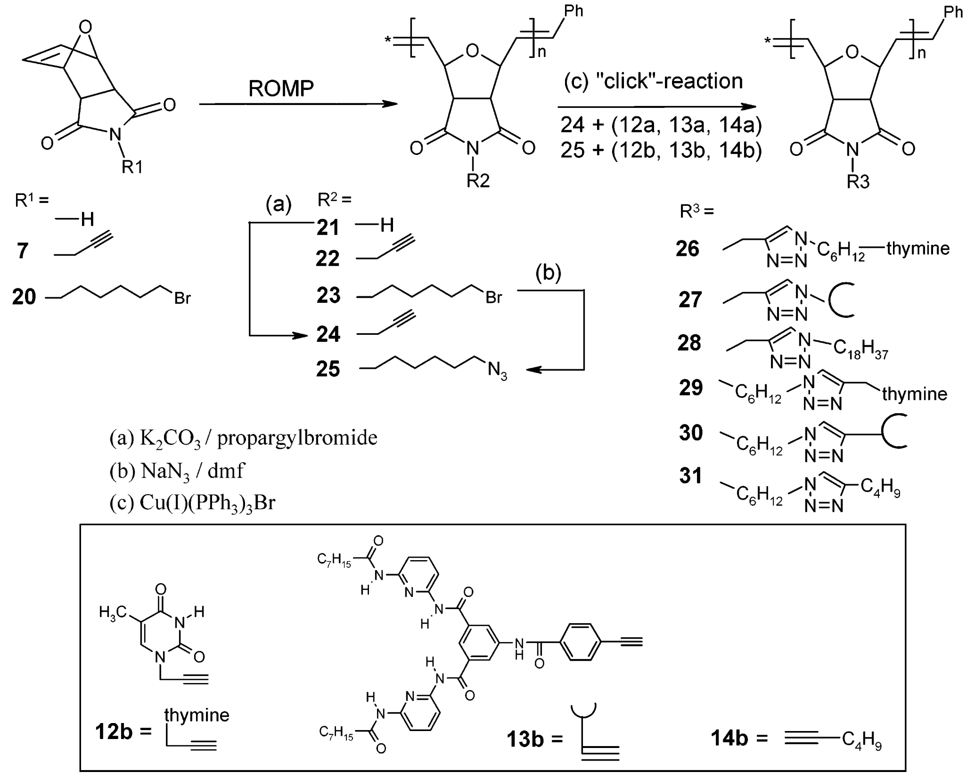
Results and Discussion

As outlined in Scheme 1, there are two approaches to combine ROMP with the Sharpless 1,3-dipolar cycloaddition ("click") reaction between azides and terminal acetylenes (1: "first ROMP–then click"). Appropriately functionalized monomers (we have used 7-oxynorbornenes) bearing an acetylene or ω-bromoalkyl moiety (R^1) can be prepared and polymerized, yielding homopolymers with azido or acetylenic side chains (R^2, R^3), respectively. Subsequent "click" reaction should then furnish the final functionalized polymers bearing the hydrogen bonding elements (R^4). Two questions are important within this reaction pathway: (a) will the azido or acetylenic moieties be compatible with the ROMP catalysts **1**–**4**, and (b) can the subsequent "click" reaction be combined with the polar moieties of the hydrogen bonding elements present in (R^4), thus allowing an efficient functionalization of the polymers (2: first "click"–then ROMP"). The second approach fixes the residues (R^4) before polymerization reactions, either by use of a conventional nucleophilic substitution reaction or via a "click" reaction. Afterward, the monomers bearing (R^4) are polymerized by the ROMP catalysts **1**–**4**. Here the primary question is whether the"click" reaction acts in competition to a 1,3-dipolar cycloaddition reaction onto the 5,6-double bond of the 7-oxynorbornene, thus competing the acetylene/azide cycloaddition reaction. We therefore have prepared a variety of monomers, following either pathway 1 or 2 to investigate the most efficient strategy for the preparation of hydrogen-bonded poly(oxynorbornenes).

