ATRP from a Norbornenyl-Functionalized Initiator: Balancing of Complementary Reactivity for the Preparation of α-Norbornenyl Macromonomers/ω-Haloalkyl Macroinitiators

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ABSTRACT: Atom transfer radical polymerization (ATRP) using a norbornenyl-functionalized initiator was established as a new synthetic method for the preparation of macromolecules that are both α-norbornenyl macromonomers and ω-haloalkyl macroinitiators. When styrene, methyl methacrylate, and *tert*-butyl methacrylate were used as monomer or constituted comonomer pairs, the (co)polymerization was well-controlled and the norbornenyl functionality was intact. The resulting homopolymer or statistical copolymer-based macromonomers had linear structures, quantitative α-norbornenyl functionality, controlled number-average molecular weights (M_n = 3600−24300 Da), and narrow monomodal molecular weight distributions (M_w/M_n = 1.07−1.35). Their ω-halide terminals further allowed them to serve as macroinitiators for the syntheses of block copolymer-based α-norbornenyl macromonomers by ATRP. In contrast, the norbornenyl functionality exhibited considerable competitive reactivity in the polymerizations of methyl acrylate and *tert*-butyl acrylate, resulting in mixed linear and branched macromonomers/macroinitiators. TGA analysis of α-norbornenyl macromonomers showed that the presence of norbornenyl functionality appreciably enhanced their thermal stability.

Introduction

Macromonomers are important precursors for supermolecular construction and have been utilized broadly in the syntheses of graft polymers, star polymers, polymer brushes, and polymer-based nanomaterials.[1−17] Among various macromonomers that have been reported, macromonomers with a terminal norbornenyl group have attracted increasing attention, due to their unusually high reactivity relative to that of most other types of macromonomers and their interesting applications in the preparation of complex polymers with novel topologies.[18−36] In contrast to typical vinyl-ended macromonomers that have relatively limited reactivity when their number-average molecular weights (M_n) exceed several thousand Daltons (Da), norbornenyl-ended macromonomers with M_n up to 10 kDa still maintain significant reactivity in ring-opening metathesis polymerization (ROMP).[20,26,31] The high reactivity of norbornenyl-ended macromonomers can be ascribed to two reasons. First, the norbornenyl group is highly strained, and therefore, with the relief of ring strain as the driving force, ROMP is thermodynamically highly favorable for norbornenyl derivatives, including macromonomers. Second, relative to typical chain polymerization of vinyl-ended macromonomers, ROMP of norbornenyl-ended macromonomers is less sterically unfavorable. The lower steric environment results from the poly(norbornene-macromonomer)-based backbones having their branching grafts less densely populated than do typical poly(vinyl-macromonomer)s, which extend a graft from every other carbon atom along the backbone. Due to their high reactivity, norbornenyl-ended macromonomers can be polymerized by ROMP in a well-controlled manner to yield complex polymers with specific topological control.

Spherelike and bottlebrush-like poly(macromonomers) have been obtained by homopolymerization of homopolymer-based norbornenyl-ended macromonomers by several groups.[20−22,26,28,30−32,36] Héroguez and co-workers[23,29] and Nomura et al.[31] have utilized more complicated synthetic designs using norbornenyl-ended macromonomers and, thereby, have achieved the preparation of a series of complex polymers with interesting macromolecular architectures, including core−shell spherelike poly(macromonomers), Janus-type spherelike poly(macromonomers), umbrella-like star copolymers, and dumbbell-shaped copolymers. Because such polymeric topologies can be converted theoretically into novel polymeric nanostructures by selective cross-linking techniques,[37,38] we were attracted to norbornenyl-ended macromonomers and have studied their synthesis.

Similar to most other types of macromonomers, norbornenyl-ended macromonomers have been prepared through two generalized synthetic strategies: polymerization from a functional initiator and terminal functionalization by postpolymerization reaction (including end-capping of living polymers). Typically, polymerization from functional initiators yields macromonomers with quantitative α-functionalization, and if living polymerization techniques are used, the resulting macromonomers have also well-controlled M_n and narrow molecular weight distribution. However, this synthetic strategy generally requires inertness or negligible reactivity of the functionality contained within the initiator under the polymerization conditions, which causes difficulties with direct incorporation of unsaturated groups to be utilized later as the macromonomer polymerizable unit. Only anionic polymerization (including anionic ring-opening polymerization) and cationic ring-opening polymerization using norbornenyl-func-

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tionalized initiators have been reported, and therefore, relatively limited types of norbornenyl-terminated macromonomers have been obtained by this strategy.[21−25,28,29,34−36] Norbornenyl-terminated macromonomers can be prepared alternatively by terminal functional group transformation of other types of terminal-functionalized polymers.[18−20,26,30−32] However, quantitative terminal unsaturation may not be guaranteed especially when macromonomers with relatively high M_n are targeted.

Atom transfer radical polymerization (ATRP) is a powerful polymerization technique for the preparation of a broad range of polymers with accurate structural control.[39−41] By using a functional initiator, ATRP can yield well-defined terminal-functionalized polymers readily, including macromonomers. To date, macromonomers with polymerizable groups including allyl,[42−44] vinyl ether,[44,45] vinyl ester,[46−49] lactone,[50] epoxy,[51] thiophene,[52] and pyrrole[53] have been prepared by this synthetic strategy, whereby each of these polymerizable groups is not susceptible or has little susceptibility to polymerization under ATRP conditions.

We hypothesized that the norbornenyl group could serve as a polymerizable unit in a functional initiator for the preparation of macromonomers by ATRP, because the norbornenyl group has only low reactivity in radical polymerizations. Therefore, a norbornenyl-functionalized bromoester was synthesized and studied as an initiator in ATRP as a new and convenient synthetic method for the preparation of α-norbornenyl macromonomers. A range of homopolymer and statistical copolymer-based α-norbornenyl macromonomers, most with well-defined structure, were obtained. Because ATRP requires less stringent reaction conditions, but is applicable for more vinyl monomers and suitable for more types of copolymerizations than ionic polymerization, our method by ATRP extends significantly the synthetic scope of α-norbornenyl macromonomers.

Experimental Section

Materials. All chemicals were purchased from Aldrich unless otherwise noted. CuCl (99.995+%), $CuCl_2$ (99.999%), CuBr (99.999%), $CuBr_2$ (99.999%), acetone (99.5+%), anisole (99.7%), 2-bromoisobutyryl bromide (98%), 1,10-dibromodecane (97%), dimethyl sulfoxide (DMSO, 99.6+%), methyl ethyl ketone (MEK, 99.5+%), sodium hydride (95%), sodium hydroxide (97+%), pyridine (99+%), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA, 99.5+%), and *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA, 99%) were used as received. Styrene (St, 99+%), methyl methacrylate (MMA, 99%), *tert*-butyl methacrylate (*t*BMA, 98%), methyl acrylate (MA, 99%) and *tert*-butyl acrylate (*t*BA, 98%) were distilled over CaH_2 and stored under argon at 4 °C. *exo*-5-Norbornene-2-methanol was separated from 5-norbornene-2-methanol (98%, mixture of *endo* and *exo*) following the literature method.[54]

Characterization Methods. Infrared spectra were obtained on a Perkin-Elmer Spectrum BX FT-IR system using diffuse reflectance sampling accessories. ^{1}H NMR spectra were recorded at 300 or 600 MHz on solutions in $CDCl_3$ on a Varian Mercury 300 or Varian Unity 600 spectrometer, respectively, with the solvent proton signal as standard. ^{13}C NMR spectra were recorded at 150.8 MHz on solutions in $CDCl_3$ on a Varian Unity 600 spectrometer with the solvent carbon signal as standard.

