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Two Distinct, Reactive Polymers Derived from a Single Norbornenyl−Methacryloyl Bifunctional Monomer by Selective ATRP or ROMP

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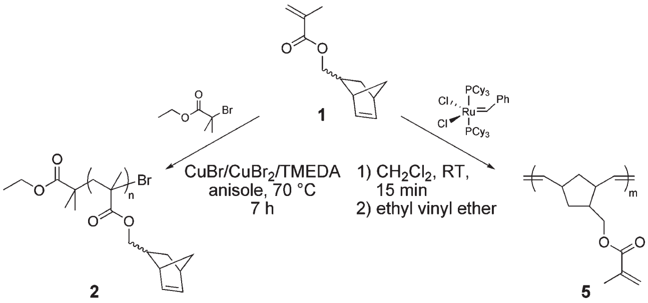
The synthesis of well-defined polymers bearing reactive functionalities has great importance because of their potential capabilities as building blocks for the construction of smart materials and advanced macromolecular architectures. Decoration of functionalities along a polymer backbone, which can be achieved by the direct polymerization of functional monomers, can incorporate high densities of groups for ultimate utility in modification of polymer compositions, structures, and properties. Direct polymerization of functional monomers also provides for an atom efficient route toward complex materials, relative to postpolymerization modification reactions or protection−deprotection strategies. In this work, we were interested in the production of two distinctly different polymers, in terms of their backbone structures and side chain functionalities, by direct, selective, orthogonal polymerizations of a single bifunctional monomer.

Recently, both controlled radical polymerization (CRP) and ring-opening (metathesis) polymerization (RO(M)P) have been shown to be effective methods to synthesize functional polymers bearing terminal alkenyl,[1−4] cycloalkenyl,[5,6] norbornenyl,[7,8] alkynyl,[9−12] and methacryloyl pendant groups.[13−17] Moreover, these two polymerization mechanisms can proceed orthogonally. Therefore, a bifunctional monomer of this study was designed as a single monomer bearing both a CRP-reactive and a ROMP-reactive unit to allow for either CRP or ROMP to be performed. Specifically, conditions were optimized to achieve selective atom transfer radical polymerization (ATRP) and ROMP of 5-norbornene-2-methylene methacrylate (**1**), a bifunctional monomer having both a methacryloyl (MA) unit (ATRP reactive) and a norbornenyl (Nb) unit (ROMP reactive). In addition to interesting aspects of selective polymerizations of this monomer, the resulting polymers from one single monomer possess different types of backbone structures, functional side chain units, and properties (Scheme 1). For instance, while this work was under review, Li and co-workers reported reversible addition−fragmentation chain transfer (RAFT) polymerization of this bifunctional monomer, aiming to obtain unique norbornenyl-functionalized hyperbranched structures;[18] in our study, however, we were interested in the preparation of well-defined functional linear polymers.

The radical polymerization of the methacrylate headgroup, uniquely, in the presence of the norbornenyl group, was investigated initially. Since the bifunctional monomer **1** has a MA group and a Nb functionality, radical polymerization of **1** could be considered as copolymerization of two types of unsaturations. Quantitative analysis using Alfrey−Price equations[19] and the Q and e values (MA: $Q_1 = 0.78$, $e_1 = 0.45$; Nb: $Q_2 = 0.02$, $e_2 = -1.00$) gave estimated reactivity ratios of $r_1 \approx 20$ and $r_2 \approx 0.006$. These values indicate that the MA groups have significantly higher reactivities than do the Nb groups and further suggest that the radical polymerization of **1** is essentially a homopolymerization of the substituted MA groups.

Scheme 1. Selective Polymerization of 1 by Either ATRP or ROMP To Afford Two Distinctly Different Reactive Polymers



Selective atom transfer radical homopolymerization of **1** was investigated by using ethyl 2-bromoisobutyrate (EBiB) as initiator, $CuBr/CuBr_2$/*N*,*N*,*N*′,*N*′′,*N*′′-pentamethyldiethylenetriamine (PMDETA) or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) as catalyst, and anisole (67 vol %) as solvent at 65−80 °C. ^1H NMR spectroscopy was used to determine the monomer conversions and number-averaged molecular weights (M_n). Gel permeation chromatography (GPC) was used to analyze the molecular weights and polydispersities (PDI). As shown in Table 1, less control of polymerization with relatively high PDIs was observed for the ATRP of **1** without $CuBr_2$ as a deactivator (entry 1), with highly active PMDETA as ligand (entries 1 and 2),[20] at high monomer conversions (>45%, entries 2 and 3) or at high temperature (80 °C, entry 4). Among all the entries, selective ATRP of **1** at 70 °C with a feed ratio of [**1**]:[EBiB]:[CuBr]:[$CuBr_2$]:[TMEDA] = 100:1:1:0.1:2 (entry 5), quenched at 7.0 h when conversion of **1** had reached 42%, resulted in Nb-functionalized poly(methacrylate), PNbMA, **2**, with a monomodal molecular weight distribution and a PDI of 1.14.