Monomers. The synthesis of the monomers **6**–**11** (Scheme 2) starts from the imide **5**. Monomer **6** (bearing a *N*-6-(5-methyl-2,4-dioxo-3,4-dihydro-2*H*-pyrimidin-1-yl)hexyl moiety), monomer **7** (bearing a *N*-propargyl-moiety), and monomer **8** (bearing a simple *n*-hexyl moiety) can be prepared from **5** by simple nucleophilic substitution reaction using DMF/K$_2$CO$_3$ in 81%, 92%, and 98% yield, respectively. Using a similar conventional nucleophilic substitution protocol, monomer **20** (Scheme 3) (bearing a 6-bromohexyl moiety) was prepared from monomer **5** and 1,6-dibromohexane.

Starting from monomer **7**, a direct Sharpless "click" reaction with the building blocks **12a**, **13a**, and **14a** was probed, yielding the monomers **9**, **10**, and **11**. All reactions proceeded smoothly in DMF by use of bromotris(triphenylphosphine)copper(I) and *N*,*N*-diisopropylethylamine as the catalytic system, indicating quantitative conversion by NMR spectroscopy. Isolated yields

Scheme 3



ranged from 79% (**9**), 81% (**10**), to 96% (**11**) for the octadecyl azide (**14a**) as nonpolar moiety. Thus, it is demonstrated that the 1,3-dipolar cycloaddition represents an excellent tool to functionalize the 7-oxynorbornenes under these mild conditions nearly quantitatively. Changing 7-oxynorbornene to norbornene derivatives did not yield the desired products, since the concurring 1,3-dipolar addition to the 5,6-double bond of the norbornene was more pronounced than in the case of the corresponding oxynorbornene derivatives (data not shown). These results are in compliance with the higher ring strain in norbornenes in comparison to 7-oxynorbornenes,[35] thus favoring the addition to the 5,6-double bond over the acetylenic moiety. Thus, a norbornene derivative bearing an ω-azido moiety cannot be prepared.

Polymerization. Monomers **5**, **6**–**11**, and **20** were subjected to ROMP polymerization, furnishing the polymers **15**–**19** and **21**–**23**. Polydispersities and molecular weights are shown in Table 1. It is evident that in most cases the best results are achieved by use of the conventional Grubbs I catalyst **1**, yielding polymers with polydispersities in the range from 1.1 to 1.3. The Hoveyda-type catalyst **3** and **4** as well as the second-generation Grubbs catalyst **2** indicated less useful results. *N*-Propargyl-7-oxynorbornene (**7**) yields broad molecular weight distributions, although with a relatively defined molecular weight (entries 11 and 12). Clearly, this monomer cannot be used for the preparation of poly(oxynorbornenes) bearing reactive acetylenic side chains, presumably due to a competing reactivity of the acetylenic moiety with the ROMP catalyst. In line with previous investigations by Weck et al.[13,15,16] and Sleiman et al.[14, 19] are the results of monomer **6** bearing a thymine moiety at the chain end (entry 10): here a polydispersity of 1.2 is achieved with catalyst **1**, thus for the first time opening an efficient direct synthesis of poly(norbornenes) bearing pendant thymine side chains. The monomers bearing the triazole moiety (**9**, **10**) with the hydrogen bonding moieties (entries 18 and 19) yield polymers with low polydispersities. As evident by NMR spectroscopy, the triazole moieties are preserved throughout the ROMP process (resonances in ^{1}H NMR: 7.92 ppm (triazole-H)). The polymerization of monomer **9** (entry 18), however, is limited by its poor solubility of the final polymer in dichloromethane. In a similar manner, monomer **11** (bearing a nonpolar octadecyl moiety bound to the oxynorbornene via a triazole moiety, entry 20) can be polymerized with catalyst **1** with a narrow polydispersity. Thus, the “first click”–“then ROMP” methodology is a viable strategy to produce a variety of side chain-functionalized poly(oxynorbornenes) by the ROMP process.