Gel permeation chromatography (GPC) was conducted on a Waters 1515 HPLC (Waters Chromatography, Inc.) equipped with a Waters 2414 differential refractometer, a PD2020 dual-angle (15° and 90°) light-scattering detector (Precision Detectors, Inc.), and a three-column series PL gel 5μm Mixed C, 500 Å, and 10^4 Å, 300 × 7.5 mm columns (Polymer Laboratories Inc.). The system was equilibrated at 35 °C in anhydrous THF, which served as the polymer solvent and eluent with a flow rate of 1.0 mL/min. Polymer solutions were prepared at a known concentration (ca. 3 mg/mL), and an injection volume of 200 μL was used. Data collection and analysis were performed, respectively, with Precision Acquire software and Discovery 32 software (Precision Detectors, Inc.). The inter-detector delay volume and the light-scattering detector calibration constant were determined by calibration using a nearly monodispersed polystyrene standard (Pressure Chemical Co., M_p = 90 kDa, M_w/M_n < 1.04). The differential refractometer was calibrated with standard polystyrene reference material (SRM 706 NIST), of known specific refractive index increment d*n*/d*c* (0.184 mL/g). The d*n*/d*c* values of the analyzed polymers were then determined from the differential refractometer response.

Thermogravimetric analysis (TGA) was performed on a TGA/SDTA851^e instrument (Mettler-Toledo, Inc.) measuring the total mass loss on approximately 10 mg samples from 25 to 600 °C at a heating rate of 10 °C/min in a nitrogen flow of 50 mL/min. Glass transition temperature (T_g) determinations were performed by using differential scanning calorimetry (DSC) on a DSC822^e instrument (Mettler-Toledo, Inc.) in a temperature range of −50 to 180 °C with a heating rate of 10 °C/min under nitrogen. For both TGA and DSC, data were acquired and analyzed with STAR^e software (Mettler-Toledo, Inc.). The T_g values were taken at the midpoint of the inflection tangent, upon the third heating scans.

Elemental analyses were conducted by M-H-W Laboratories (Phoenix, AZ) as a typical commercial service.

***exo*-5-(10-Bromo-decyloxymethyl)-bicyclo[2.2.1]hept-2-ene.** In a 100 mL flask with a stirring bar, sodium hydride (1.80 g, 71.3 mmol) was added slowly into a THF solution of *exo*-5-norbornene-2-methanol (5.98 g, 48.2 mmol). After stirring for 10 min, 1,10-dibromodecane (78.2 g, 261 mmol) was added, and then the reaction mixture was heated at reflux for 48 h. The reaction mixture was allowed to cool to room temperature, and water was added dropwise to consume the remaining sodium hydride. After THF was removed under reduced pressure, the reaction mixture was partitioned between water and CH_2Cl_2. The organic phase was dried over $MgSO_4$, concentrated in vacuo, and separated using flash chromatography eluting with hexane, increasing polarity to 50% CH_2Cl_2−hexane, to give the targeted product as a colorless oil: yield 11.5 g (70%). IR: 3150−2700, 1609, 1569, 1464, 1368, 1334, 1252, 1187, 1125, 920, 903, 857, 834, 787, 713, 646 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 1.07−1.99 (m, 21H, C*H* and 10 × CH_2), 2.75 (s, 1H, C*H*), 2.81 (s, 1H, C*H*), 3.26−3.58 (m, 6H, CH_2OCH_2 and CH_2Br), 6.03−6.16 (m, 2H, C*H*=C*H*). ^{13}C NMR (150.8 MHz, $CDCl_3$, ppm) δ: 26.5, 28.4, 29.1, 29.7, 30.0, 33.1, 34.0, 39.2, 41.8, 44.0, 45.4, 71.3, 75.7, 137.0. Anal. Calcd for $C_{18}H_{31}OBr$: C, 62.97; H, 9.10; Br, 23.27. Found: C, 63.00; H, 8.98; Br, 23.23.

***exo*-10-(Bicyclo[2.2.1]hept-5-en-2-ylmethoxy)-decan-1-ol.** To a 500 mL flask with a stirring bar was added sodium hydroxide (4.00 g, 100 mmol), *exo*-5-(10-bromo-decyloxymethyl)-bicyclo[2.2.1]hept-2-ene (8.00 g, 23.3 mmol), and 75% DMSO−H_2O (150 mL). The reaction mixture was heated at 80−85 °C for 12 h and then concentrated in vacuo. The residue was partitioned between water and CH_2Cl_2. The organic phase was dried over $MgSO_4$, evaporated to dryness under reduced pressure at elevated temperature, and separated using flash chromatography eluting with 50% CH_2Cl_2−hexane, increasing polarity to 3% methanol−CH_2Cl_2, to give the targeted product as a colorless oil: yield 5.10 g (78%). IR: 3600−3200, 3150−2700, 1609, 1569, 1464, 1368, 1335, 1280, 1251, 1226, 1158, 1123, 1059, 903, 857, 834, 787, 778, 710, 662 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 1.06−1.46 (m, 16H, 8 × CH_2), 1.46−1.76 (m, 5H, CH and 2 × CH_2), 2.21 (s, 1H, O*H*), 2.75 (s, 1H, C*H*), 2.80 (s, 1H, C*H*), 3.25−3.51 (m, 4H, CH_2OCH_2), 3.64 (t, 2H, J = 6.6 Hz, CH_2OH), 6.03−6.16 (m, 2H, C*H*=C*H*). ^{13}C NMR (150.8 MHz, $CDCl_3$, ppm) δ: 26.0, 26.6, 29.8, 30.0, 33.1, 39.1, 41.8, 44.0, 45.4, 53.7, 63.2, 71.3, 75.6, 137.0. Anal. Calcd for $C_{18}H_{32}O_2$: C, 77.09; H, 11.50. Found: C, 76.91; H,11.42.

***exo*-Norbornenyl-Functionalized ATRP Initiator, 1.** In a 100 mL flask with a stirring bar, 2-bromoisobutyryl bromide (2.79 g, 11.9 mmol) was added dropwise into a THF solution of *exo*-10-(bicyclo[2.2.1]hept-5-en-2-ylmethoxy)-decan-1-ol (1.70 g, 6.07 mmol) and pyridine (1.96 g, 24.6 mmol). The reaction mixture was stirred at room temperature for 22 h, concentrated in vacuo, and partitioned between water and CH_2Cl_2. The organic phase was dried over $MgSO_4$, evaporated to dryness under reduced pressure at elevated temperature, and separated using flash chromatography eluting with 50% CH_2Cl_2–hexane, increasing polarity to 2% methanol–CH_2Cl_2, to give the targeted product as a colorless oil: yield 2.41 g (93%). IR: 3150–2700, 1742, 1609, 1568, 1466, 1388, 1379, 1336, 1285, 1175, 1122, 1011, 976, 923, 903, 857, 834, 788, 778, 762, 709 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, ppm) δ: 1.05–1.49 (m, 16H, 8 × C*H*$_2$), 1.49–1.80 (m, 5H, CH and 2 × C*H*$_2$), 1.96 (s, 6H, 2 × C*H*$_3$), 2.76 (s, 1H, C*H*), 2.81 (s, 1H, C*H*), 3.25–3.52 (m, 4H, C*H*$_2$OC*H*$_2$), 4.18 (t, 2H, J = 6.6 Hz, C*H*$_2$OCO), 6.02–6.16 (m, 2H, C*H*=C*H*). ^{13}C NMR (150.8 MHz, $CDCl_3$, ppm) δ: 26.0, 26.3, 28.5, 29.3, 29.6, 29.9, 31.0, 39.0, 41.7, 43.9, 45.2, 56.2, 66.3, 71.3, 75.6, 136.8, 172.0. Anal. Calcd for $C_{22}H_{37}OBr_3$: C, 61.53; H, 8.68; Br, 18.81. Found: C, 61.76; H, 8.49; Br, 18.76.

General Polymerization Procedure. To a preflamed round-bottom flask was added initiator **1**, catalyst (CuCl or CuBr), ligand (PMDETA or TMEDA), and monomer (St, MMA, *t*BMA, MA, or *t*BA) or comonomers (St–MMA, St–*t*BMA, MMA–*t*BMA). Deactivator ($CuCl_2$ or $CuBr_2$) and solvent (anisole, MEK, or acetone) were also added in some trials. After the flask was sealed with a rubber septum, the reaction mixture was degassed by at least three freeze–pump–thaw cycles and then heated at a consistent temperature (60–84 °C) with an oil bath.