The well-defined structure of **2** was also verified by both ^1H NMR spectroscopy and GPC. As shown in Figure 1a, the ratio of the resonance intensities of the two norbornenyl protons vs methylene protons ($-OCH_2-$) in **2** was 1.99:2.00, indicating, essentially, an absence of side reactions on the pendant Nb groups. The molecular weight determined by GPC (M_n^{GPC}) was measured to be 8270 Da, in good agreement with the theoretical value ($M_n^{calc} = 9110$ Da), calculated from the monomer conversion as determined by ^1H NMR spectroscopy.

To further identify the controlled characteristics of the ATRP of **1**, the relationships of monomer conversions vs M_n and PDI values of the resulting polymers and the polymerization kinetics were also investigated. As shown in Figure 2a, ATRP of **1** ([**1**]:[EBiB]:[CuBr]:[$CuBr_2$]:[PMDETA] = 100:1:1:0.2:2, 67 vol % anisole, at 65 °C) followed linear first-order kinetics, showing a constant concentration of active species for up to 3.0 h. These conditions were applied in order to reach control over the polymerization process, employing increased levels of deactivator ($CuBr_2$) to reduce the polymerization rate[21] as compared with entry 2, Table 1. Below 48% monomer conversion, excellent linear agreement between M_ns and monomer conversions were

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Table 1. ATRP of 5-Norbornene-2-methylene Methacrylate, 1[a]

entry	L	[**1**]:[I]:[CuBr]:[CuBr$_2$]:[L]	T (°C)	t (h)	conv (%)	M_n^{calc} (Da)	M_n^{GPC} (Da)	PDI
1	P	100:1:1:0:2	70	0.5	60	12840	13000	1.36
2	P	100:1:1:0.1:2	65	1.2	60	12840	22000	1.26
3	T	44:1:1:0.1:2	70	7.4	55	5250	7900	1.24
4	T	100:1:1:0.1:2	80	4.8	46	9880	8880	1.61
5	T	100:1:1:0.1:2	70	7.0	42	9110	8270	1.14

[a] L = ligand; I = initiator (ethyl 2-bromoisobutyrate); P = PMDETA; T = TMEDA; T = temperature; t = time; conv = monomer conversion, measured by ^{1}H NMR spectroscopy; M_n^{calc} = calculated number-average molecular weight based on monomer conversions measured by ^{1}H NMR spectroscopy; M_n^{GPC} = number-average molecular weight measured by GPC, relative to polystyrene standards; PDI = polydispersity index measured by GPC.

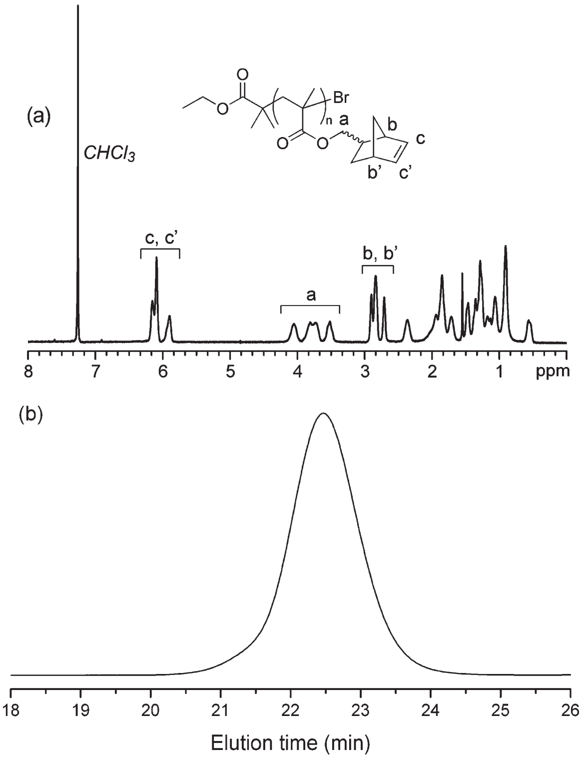


Figure 1. Atom transfer radical homopolymerization of 5-norbornene-2-methylene methacrylate, **1**: (a) ^{1}H NMR spectrum of **2** (300 MHz, CDCl$_3$; Table 1, entry 5); (b) GPC profile of **2** (THF eluent; Table 1, entry 5).

obtained, and the resulting polymers also maintained narrow molecular weight distributions (PDI = 1.12−1.18) (Figure 2b). Such results verified the controlled characteristics of the selective ATRP of **1**. However, it was noticed that after the monomer conversion reached 50% at 3.5 h a high-MW shoulder on the GPC profile (Figure 2c) was observed, suggesting a minor occurrence of reactions of the Nb, presumably due to the increased molar ratio of the Nb groups to the remaining MA vinyl groups.