Table 2. Results (M_n, M_w/M_n) Transformations of the ROMP Polymers 21 and 23–25

entry	polymer (educt)	M_n (educt)	PDI (educt)	polymer (product)	M_n (product)	PDI (product)
1	**21**	2540	1.1	**24**	3500	1.2
2	**21**	2990	1.1	**24**	3535	1.1
3	**21**	4020	1.1	**24**	5240	1.1
4	**23**	3070	1.1	**25**	3480	1.2
5	**23**	3170	1.1	**25**	3530	1.2
6	**23**	2990	1.1	**25**	3770	1.2
7	**23**	2975	1.1	**25**	2624	1.2
8	**24**	3535	1.1	**26**	*a*	*a*
9	**24**	3535	1.1	**27**	10930	1.5
10	**24**	3535	1.1	**28**	7615	1.2
11	**25**	3480	1.2	**29**	*a*	*a*
12	**25**	3480	1.2	**30**	8080	3.8
13	**25**	3480	1.2	**31**	4770	1.5

[a] No GPC in THF possible.

Alternatively, we have investigated the “first ROMP”–then “click” approach (Scheme 3). Here, monomer **20** is polymerized best by Grubbs I **1** catalyst in dichloromethane, yielding polymer **23** in high yield and with narrow polydispersities. Subsequent transformation of

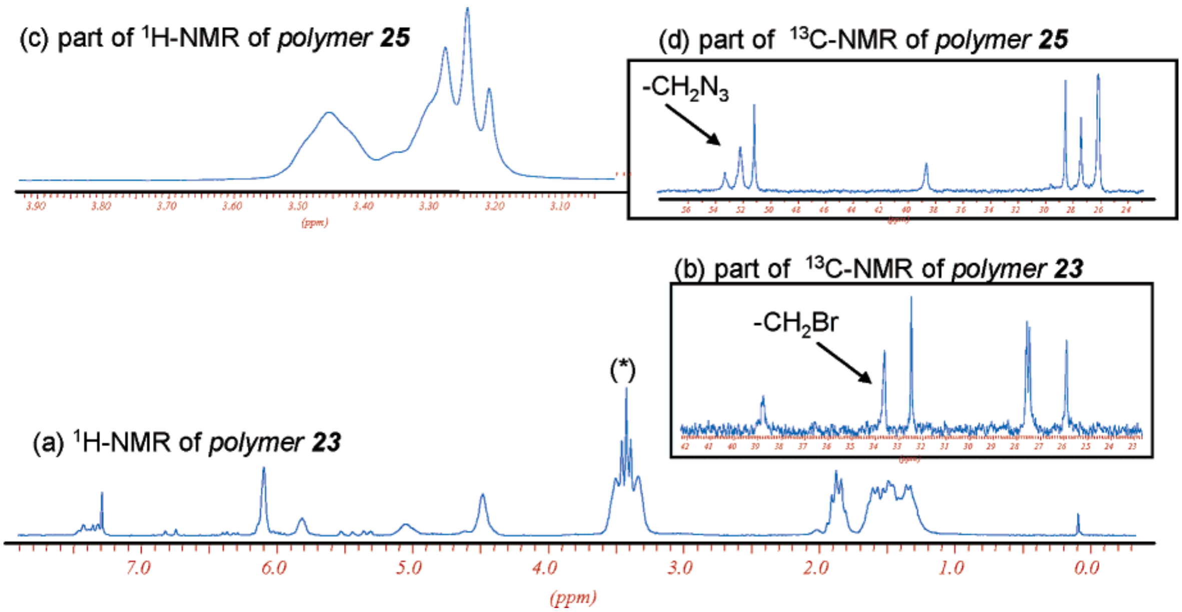


Figure 1. ^{1}H and ^{13}C NMR spectra for the substitution from polymer **23** to polymer **25**. (a) ^{1}H NMR of polymer **23**. (b) ^{13}C NMR of polymer **23**. (c) ^{1}H NMR (region between 4.0 and 5.0 ppm) of polymer **25**. (d) ^{13}C NMR (aliphatic region) of polymer **25**.