For each of the trials in which polymerization processes were monitored, aliquots of the reaction mixture were withdrawn from the flask with a degassed dry syringe at time intervals. Parts of these aliquots were analyzed directly by ^1H NMR spectroscopy to determine the conversion(s) of monomer or comonomers based on the resonance intensity of the vinyl protons of the remaining monomer or comonomers. Parts of these aliquots were passed through neutral alumina, concentrated, precipitated into methanol or pentane, collected by filtration, dried in vacuo, and then analyzed by GPC to determine the molecular weights and molecular weight distributions.

For each trial, when the desired polymerization time was attained, polymerization was quenched by cooling the reaction mixture to room temperature. After determination of conversion(s) of monomer or comonomers by ^1H NMR spectroscopy, the reaction mixture was diluted by the addition of THF, passed through a neutral alumina column, concentrated in vacuo, and precipitated twice into 10-fold excess of a nonsolvent (methanol for polymerization of St and copolymerization of St–MMA; pentane for polymerization of MMA; 50% methanol–water for polymerizations of *t*BMA, MA, and *t*BA and copolymerizations of St–*t*BMA and MMA–*t*BMA). The polymer recovered was then dried in vacuo for 1–2 days.

α-*exo*-Norbornenyl Polystyrene, 2. This was prepared from a polymerization mixture of styrene (18.7 g, 180 mmol), initiator **1** (386 mg, 0.900 mmol), CuBr (129 mg, 0.899 mmol), and PMDETA (312 mg, 1.80 mmol) at 70 °C. The polymerization process was monitored by withdrawing aliquots of the reaction mixture for analysis at polymerization times of 2, 5, 9, 14, 20, and 27 h. Finally, the polymerization (~5.0 mL of reaction mixture remained) was quenched at 35 h, and the isolated yield was 3.01 g (96%; based on the relative amount of remaining reaction mixture and 69% conversion of styrene as measured by ^1H NMR spectroscopy). M_n^{NMR} = 15.2 kDa, M_n^{GPC} = 16.2 kDa, M_w/M_n^{GPC} = 1.07. T_g = 95 °C. IR: 3100–2800, 1600, 1582, 1493, 1452, 1371, 1181, 1068, 1028, 910, 759, 735, 704 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, ppm) δ: 0.85–2.57 (br m, C*H*$_2$ and C*H* of polystyrene backbone and C*H*, 2 × C*H*$_3$, and 9 × C*H*$_2$ of unit from **1**), 2.78 (s, C*H* of unit from **1**), 2.83 (s, C*H* of unit from **1**), 3.30–3.67 (m, C*H*$_2$OC*H*$_2$ and C*H*$_2$OCO of unit from **1**), 4.39–4.62 (m, terminal C_6H_5CHBr), 6.07–6.18 (m, C*H*=C*H* of unit from **1**), 6.31–7.35 (br m, Ar*H*). ^{13}C NMR (150.8 MHz, $CDCl_3$, ppm) δ: 37.8–46.9, 125.8, 128.2, 145.5. TGA in N_2: 220–370 °C, 5% mass loss; 370–450 °C, 90% mass loss.

α-*exo*-Norbornenyl Poly(MMA), 3. Sample **3a** was prepared from the polymerization mixture of MMA (4.68 g, 46.8 mmol), initiator **1** (100 mg, 0.233 mmol), CuCl (23.2 g, 0.234 mmol), TMEDA (54.4 mg, 0.468 mmol), and anisole (5.0 mL) at 70 °C. The polymerization process was monitored by withdrawing aliquots of the reaction mixture for analysis at polymerization times of 2, 5, 9, 14, 20, and 27 h. Finally, the polymerization (~3.2 mL of reaction mixture remained) was quenched at 35 h, and the isolated yield was 1.90 g (97%; based on the relative amount of remaining reaction mixture and 65% conversion of MMA as measured by ^1H NMR spectroscopy). M_n^{NMR} = 14.5 kDa, M_n^{GPC} = 13.8 kDa, M_w/M_n^{GPC} = 1.07. T_g = 105 °C. TGA in N_2: 220–345 °C, 10% mass loss; 345–420 °C, 87% mass loss.

Sample **3b** was prepared from the polymerization mixture of MMA (9.00 g, 90.0 mmol), initiator **1** (193 mg, 0.450 mmol), CuCl (44.5 mg, 0.450 mmol), $CuCl_2$ (3.0 mg, 0.023 mmol), TMEDA (110 mg, 0.945 mmol), and anisole (9.7 mL) at 70 °C. At polymerization times of 1 and 2 h, aliquots of the reaction mixture were withdrawn from the flask with a degassed dry syringe, but ^1H NMR analysis showed very low conversions of MMA (<3%). Finally, the polymerization (~18 mL of reaction mixture remained) was quenched at 11 h, and the isolated yield was 0.80 g (58%; based on the relative amount of remaining reaction mixture and 15% conversion of MMA as measured by ^1H NMR spectroscopy). M_n^{NMR} = 3. 50 kDa, M_n^{GPC} = 3.60 kDa, M_w/M_n^{GPC} = 1.07. T_g = 75 °C. IR: 3100–2800, 1747, 1702, 1490, 1459, 1388, 1282, 1206, 1064, 993, 922, 843, 742 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, ppm) δ: 0.67–2.10 (m, C*H*$_2$ and *CH*$_3$ of MMA units except the one at ω-terminal, and C*H*, 2 × C*H*$_3$, and 9 × C*H*$_2$ of unit from **1**), 2.43 (s, C*H*$_2$ of ω-terminal MMA unit), 2.73 (s, C*H* of unit from **1**), 2.78 (s, C*H* of unit from **1**), 3.25–3.48 (m, C*H*$_2$OC*H*$_2$ of unit from **1**), 3.58 (s, OC*H*$_3$ of MMA units except the one at ω-terminal), 3.75 (s, OC*H*$_3$ of ω-terminal MMA unit), 3.91–4.05 (m, C*H*$_2$-OCO of unit from **1**), 6.02–6.11 (m, C*H*=C*H* of unit from **1**). ^{13}C NMR (150.8 MHz, $CDCl_3$, ppm) δ: 16.4, 18.8, 26.0, 26.2, 28.5, 29.3, 29.5, 29.8, 38.9, 41.6, 43.8, 44.6, 45.0, 51.9, 52.4–53.8, 54.5, 64.8, 66.5, 71.2, 75.6, 136.7, 177.0, 177.9, 178.2. TGA in N_2: 130–350 °C, 10% mass loss; 350–450 °C, 86% mass loss.

α-*exo*-Norbornenyl Poly(*t*BMA), 4. Sample **4a** was prepared from a polymerization mixture of *t*BMA (4.38 g, 30.8 mmol), initiator **1** (66.1 mg, 0.154 mmol), CuCl (15.2 mg, 0.154 mmol), PMDETA (53.3 mg, 0.308 mmol), and anisole (5.0 mL) at 70 °C for 2 h. Isolated yield: 2.83 g (97%; based on 65% conversion of *t*BMA as measured by ^1H NMR spectroscopy). M_n^{NMR} = 23.0 kDa, M_n^{GPC} = 24.3 kDa, M_w/M_n^{GPC} = 1.12. T_g = 115 °C. IR: 3050–2800, 1730, 1478, 1457, 1392, 1368, 1274, 1253, 1165, 1035, 967, 918, 875, 849, 735 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$, ppm) δ: 0.65–2.33 (br m, C*H*$_2$ of *t*BMA units except the one at ω-terminal, C*H*$_3$ of *t*BMA units, and C*H*, 2 × C*H*$_3$, and 9 × C*H*$_2$ of unit from **1**), 2.46 (br m, C*H*$_2$ of ω-terminal *t*BMA unit), 2.74 (s, C*H* of unit from **1**), 2.80 (s, C*H* of unit from **1**), 3.27–3.49 (m, C*H*$_2$OC*H*$_2$ of unit from **1**), 3.90–4.12 (m, C*H*$_2$OCO of unit from **1**), 6.02–6.12 (m, C*H*=C*H* of unit from **1**). ^{13}C NMR (150.8 MHz, $CDCl_3$, ppm) δ: 18.0, 18.7, 28.0, 46.4, 46.7, 80.8, 81.0, 176.9, 177.4. TGA in N_2: 180–260 °C, 45% mass loss; 260–400 °C, 5% mass loss; 400–460 °C, 45% mass loss.