The controlled characteristics of ATRP allow ready preparation of a broad range of block copolymers. Therefore, we investigated chain extension polymerizations of **1** from a poly(methyl methacrylate) (PMMA) macroinitiator and polymerizations of methyl methacrylate (MMA) from a Nb-functionalized macroinitiator **2** via ATRP, for the preparation of Nb side chain functionalized diblock copolymers (Scheme 2). Using PMMA (M_n^{GPC} = 10 100 Da, PDI = 1.06) as the macroinitiator, chain extension ATRP of **1** ([**1**]:[PMMA]:[CuBr]:[CuBr$_2$]:[PMDETA] = 189:1:3.0:0.1:6, at 70 °C, in 86 vol % of anisole as solvent) resulted in well-defined diblock polymer PMMA-*b*-PNbMA, **3**, after 7.0 h and a conversion of **1** of 11%. Chain extension of **2** (M_n^{GPC} = 8270 Da, PDI = 1.14) with MMA ([MMA]:[**2**]:[CuBr]:[CuBr$_2$]:[PMDETA] = 200:1:1.5:0.2:3, at 70 °C, in 79 vol % of anisole as solvent) quenched at 7.0 h with 12% conversion of MMA afforded diblock copolymer PNbMA-*b*-PMMA, **4**. As shown in Figure 3, the formation of diblock copolymers **3**

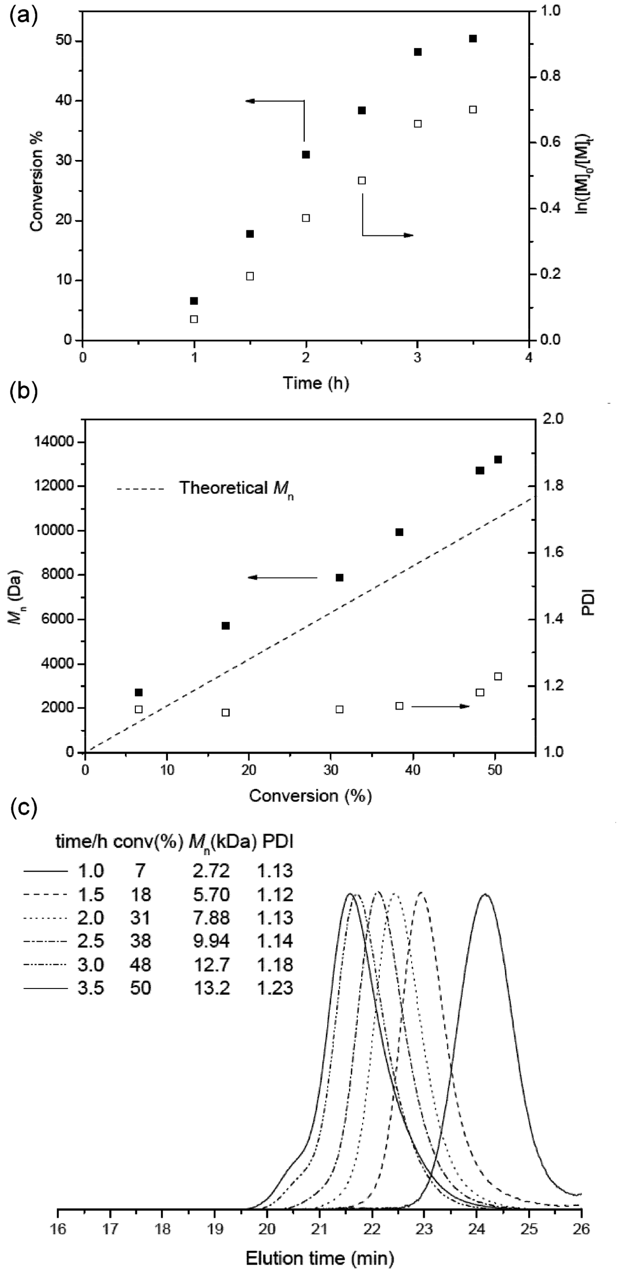


Figure 2. Kinetic plots for the ATRP of **1**: (a) time dependence of monomer conversions and ln([M]$_0$:[M]$_t$) (polymerization conditions: [**1**]:[EBiB]:[CuBr]:[CuBr$_2$]:[PMDETA] = 100:1:1:0.2:2, vol 67% anisole, at 65 °C); (b) dependence of M_n^{GPC} and PDI relative to monomer conversions; (c) evolution of GPC traces during ATRP of **1**.