Table 3. Results (M_n, M_w/M_n) of the Diblock Copolymers 32−34

monomer 1	monomer 2	catalyst	polymer	$M_{n,homo,th}$	$M_{n,homo,GPC}$	PDI_{homo}	$M_{n,block,th}$	$M_{n,block,GPC}$	PDI block	solvent
8	**5**	**1**	**32**	2989	2880	1.2	6301	4350	1.2	CH_2Cl_2
6	**8**	**1**	**33**	1867	2190	1.2	5607	4700	1.2	CH_2Cl_2
20	**8**	**1**	**34**	3282	2987	1.1	4986	4580	1.1	CH_2Cl_2

polymer **23** with NaN_3/DMF furnishes the azido-functionalized polymer **25** in quantitative yield (see Figure 1 and Table 2). This postmodification process is highly efficient, in that the ω-bromohexyl moieties are quantitatively exchanged against the ω-azidohexyl moieties as visible in ^{1}H NMR (3.35 ppm for the $-CH_2-Br$ vs 3.24 ppm for the $-CH_2-N_3$). ^{13}C NMR was even more apt in monitoring the progress of the reaction. The resonance at 33.61 ppm ($-CH_2Br$ in polymer **23**) changes completely to 53.33 ppm ($-CH_2N_3$) in polymer **25**. A similar synthetic strategy was applied for the preparation of poly(oxynorbornenes) **24** bearing side-chain acetylenic groups: Since the direct polymerization of monomer **7** was not satisfactory, polymer **21** was modified with propargyl bromide/K_2CO_3 in DMF, furnishing polymer **24** in quantitative yield. Again the conversion was proven by ^{1}H NMR spectroscopy. As shown in Table 2, there is no change in the polydispersities during these modification processes (i.e., transformation of polymer **21** to polymer **24** (entries 1−3); transformation of polymer **23** to polymer **25** (entries 4−7)).

Polymers **24** and **25** were then subjected to “click” reactions using monomers **12a**, **13a**, and **14a** as well as monomers **12b**, **13b**, and **14b**. Completeness of the functional group transformation was proven by several methods: (a) NMR spectroscopy indicates the loss of the acetylenic groups in polymer **24** (1.7−2.0 ppm) as well as the azido moieties in polymer **25** (3.44 ppm) during the reaction. In parallel, new resonances corresponding to the CH_2-triazole moiety appear at 4.33 and 4.91 ppm, together with the triazole-H at 8.08 ppm (see Supporting Information). ^{13}C NMR spectroscopy shows the triazole resonances (polymer **29**) at 142.0 and 124.3 ppm. (b) IR spectroscopy shows a complete loss of the azido moiety (2100 cm^{-1}) in polymer **25** during reaction. (c) The NMR spectra of the final product polymers **26**−**28** and **29**−**31** are in accordance with the attachment of the functional groups (see Experimental Section and Supporting Information). (d) There is a dramatic change in solubility of all polymers, in particular polymers **26** and **29** (those bearing the complex hydrogen bonding pattern).

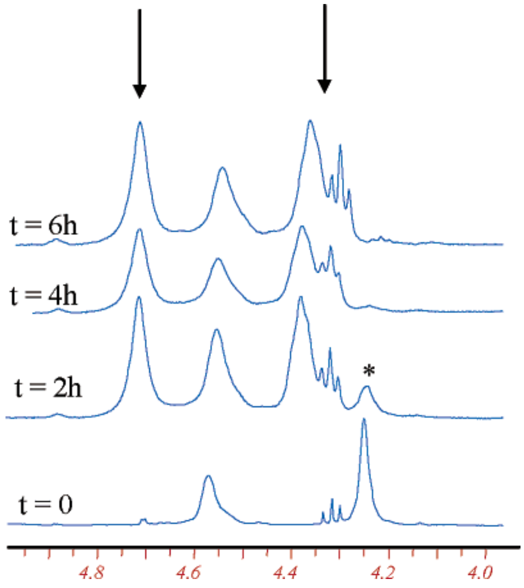
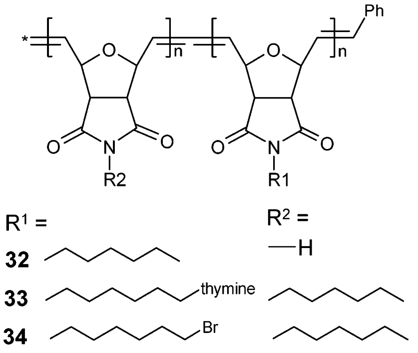