Sample **4b** was prepared from a polymerization mixture of initiator **1** (66.1 mg, 0.154 mmol), CuCl (15.2 mg, 0.154 mmol), PMDETA (53.3 mg, 0.308 mmol), *t*BMA (4.38 g, 30.8 mmol), and MEK (5.0 mL) at 70 °C for 2 h. Isolated yield: 2.49 g (94%; based on 59% conversion of *t*BMA as measured by ^1H NMR spectroscopy). M_n^{NMR} = 20.3 kDa, M_n^{GPC} = 22.8 kDa, M_w/M_n^{GPC} = 1.14. T_g = 117 °C. TGA in N_2: 180–260 °C, 43% mass loss; 260–400 °C, 5% mass loss; 400–460 °C, 46% mass loss.

α-*exo*-Norbornenyl Poly(MA), 5. Sample **5a** was prepared from a polymerization mixture of MA (4.78 g, 55.5 mmol), initiator **1** (118 mg, 0.276 mmol), CuBr (39.7 mg, 0.276 mmol),

and PMDETA (47.7 mg, 0.276 mmol) at 60 °C for 2 h. Isolated yield: 2.10 g (76%; based on 55% conversion of MA as measured by ^{1}H NMR spectroscopy). M_n^{NMR} = 15.7 kDa, M_n^{GPC} = 14.3 kDa, M_w/M_n^{GPC} = 1.23 (bimodal distribution). T_g = 11 °C. TGA in N_2: 220−370 °C, 5% mass loss; 370−450 °C, 90% mass loss.

Sample **5b** was prepared from the polymerization mixture of MA (4.78 g, 55.5 mmol), initiator **1** (118 mg, 0.275 mmol), CuBr (39.7 mg, 0.276 mmol), $CuBr_2$ (3.1 mg, 0.014 mmol), and PMDETA (47.7 mg, 0.276 mmol) at 60 °C for 2 h. Isolated yield: 1.52 g (75%; based on 40% conversion of MA by ^{1}H NMR). M_n^{NMR} = 8.95 kDa, M_n^{GPC} = 9.03 kDa, M_w/M_n^{GPC} = 1.14 (bimodal distribution). T_g = 8 °C. IR: 3100−2800, 1752, 1711, 1454, 1381, 1277, 1180, 1058, 976, 918, 829, 733 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ: 1.05−2.12 (m, CH_2 of MA units, and CH, 2 × CH_3, and 9 × CH_2 of unit from **1**), 2.15−2.53 (br m, CH of MA units except the one at ω-terminal), 2.73 (s, CH of unit from **1**), 2.79 (s, CH of unit from **1**), 3.27−3.48 (m, CH_2-OCH_2 of unit from **1**), 3.66 (s, OCH_3 of MA units except the one at ω-terminal), 3.81 (s, OCH_3 of ω-terminal MA unit), 4.00 (t, J = 6.6 Hz, CH_2OCO of unit from **1**), 4.24 (m, CH of ω-terminal MA unit), 6.01−6.12 (m, CH═CH of unit from **1**). ^{13}C NMR (150.8 MHz, $CDCl_3$, ppm) δ: 29.7, 34.2−36.4, 41.3, 41.5, 51.9, 136.9, 175.1. TGA in N_2: 220−360 °C, 5% mass loss; 360−450 °C, 90% mass loss.

α-*exo*-Norbornenyl Poly(*t*BA), 6. This was prepared from the polymerization mixture of *t*BA (4.38 g, 30.8 mmol), initiator **1** (115 mg, 0.268 mmol), CuBr (19.0 mg, 0.133 mmol), $CuBr_2$ (2.0 mg, 0.0090 mmol), PMDETA (24.0 mg, 0.139 mmol), DMB (183 mg, 1.32 mmol), and acetone (2.0 mL) at 84 °C for 14 h. Isolated yield: 2.30 g (91%; based on 55% conversion of *t*BA by ^{1}H NMR). M_n^{NMR} = 20.8 kDa, M_n^{GPC} = 19.4 kDa, M_w/M_n^{GPC} = 1.14 (bimodal distribution). T_g = 42 °C. IR: 3100−2800, 1741, 1704, 1480, 1454, 1396, 1373, 1281, 1184, 1110, 1035, 917, 850, 736 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ: 0.97−1.99 (br m, CH_2 and CH_3 of *t*BA units, and CH, 2 × CH_3, and 9 × CH_2 of unit from **1**), 2.08−2.43 (br m, CH of MA units except the one at ω-terminal), 2.74 (s, CH of unit from **1**), 2.79 (s, CH of unit from **1**), 3.27−3.49 (m, CH_2OCH_2 of unit from **1**), 4.01 (br, CH_2OCO of unit from **1**), 4.04−4.19 (m, CH of ω-terminal *t*BA unit), 5.98−6.09 (m, CH═CH of unit from **1**). ^{13}C NMR (150.8 MHz, $CDCl_3$, ppm) δ: 28.3, 36.0, 37.6, 41.4−42.8, 80.6, 174.3. TGA in N_2: 180−230 °C, 40% mass loss; 230−460 °C, 50% mass loss.

α-*exo*-Norbornenyl Poly(MMA)-*b*-Poly(*t*BMA), 7. This was prepared from the polymerization mixture of *t*BMA (1.75 g, 12.3 mmol), **3** (472 mg, 0.0342 mmol), CuCl (3.4 mg, 0.034 mmol), PMDETA (11.8 mg, 0.068 mmol), and anisole (2.5 mL) at 70 °C for 12 h. Isolated yield: 1.12 g (69%; based on 66% conversion of *t*BMA as measured by ^{1}H NMR spectroscopy). M_n^{NMR} = 35.1 kDa, M_n^{GPC} = 36.9 kDa, M_w/M_n^{GPC} = 1.12. Mol fractions of MMA and *t*BMA units were 47% and 53% as determined by ^{1}H NMR spectroscopy. T_g (PMMA) = 98 °C, T_g (P*t*BMA) = 118 °C. IR: 3100−2750, 1743, 1700, 1489, 1395, 1371, 1282, 1204, 1066, 1036, 969, 922, 852, 742 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ: 0.58−2.35 (br m, CH_2 and CH_3 of MMA and *t*BMA units except the CH_2 at terminal *t*BMA unit, and CH, 2 × CH_3, and 9 × CH_2 of unit from **1**), 2.44 (br m, CH_2 of ω-terminal *t*BMA unit), 2.72 (s, CH of unit from **1**), 2.77 (s, CH of unit from **1**), 3.25−3.44 (m, CH_2OCH_2 of unit from **1**), 3.58 (s, OCH_3 of MMA units), 3.91−4.08 (m, CH_2OCO of unit from **1**), 6.00−6.10 (m, CH═CH of unit from **1**). ^{13}C NMR (150.8 MHz, $CDCl_3$, ppm) δ: 16.7, 17.9, 18.8, 28.0, 44.7, 45.1, 46.3, 46.6, 51.6−55.3, 80.6, 81.0, 176.7−178.4. TGA in N_2: 180−255 °C, 30% mass loss; 255−355 °C, 5% mass loss; 355−450 °C, 58% mass loss.