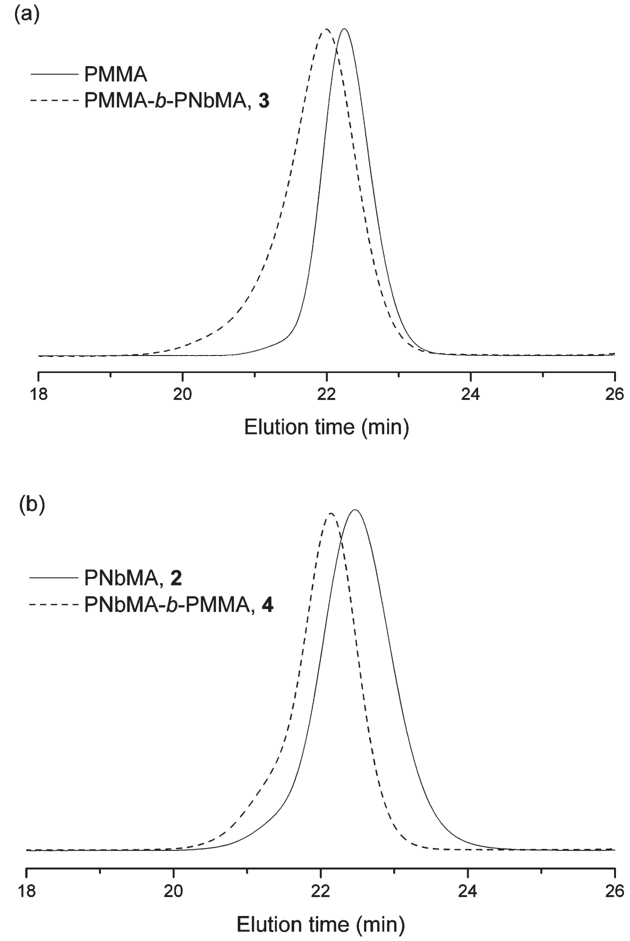
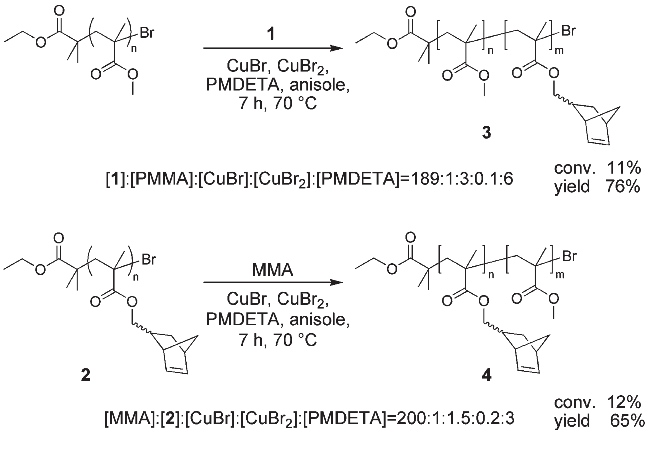


Figure 3. Overlaid GPC profiles of (a) PMMA and PMMA-*b*-PNbMA, **3**, and (b) PNbMA, **2**, and PNbMA-*b*-PMMA, **4**.

Scheme 2. Regio-Functionalized Diblock Copolymers 3 and 4 Prepared by Atom Transfer Radical Block Copolymerizations of 1 from PMMA Macroinitiator or ATRP of MMA from Macroinitiator 2



(M_n^{GPC} = 12 800 Da, M_n^{cal} = 14 300 Da, PDI = 1.16) and **4** (M_n^{GPC} = 11 300 Da, M_n^{cal} = 10 800 Da, PDI = 1.11) were verified by the shifts of the GPC profiles of the resulting diblock structures to shorter retention times compared with those of their macroinitiator precursors. Moreover, the good agreement between the experimental and theoretical molecular weights and the monomodal molecular weight distributions of both diblock copolymers illustrated the quantitative initiation efficiency and tunability of the length of Nb-functionalized blocks.