Figure 2. Kinetic progress of the Sharpless “click” reaction from polymer **24** in polymer **28**. ^{1}H NMR spectra were taken directly in perdeuterated DMF with polymer **24**, 1-octadecyl azide (**14a**), and Cu(I)(PPh$_3$)$_3$Br. Time scale: $t = 0$, $t = 2$ h, $t = 4$ h, $t = 6$ h. The $-N-CH_2$-acetylene resonance of polymer **24** is marked with a (*) and the new resonances of polymer **28** with an arrow.

We have also studied the kinetic progress of the Sharpless click reaction monitoring the reaction of polymer **24** with 1-octadecylazide (**14b**) by ^{1}H NMR

Scheme 4



spectroscopy (see Figure 2). The reaction starts quickly and indicates the loss of the N$-$CH$_2$-acetylene moiety (4.24 ppm (*)) within 4 h. As the reaction progresses, the $-$N$-$CH$_2$-triazole resonance (4.72 ppm) as well as the $-$CH$_2$-triazole resonance (4.3$-$4.4 ppm) emerges (both marked with an arrow in Figure 2). This altogether shows that the "click" reaction proceeds relatively fast, clean, and with high efficiency.

As a first step toward the extension of our concept to block copolymers, we have prepared the diblock copolymers **32**$-$**34**, as shown in Scheme 4 and Table 3. In particular, low polydispersities of polymer **34** will offer future transfer of the before mentioned concept toward block copolymers.

Conclusion

In the present paper we have demonstrated the efficient combination of the ROMP process with a subsequent 1,3-dipolar cycloaddition process (Sharpless "click" reaction). Two approaches can be used to achieve a modular synthetic approach toward side-chain modified poly(oxynorbornenes): (a) applying the "click" reaction to 7-oxynorbornenes bearing an acetylenic moiety (i.e., transforming monomer **7** into monomers **9**$-$**11**) and subsequently polymerizing by use of catalyst **1** to yield polymers **16**$-$**19**. (b) Applying the ROMP process to monomers **5** and **20** and subsequently transforming the polymers to the corresponding azido and acetylenic polymers **24** and **25**. The following click reaction then furnished the final polymers **26**$-$**31** bearing hydrogen bonding donor/acceptor moieties or simple hydrophobic residues. Both strategies complement existing synthetic methodologies and represent an excellent method for the functionalization of poly(oxynorbornenes) with a high tolerance of functional groups. Investigations to transfer this methodology toward block copolymers are currently conducted in our laboratories.

Acknowledgment. We thank the Austrian Science Fund (FWF, Project 14844-CHE) for financial support.

Supporting Information Available: NMR spectra of **7**, **9**, **10**, **11** and the polymers **19**, **21**, **23**, **25**, **26**, and **29**; IR spectra of polymers **23**, **25**, **29**, **30**, and **31**; and GPC traces of polymers **21**, **23**, **24**, **25**, and **28**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Grubbs, R. H. *Handbook of Metathesis*; Wiley VCH: New York, 2003; Vol. 3.

(2) For recent reviews see: (a) Riegler, S.; Slugovc, C.; Trimmel, G.; Stelzer, F. *Macromol. Symp.,* in press. (b) Slugovc, C. *Macromol. Rapid Commun.* **2004**, *25*, 1238$-$1297.

(3) Watson, K. J.; Park, S.-J.; Im, J.-H.; Nguyen, S. T. *Macromolecules* **2001**, *34*, 3507$-$3509.