α-*exo*-Norbornenyl Poly(St-*co*-MMA), 8. Sample **8a** was prepared from a polymerization mixture of St (0.48 g, 4.6 mmol), MMA (1.38 g, 13.8 mmol), **1** (39.5 mg, 0.092 mmol), CuBr (13.2 mg, 0.092 mmol), PMDETA (31.8 mg, 0.184 mmol), and anisole (2.0 mL) at 70 °C for 20 h. Isolated yield: 0.95 g (67%; based on 68% conversion of St and 76% conversion of MMA as determined by ^{1}H NMR spectroscopy). M_n^{NMR} = 18.6 kDa, M_n^{GPC} = 18.0 kDa, M_w/M_n^{GPC} = 1.19. Mol fractions of St and MMA units are 28% and 72% by ^{1}H NMR. T_g = 101 °C. TGA in N_2: 220−345 °C, 5% mass loss; 345−430 °C, 90% mass loss.

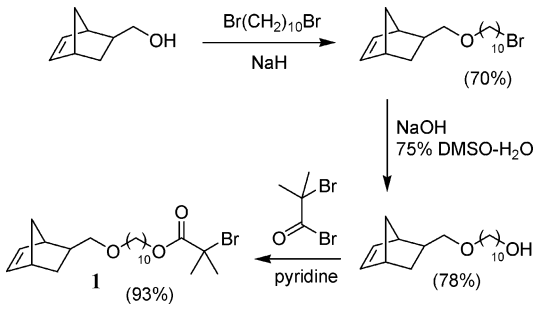
Sample **8b** was prepared from a polymerization mixture of St (1.92 g, 18.4 mmol), MMA (1.84 g, 18.4 mmol), **1** (78.9 mg, 0.184 mmol), CuBr (26.4 mg, 0.184 mmol), PMDETA (63.7 mg, 0.368 mmol), and anisole (4.0 mL) at 70 °C. The polymerization process was monitored by withdrawing aliquots of the reaction mixture for analysis at polymerization times of 2, 5, 9, and 14 h. Finally, the copolymerization (∼7.0 mL of reaction mixture remained) was quenched at 20 h, and the isolated yield was 0.93 g (81%; based on the relative amount of remaining reaction mixture and 29% conversion of St and 28% conversion of MMA as measured by ^{1}H NMR spectroscopy). M_n^{NMR} = 9.30 kDa, M_n^{GPC} = 8.86 kDa, M_w/M_n^{GPC} = 1.09. Mol fractions of St and MMA units are 51% and 49% as determined by ^{1}H NMR spectroscopy. T_g = 87 °C. IR: 3100−2800, 1752, 1711, 1454, 1381, 1277, 1180, 1058, 976, 918, 829, 733 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ: 0.20−2.63 (br m, CH and CH_2 of St units, CH_2 and CH_3 of MMA units, and CH, 2 × CH_3, and 9 × CH_2 of unit from **1**), 2.63−4.13 (br m, OCH_3 of MMA unit, 2 × CH, CH_2OCH_2, and CH_2OCO of unit from **1**), 4.21−4.65 (m, terminal C_6H_5CHBr), 6.02−6.14 (m, CH═CH of unit from **1**), 6.42−7.44 (br m, ArH of St units). ^{13}C NMR (150.8 MHz, $CDCl_3$, ppm) δ: 17.7−23.3, 26.3, 29.9, 36.9−42.1, 43.8−53.5, 71.5, 75.7, 126.2, 128.3, 137.0, 142.8−147.3, 174.7−177.9. TGA in N_2: 220−355 °C, 5% mass loss; 355−450 °C, 90% mass loss.

Sample **8c** was prepared from a polymerization mixture of St (1.44 g, 13.8 mmol), MMA (0.46 g, 4.6 mmol), **1** (39.5 mg, 0.092 mmol), CuBr (13.2 mg, 0.092 mmol), PMDETA (31.8 mg, 0.184 mmol), and anisole (2.0 mL) at 70 °C for 20 h. Isolated yield: 0.40 g (68%; based on 27% conversion of St and 35% conversion of MMA as measured by ^{1}H NMR spectroscopy). M_n^{NMR} = 7.00 kDa, M_n^{GPC} = 6.33 kDa, M_w/M_n^{GPC} = 1.06. Mol fractions of St and MMA units are 68% and 32% as determined by ^{1}H NMR spectroscopy. T_g = 79 °C. TGA in N_2: 220−350 °C, 5% mass loss; 350−450 °C, 90% mass loss.

α-*exo*-Norbornenyl Poly(St-*co*-*t*BMA), 9. This was prepared from a polymerization mixture of St (0.96 g, 9.2 mmol), *t*BMA (1.31 g, 9.2 mmol), **1** (39.5 mg, 0.092 mmol), CuBr (13.2 mg, 0.092 mmol), PMDETA (31.8 mg, 0.184 mmol), and anisole (0.64 mL) at 70 °C for 20 h. Isolated yield: 0.52 g (69%; based on 28% conversion of St and 34% conversion of *t*BMA as measured by ^{1}H NMR spectroscopy). M_n^{NMR} = 7.61 kDa, M_n^{GPC} = 8.94 kDa, M_w/M_n^{GPC} = 1.35. Mol fractions of St and *t*BMA units are 45% and 55% as measured by ^{1}H NMR spectroscopy. T_g = 101 °C. IR: 3100−2800, 1739, 1600, 1582, 1492, 1453, 1384, 1274, 1209, 1074, 1030, 989, 912, 845, 761, 738, 705 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ: −0.10 to 2.73 (br m, CH and CH_2 of St units, CH_2 and CH_3 of *t*BMA units, and CH, 2 × CH_3, and 9 × CH_2 of unit from **1**), 2.76 (s, CH of unit from **1**), 2.81 (s, CH of unit from **1**), 3.27−4.11 (m, CH_2OCH_2, and CH_2OCO of unit from **1**), 6.03−6.13 (m, CH═CH of unit from **1**), 6.30−7.41 (br m, ArH of St units). ^{13}C NMR (150.8 MHz, $CDCl_3$, ppm) δ: 17.2−23.6, 24.2, 26.2, 26.6, 28.0, 29.8, 37.6−41.0, 41.6, 43.3−53.6, 71.4, 75.6, 80.2, 126.1, 128.4, 136.8, 145.1, 147.5, 175.7−176.9. TGA in N_2: 180−265 °C, 20% mass loss; 265−370 °C, 8% mass loss; 370−440 °C, 67% mass loss.

α-*exo*-Norbornenyl Poly(MMA-*co*-*t*BMA), 10. This was prepared from a polymerization mixture of MMA (0.92 g, 9.2 mmol), *t*BMA (1.31 g, 9.2 mmol), **1** (39.5 mg, 0.092 mmol), CuBr (13.2 mg, 0.092 mmol), PMDETA (31.8 mg, 0.184 mmol), and anisole (0.64 mL) at 70 °C for 2 h. Isolated yield: 1.34 g (86%; based on 66% conversion of MMA and 69% conversion of *t*BMA as measured by ^{1}H NMR spectroscopy). M_n^{NMR} = 19.5 kDa, M_n^{GPC} = 22.4 kDa, M_w/M_n^{GPC} = 1.25. Mol fractions of MMA and *t*BMA units are 49% and 51% by ^{1}H NMR. T_g = 107 °C. IR: 3100−2800, 1728, 1457, 1392, 1367, 1249, 1152, 1036, 969, 918, 847, 734 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ: 0.56−2.21 (br m, CH_3 of MMA and *t*BMA units, CH_2 of MMA and *t*BMA units except the one at ω-terminal, and CH, 2 × CH_3, and 9 × CH_2 of unit from **1**), 2.45 (m, CH_2 of ω-terminal MMA/*t*BMA units), 2.72 (s, CH of unit from **1**), 2.78 (s, CH of unit from **1**), 3.24−3.47 (m, CH_2OCH_2 of unit from **1**), 3.57 (s, OCH_3 of MMA units except the one at ω-terminal),

Scheme 1



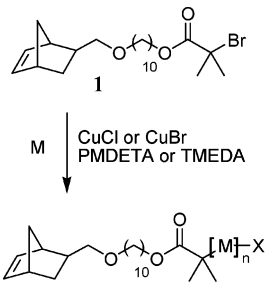
3.79 (s, OCH_3 of ω-terminal MMA units), 3.88−4.10 (m, CH_2-OCO of unit from **1**), 6.01−6.10 (m, CH=CH of unit from **1**). ^{13}C NMR (150.8 MHz, $CDCl_3$, ppm) δ: 16.7, 17.9, 18.8, 28.0, 44.7, 45.1, 46.3, 46.6, 51.6−55.3, 81.0, 80.6, 176.7−178.4. TGA in N_2: 180−255 °C, 25% mass loss; 255−380 °C, 10% mass loss; 380−450 °C, 60% mass loss.