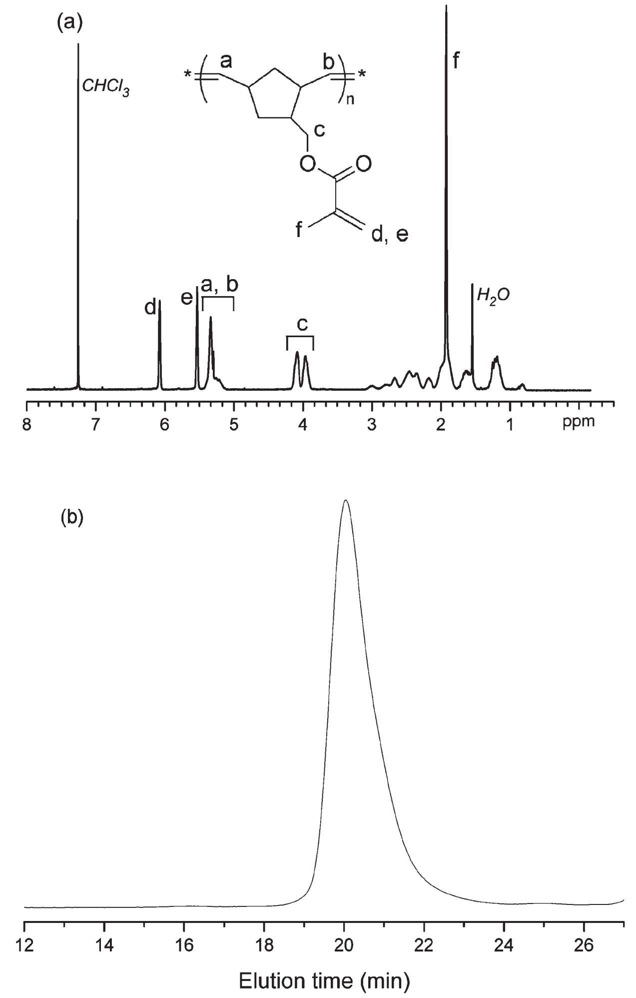


Figure 4. (a) ^{1}H NMR spectrum of **5** (300 MHz, $CDCl_3$). (b) GPC (THF eluent) profile of **5**.

Because the MA group and Nb group in monomer **1** also have different reactivities toward alkene metathesis reaction, selective ROMP homopolymerization of **1** was studied by using Grubbs' catalyst (first generation) $RuCl_2(CHC_6H_5)[P(C_6H_{11})_3]_2$ under diluted condition using CH_2Cl_2 as solvent ([**1**]:[Ru] = 100:1, concentration of **1** = 0.025 g/mL, in CH_2Cl_2). As measured by ^{1}H NMR spectroscopy, nearly complete conversion of **1** was observed after 15 min at room temperature by the disappearance of ^{1}H NMR resonances of Nb alkenyl protons (5.8−6.2 ppm). After termination with ethyl vinyl ether followed by purification, the resulting methacrylate-functionalized polynorbornene (PMANb, **5**) was found to have a M_n^{GPC} of 34 600 Da and monomodal MW distribution with a PDI of 1.18 (Figure 4b). The successful incorporation of pendant MA units on the side chain was supported by ^{1}H NMR spectroscopy (Figure 4a), with the appearance of the MA vinyl protons and methylene protons, having an integration area ratio of 1.97:2.00, which further confirmed the good selectivity of ROMP for the norbornenyl unit with little to no cross metathesis of the methacryloyl units.

In summary, by taking advantage of the difference of reactivities of two unsaturated groups in bifunctional monomer 5-norbornene-2-methylene methacrylate (**1**), both selective ATRP and selective ROMP of **1** were successfully achieved to prepare two types of well-defined polymers with nearly quantitative installation of Nb groups pendant on polymethacrylate backbones or side chain MA groups pendant on polynorbornene backbones. Although ROMP could proceed to quantitative conversion without adverse effects, ATRP was limited to less than ca. 50% conversion of the MA units to avoid significant side reactions of the Nb units and obtain a linear polymer of uniform structure and narrow molecular weight distribution. Well-defined regio-functionalized diblock copolymers containing a PMMA segment and a PNbMA segment have also been synthesized by chain extension ATRP from both PMMA and PNbMA macroinitiators. We believe that this direct route to versatile alkene-functionalized homopolymers and block copolymers is highly attractive and, further, that these functional materials can be used as building blocks for the construction of advanced macromolecular architectures. Moreover, the imbedded functional groups can also serve as reactive sites for further conjugation, modification, or cross-linking by using robust, efficient, and orthogonal (REO)[2,22,11] chemical reactions.

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Supporting Information Available: Text giving experimental procedures and characterization data of homo- and copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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