(4) Mortell, K. H.; Gingras, M.; Kiessling, L. L. *J. Am. Chem. Soc.* **1994**, *116*, 12053$-$3509.

(5) (a) Micklefield, J. *Curr. Med. Chem.* **2001**, *8*, 1157$-$1179. (b) Han, M. J.; Chang, J. Y. *Adv. Polym. Sci.* **2000**, *153*, 1$-$36. (c) Gibson, V. C.; Marshall, E. L.; North, M.; Robson, D. A.; Williams, P. J. *Chem. Commun.* **1997**, 1095$-$1096. (d) Davies, R. G.; Gibson, V. C.; Hursthouse, M. B.; Light, M. E.; Marshall, E. L.; North, M.; Robson, D. A.; Thompson, I.; White, A. J. P.; Williams, D. J.; Williams, P. J. *J. Chem. Soc., Perkin. Trans. 1* **2001**, 3365$-$3381.

(6) Maynard, H. D.; Sheldon, Y. O.; Grubbs, R. H. *Macromolecules* **2000**, *33*, 6239$-$6248.

(7) Percec, V.; Schlueter, D.; Ronda, J. C.; Johansson, G.; Ungar, G.; Zhou, J. P. *Macromolecules* **1996**, *29*, 1464$-$1472.

(8) Nyce, G. W.; Glauser, T.; Connor, E. F.; Mock, A.; Waymouth, R. M.; Hedrick, J. L. *J. Am. Chem. Soc.* **2003**, *125*, 3046$-$3056. (b) Allcock, H. R.; deDenus, C. R.; Prange, R.; Laredo, W. R. *Macromolecules* **2001**, *34*, 2757$-$2765.

(9) (a) Ky Hirschberg, J.; Brunsveld, L.; Ramzi, A.; Vekemans, J. A. J.; Sijbesma, R. P.; Meijer, E. W. *Nature (London)* **2000**, *38*, 2870$-$2872. (b) Sartorius, J.; Schneider, H.-J. *Chem.—Eur. J.* **1996**, *11*, 1446$-$1452. (c) Farnik, D.; Kluger, C.; Kunz, M. J.; Machl, D.; Petraru, L.; Binder, W. H. *Macromol. Symp.* **2004**, *217*, 247$-$266. (d) Binder, W. H. *Monatsh. f. Chemie* **2004**, in press.

(10) Schubert, U. S.; Eschbaumer, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 2892$-$2926.

(11) Meyer, E.; Castellano, R. K.; Diederich, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 1210$-$1250.

(12) Bergbreiter, D. E. *Angew. Chem., Int. Ed.* **1999**, *38*, 2870$-$2872.

(13) Higley, M. N.; Pollino, J. M.; Hollenbeak, E.; Weck, M. *Polym. Prepr.* **2003**, *44*, 463.

(14) Bazzi, H. S.; Sleiman, H. F. *Macromolecules* **2002**, *35*, 9617$-$9620.

(15) (a) Stubbs, L. P.; Adams, J.; Weck, M. *Polym. Prepr.* **2002**, *43*, 545. (b) Stubbs, L. P.; Weck, M. *Chem.—Eur. J.* **2003**, *9*, 992$-$999.

(16) Pollino, J. M.; Stubbs, L. P.; Weck, M. *Macromolecules* **2003**, *36*, 2230$-$2234.

(17) Bazzi, H. S.; Bouffard, J.; Sleiman, H. F. *Macromolecules* **2003**, *36*, 7899$-$7902.

(18) Drechsler, U.; Thibault, R. J.; Rotello, V. M. *Macromolecules* **2002**, *35*, 9621$-$9623.

(19) Bazzi, H. S.; Bouffard, J.; Sleiman, H. F. *Polym. Prepr.* **2002**, *43*, 1081$-$1082.

(20) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004$-$2021.