Results and Discussion

Design and Synthesis of Norbornenyl-Functionalized ATRP Initiator, 1. A norbornenyl-functionalized ATRP initiator, **1**, was designed by combining an *exo*-norbornenyl functionality and an α-bromoisobutyrate functionality with a $-CH_2O(CH2)_{10}-$ spacer. A three-step synthesis was followed (Scheme 1) to afford **1** in an overall yield of 51%, relative to the *exo*-5-norbornene-2-methanol starting material. The *exo*-norbornenyl stereochemistry was preferred, as it presents the carbon−carbon double bond for reaction with less steric hindrance from the substituents, in comparison to that of the *endo*-norbornenyl functionality, and therefore has significantly higher reactivity in ROMP.[55−61] The α-bromoisobutyrate functionality possesses high ATRP initiation capacity due to the two methyl groups, along with one bromine substituent, on the α-carbon of the ester group. The existence of the relatively long $-CH_2O(CH_2)_{10}-$ spacer can reduce unfavorable steric influence on the norbornenyl functionality, and thus it is helpful to further maintain the high ROMP reactivity of the *exo*-norbornenyl functionalities on the macromonomers formed by ATRP initiated by **1**. A similar compound, containing a norbornenyl functionality (mixture of *exo* and *endo*) and an α-bromopropionate, was reported by Kriegel et al.[62] It is interesting that the approach taken was opposite to that described herein, rather the norbornenyl unit was utilized first to undergo ROMP-based copolymerization, followed by ATRP to produce graft copolymers. In contrast, our intentions were to prepare densely grafted (block) copolymers via homopolymerization of various macromonomers, which required a high degree of control over the norbornenyl stereochemistry and optimization of the ATRP initiator efficiency.

Synthesis and Characterization of Homopolymer-Based α-*exo*-Norbornenyl Macromonomers/ω-Haloalkyl Macroinitiators. Atom transfer radical homopolymerizations of styrene (St), methyl methacrylate (MMA), *tert*-butyl methacrylate (*t*BMA), methyl acrylate (MA), and *tert*-butyl acrylate (*t*BA) initiated by **1** were conducted to prepare a variety of homopolymer-based macromolecules with both α-*exo*-norbornenyl and ω-haloalkyl functionalities (Scheme 2; Table 1). These monomers were chosen because, relative to the norbornenyl group, they have significantly higher reactivity in radical (co)polymerization. On the basis of Q and e values, St (Q = 1.00, e = −0.80) has the highest

Scheme 2



2(M: St), **3**(M: MMA), **4**(M: *t*BMA), **5**(M: MA), **6**(M: *t*BA)

reactivity among these monomers, MMA (Q = 0.78, e = 0.40) and its analogue *t*BMA have similar reactivity, and each is significantly more reactive than MA (Q = 0.45, e = 0.64) and its analogue *t*BA; however, the norbornenyl group (Q = 0.05, e = −1.48; estimation based on norbornadiene) has only very low reactivity in radical (co)polymerization.[63] To further reduce the considerable occurrence of unwanted polymerization of the norbornenyl functionalities during the radical polymerizations to establish the macromonomer structures, a high initial molar feed ratio of monomer-to-**1** of 200 was used and monomer conversion was controlled to be below 70% for all experiments to ensure a large excess of reactive monomer relative to norbornene functionality at all times during the polymerizations. Chain-transfer reactions are also unwanted side reactions but should not be important in these polymerization systems due to the low chain-transfer constants of the monomer used[63] and the low concentrations of norbornenyl functionalities. Because we found that *exo*-norbornenyl group has only limited chemical stability under elevated temperatures (a portion of the *exo*-norbornenyl group can be converted slowly into the *endo*-norbornenyl group by heating at over 100 °C, as detected by ^{1}H NMR spectroscopy), the polymerizations were conducted at temperatures ranging from 60 to 84 °C. Typical ATRP conditions were used,[64−66] employing either CuCl or CuBr as the catalyst (if CuCl was chosen, then both chloride and bromide functionalities are expected at the ω-terminals of the resulting polymers, due to halogen exchange between the catalyst and initiation site)[67] and either PMDETA or TMEDA as the ligand. In some trials, $CuCl_2$ or $CuBr_2$ was also used as deactivator, and anisole, MEK, or acetone was used as the solvent, for better polymerization control.

Theoretically, all of the PS, PMMA, P*t*BMA, PMA, and P*t*BA-based macromolecules prepared by ATRP initiated by **1** are macromonomers with quantitative α-*exo*-norbornenyl functionality, and such an expectation was verified by quantitative ^{1}H NMR analysis of these macromonomers using a 600 MHz spectrometer with a long predelay of 30 s. As illustrated in an exemplary ^{1}H NMR spectrum (Figure 1; for PMMA-based macromonomer **3b**), the characteristic resonances of the *exo*-norbornenyl alkene protons at 6.0−6.1 ppm, which are well-separated from all other resonances, were detected. For each macromonomer, the M_n value measured by ^{1}H NMR spectroscopy end group analysis, based on the intensity of this characteristic resonance, was in excellent agreement with the M_n value determined by GPC, indicating quantitatively that one *exo*-norbornenyl group was present per polymer chain.

Table 1. Synthesis of Homopolymer-Based α-*exo*-Norbornenyl Macromonomers/ω-Haloalkyl Macroinitiators

sample	M[a]	C[b]	D[c]	L[d]	$[M]_0/[\mathbf{1}]_0/[C]_0/[D]_0/[L]_0$	solvent	T (°C)	t (h)	conv (%)[e]	M_n^{calcd} (kDa)	M_n^{GPC} (kDa)	M_n^{NMR} (kDa)	PDI
2	St	CuBr		PMDETA	200/1.0/1.0/0/2.0		70	35	69	14.8	16.2	15.2	1.07
3a	MMA	CuCl		TMEDA	200/1.0/1.0/0/2.0	anisole (50 vol %)	70	35	65	13.4	13.8	14.5	1.07
3b	MMA	CuCl	$CuCl_2$	TMEDA	200/1.0/1.0/0.05/2.1	anisole (50 vol %)	70	11	15	3.45	3.60	3.50	1.07
4a	*t*BMA	CuCl		PMDETA	200/1.0/1.0/0/2.0	anisole (50 vol %)	70	2	65	18.9	24.3	23.0	1.12
4b	*t*BMA	CuCl		PMDETA	200/1.0/1.0/0/2.0	MEK (50 vol %)	70	2	59	17.2	22.8	20.3	1.14
5a	MA	CuBr		PMDETA	200/1.0/1.0/0/2.0		60	2	55	9.91	14.3	15.7	1.23[f]
5b	MA	CuBr	$CuBr_2$	PMDETA	200/1.0/1.0/0.05/2.1		60	2	40	7.33	9.03	8.94	1.14[f]
6	*t*BA	CuBr	$CuBr_2$	PMDETA	200/1.0/0.5/0.03/0.53	acetone (20 vol %)	84	14	55	14.5	19.4	20.8	1.14[f]

[a] M: monomer. [b] C: catalyst. [c] D: deactivator. [d] L: ligand. [e] By ^{1}H NMR spectroscopy. [f] Bimodal molecular weight distribution.

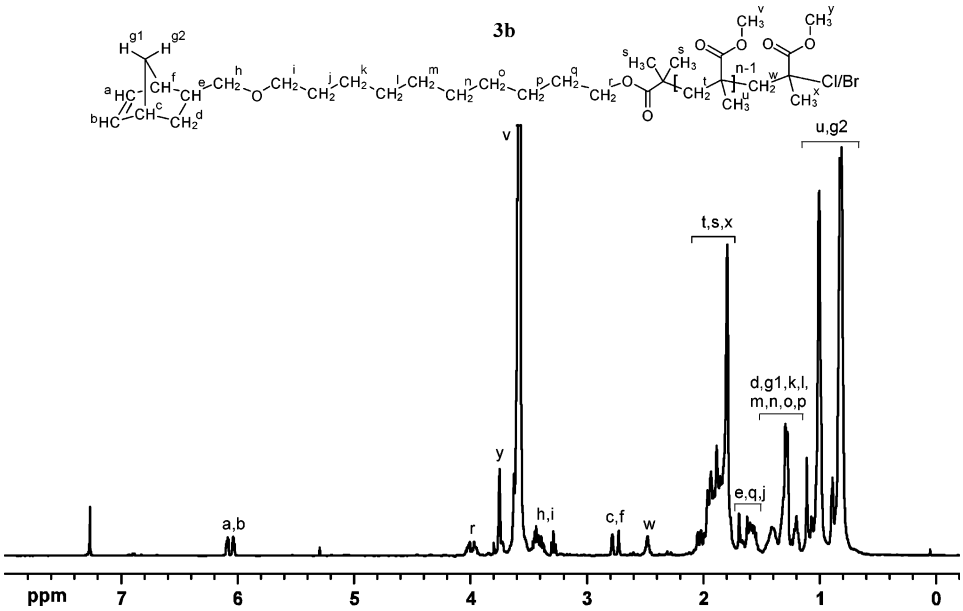


Figure 1. ^{1}H NMR (600 MHz) spectrum of α-*exo*-norbornenyl PMMA-based macromonomer **3b**.

It is a critical concern whether the norbornenyl functionality was involved in the ATRP process initiated by **1**. If the norbornenyl functionality from **1** was considerably copolymerized with the monomer used under the reaction conditions, then long-chain linear (if reinitiation did not occur from the polymerized norbornenyl unit) and/or branched (if reinitiation was to occur from the polymerized norbornenyl unit) macromonomer molecules would be formed along with the regular macromonomer structures and, therefore, would lead to broad molecular weight distribution and uncontrolled M_n for the resulting polymers. To probe the potential reactivity of the norbornenyl functionality under the synthetic conditions employed during the preparation of each of the macromonomers, the molecular weight distributions were studied by GPC (Figure 2), and comparisons between the experimental M_n values (by ^{1}H NMR and GPC) and the theoretical M_n values were also made.

As indicated by the narrow and monomodal GPC curves of PS, PMMA, and P*t*BMA-based macromonomers **2**−**4** (M_w/M_n = 1.07−1.15) and the close agreement between their experimental and theoretical M_n values, the norbornenyl group from initiator **1** was essentially intact during ATRP of styrene, MMA, and *t*BMA, and macromonomers **2**−**4** were produced with well-defined linear structures. The ATRP processes of styrene and MMA (as a representative methacrylate monomer) were further investigated by the analyses of the aliquots withdrawn from the corresponding polymerization solutions at time intervals during polymerization. Monomer conversions were obtained by ^{1}H NMR analysis of these aliquots, based on the resonances of the vinyl protons of the remaining monomer. Living polymerization characteristics with consistent radical concentration were verified by the linearity between $\ln([M]_0/[M])$ and polymerization time (Figure 3). Moreover, well-controlled polymer chain growth during the polymerizations was established based on GPC analyses of these aliquots (Figure 4), which further supported the inertness of the norbornenyl functionality under the reaction conditions for the two systems. For ATRP of styrene initiated by **1**, the experimental M_n values of the resulting polymers were in agreement with the calculated M_n values and the PDI values of the resulting polymers were low (<1.1); for ATRP of MMA initiated by **1**, after the initial stage with low monomer conversions (<20%), the experimental M_n values of the polymers were also in agreement with the calculated M_n values and the PDI values became relatively low. The MMA polymerization system could be refined by using $CuCl_2$ as deactivator, and as a result, well-defined PMMA-based macromonomer **3b** with predetermined M_n and a low PDI of 1.07 was obtained at a relatively low monomer conversion of 15%.

In contrast to the absence of norbornenyl reactivity during the well-defined polymerizations of styrene and the methacrylates, considerable reactivity of the norbornenyl functionality occurred during ATRP of MA and *t*BA. GPC chromatograms for the PMA and P*t*BA-based macromonomers **5** and **6** revealed bimodal molecular weight distributions, with the formation of high-molecular-weight components having peak molecular weights (M_p) about twice those of the M_p values of the major

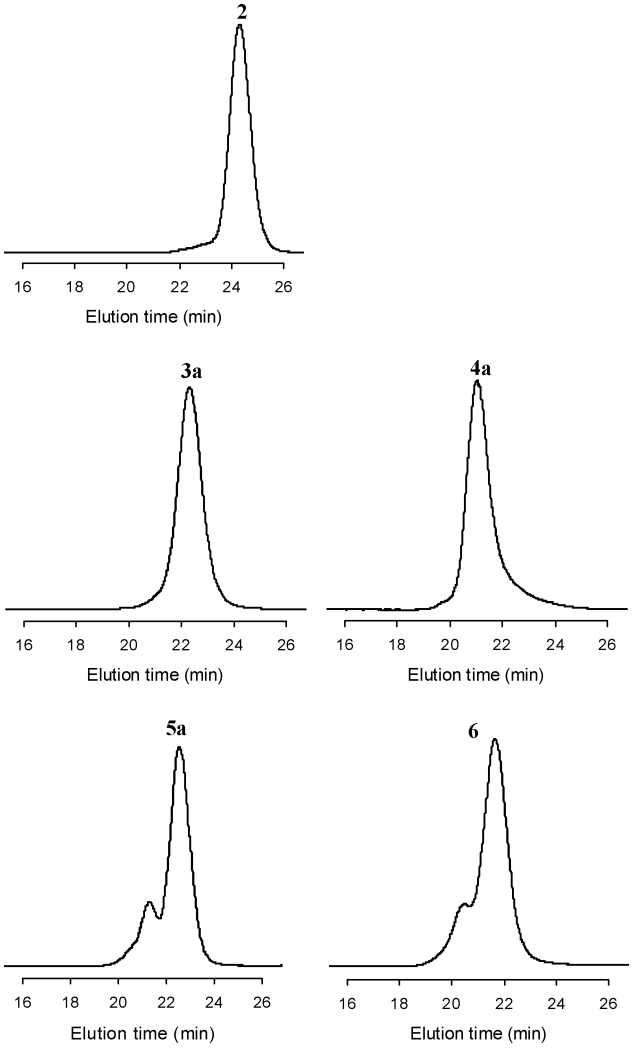


Figure 2. GPC chromatograms of homopolymer-based α-norbornenyl macromonomers **2**, **3a**, **4a**, **5a**, and **6**.