(21) Recent examples: (a) Lee, L. V.; Mitchell, M. L.; Huang, S.-J.; Fokin, V. V.; Sharpless, K. B.; Wong, C.-W. *J. Am. Chem. Soc.* **2003**, *125*, 9588$-$9589. (b) Wang, Q.; Chan, T. R.; Hilgraf, R.; Fokin, V. V.; Sharpless, K. B.; Finn, M. G. *J. Am. Chem. Soc.* **2003**, *125*, 3192$-$3193. (c) Demko, Z. P.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2113$-$2116. (d) Demko, Z. P.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2110$-$2113. (e) Perez-Balderas, F.; Ortega-Munoz, M.; Morales-Sanfrutos, J.; Hernandez-Mateo, F.; Calvo-Flores, F. G.; Calvo-Asin, J. A.; Isac-Garcia, J.; Santoyo-Gonzales, F. *Org. Lett.* **2003**, *5*, 1951$-$1954. (f) Tornoe, C. W.; Christensen, C.; Meldal, M. *J. Org. Chem.* **2002**, *67*, 3057$-$3064. (g) Speers, A. E.; Cravatt, B. F. *Chem. Biol.* **2004**, *11*, 535$-$546. An older example of the reaction: Huisgen, R.; Szeimies, G.; Möbius, L. *Chem. Ber.* **1967**, *100*, 2494$-$2507.

(22) Tsarevsky, N. V.; Dufour, B.; Matyjaszewski, K. *Polym. Prepr.* **2004**, *45*, 1065$-$1066.

(23) O'Reilly, R. K.; Hawker, C. J.; Wooley, K. L. *Polym. Prepr.* **2004**, *45*, 780.

(24) Scheel, A. J.; Komber, H.; Voit, B. I. *Macromol. Rapid Commun.* **2004**, *25*, 1175$-$1180.

(25) Lee, J. K.; Shik, Y.; Chio, I. S. *Langmuir* **2004**, *20*, 3844$-$3847.

(26) Lummerstorfer, T.; Hoffmann, H. *J. Phys. Chem. B* **2004**, *108*, 3963$-$3966.

(27) (a) Binder, W. H.; Kunz, M. J.; Kluger, C.; Hayn, G.; Saf, R. *Macromolecules* **2004**, *37*, 1749$-$1759. (b) Kunz, M. J.; Hayn, G.; Saf, R.; Binder, W. H. *J. Polym. Sci., Part A: Chem.* **2004**, *42*, 661$-$674. (c) Binder, W. H.; Kunz, M. J.; Ingolic, E. *J. Polym. Sci., Part A: Chem.* **2004**, *42*, 162$-$172. (d) Kunz, M. J.; Machl, D.; Binder, W. H. *Polym. Prepr.* **2002**, *43* (2), 410$-$411.

(28) Kwart, H.; Burchuk, I. *J. Am. Chem. Soc.* **1952**, *74*, 3094.
(29) Dalphond, J.; Bazzi, H. S.; Kahrim, K.; Sleimna, H. F. *Macromol. Chem. Phys.* **2002**, *203*, 1988−1994.
(30) Wystrach, V. P.; Erickson, J, G. *J. Am. Chem. Soc.* **1953**, 6345−6346.
(31) Lindsell, W. E.; Murray, C.; Preston, P. N.; Woodman, T. A. J. *Tetrahedron* **2000**, *56*, 1233−1245.
(32) Summers, W. A.; Lee, J. Y.; Burr, J. G. *J. Org. Chem.* **1979**, *40*, 1559−1561.
(33) Zhang, S.-Q.; Fukase, K.; Izumi, M.; Fukase, Y.; Kusumoto, S. *Synlett* **2001**, *5*, 590−596.
(34) Ulbricht, M.; Hicke, H.-G. Angew. *Makromol. Chem.* **1993**, *210*, 69−95.
(35) Samuilov, Y. D.; Movchan, A. I.; Soloveva, S. E.; Konovalov, A. I. *J. Org. Chem. USSR* **1985**, *21*, 1618−1622. (b) Huisgen, R.; Szeimies, G.; Möbius, L. *Chem. Ber.* **1967**, *100*, 2494−2507.

MA0480087