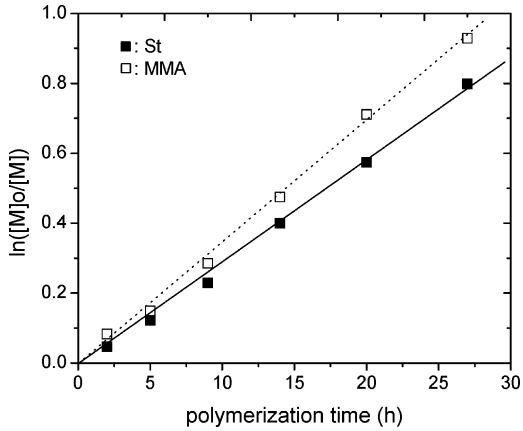


Figure 3. Time dependence of $\ln([M]_0/[M])$ for ATRP of styrene initiated by **1** (polymerization conditions: $[St]_0/[\mathbf{1}]_0/[CuBr]_0/[PMDETA]_0 = 200:1:1:2$; 70 °C) and ATRP of MMA initiated by **1** (polymerization conditions: $[MMA]_0/[\mathbf{1}]_0/[CuCl]_0/[TMEDA]_0 = 200:1:1:2$; 70 °C).

products (Figure 2). With the significant presence of the high-molecular-weight species, the experimental M_n values could be up to ca. 50% higher than their theoretical M_n values. The use of copper(II) deactivator led to better polymerization control, as indicated by decreased PDI values and improved agreement between

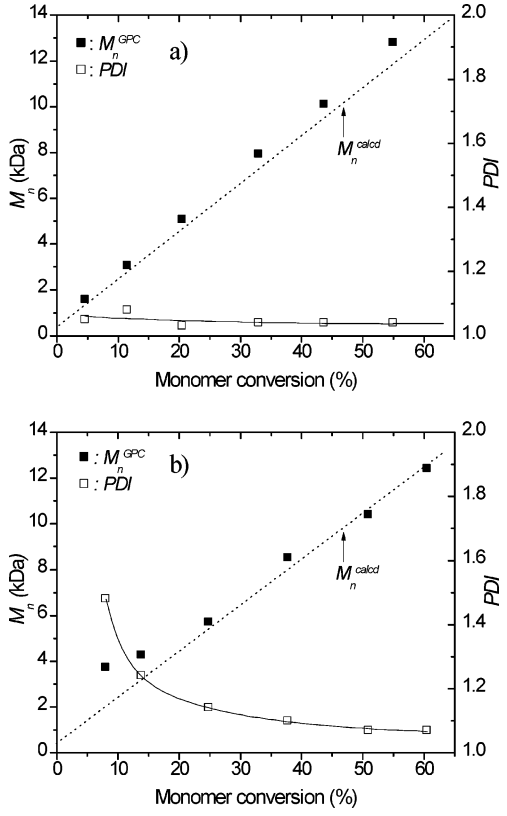


Figure 4. M_n and PDI of macromonomers vs monomer conversion for (a) ATRP of styrene initiated by **1** and (b) ATRP of MMA initiated by **1** (polymerization conditions: $[M]_0/[\mathbf{1}]_0/[CuBr]_0/[PMDETA]_0 = 200:1:1:2$; 70 °C).

experimental and theoretical M_n values, but the molecular weight distributions of the resulting polymers remained bimodal. Because under similar reaction conditions initiated by bromoesters without norbornenyl functionality, atom transfer radical polymerizations of MA and *t*BA led to well-defined homopolymers and atom transfer radical copolymerization of MA with norbornene derivatives also resulted in well-defined copolymers,[64,65,68] these bimodal molecular weight distributions suggest that, during ATRP of MA and *t*BA initiated by **1**, a small portion of norbornenyl functionality was polymerized and reinitiation from these polymerized norbornenyl functionalities could occur. Thus, these PMA and P*t*BA-based macromonomers contain mixed linear (major component) and branched (minor component) structures. Additionally, although the occurrence of bimolecular coupling of propagating radicals theoretically can also result in polymer species with unexpected high molecular weights, it should not be of significance in the current polymerization systems because only moderate monomer conversions (<60%) were reached and the initial concentrations of initiator **1** were relatively low (<0.06 M).[69]

The α-*exo*-norbornenyl macromonomers **2**−**6** retain a haloalkyl functionality on the ω-terminus and, therefore, can also serve as ATRP macroinitiators. The presence of the ω-haloalkyl functionalities in macromonomers **2**−**6** is unique, in comparison to the norbornenyl macromonomers reported previously,[18−36] and was verified by ^{1}H NMR spectroscopy. The characteristic resonances of the protons on the α-carbons to the ω-haloalkyl functionalities were detected at 4.35−4.60 ppm for PS-based macromonomer **2,** at 4.20 ppm for

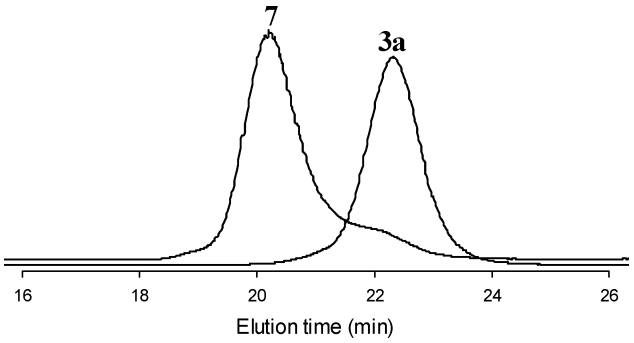
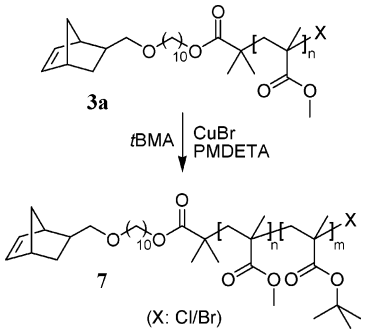


Figure 5. GPC monitoring of the formation of α-norbornenyl PMMA-*b*-P*t*BMA diblock macromonomer **7** by ATRP initiated by α-norbornenyl PMMA macromonomer **3a** (polymerization conditions: [*t*BMA]/[**3b**]/[CuCl]/[PMDETA] = 360:1:1:2; 50 vol % of anisole; 70 °C; 12 h).

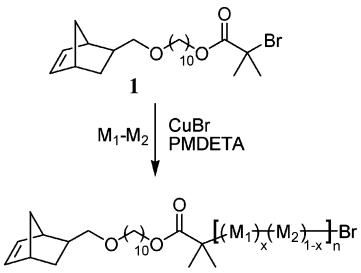
Scheme 3



PMA-based macromonomer **5**, and at 4.10 ppm for P*t*BA-based macromonomer **6.** The characteristic resonances of the methylene protons on the β-carbons to the ω-haloalkyl functionalities were detected at 2.45 ppm for PMMA-based macromonomer **3** and at 2.43 ppm for P*t*BMA-based macromonomer **4**.

Furthermore, the ATRP initiation ability of the ω-haloalkyl functionalities in macromonomers **2**−**6** was proven by an ATRP experiment using PMMA-based **3b** as macroinitiator (Scheme 3). ATRP of *t*BMA initiated by **3b** was performed utilizing PMDETA together with CuCl as the ligand/catalyst system at 70 °C in 50 vol % of anisole for 12 h ([*t*BMA]/[**3b**]/[CuCl]/[PMDETA] = 360:1:1:2) and allowed to proceed to 66% conversion of *t*BMA.[70] The formation of PMMA-*b*-P*t*BMA-based α-*exo*-norbornenyl diblock macromonomer **7** was verified by GPC analysis (Figure 5). Although the GPC chromatogram of **7** shows a low-molecular-weight tail, suggesting a slow initiation relative to propagation, quantitative initiation from ω-haloalkyl functionality of **3b** was supported by ^{1}H NMR analysis of **7** based on the absence of the characteristic resonances of the methoxy proton of the ω-terminal MMA unit at 3.75 ppm. Quantitatively, the retention of the α-*exo*-norbornenyl functionality in **7** was verified through the excellent agreement between its M_n by GPC (36.9 kDa) and its M_n by ^{1}H NMR spectroscopy (35.1 kDa), based on the characteristic resonances of its α-*exo*-norbornenyl alkene protons at 6.00−6.10 ppm. Additionally, the presence of the ω-haloalkyl functionality in **7** was supported by the characteristic ^{1}H NMR resonances of the methylene protons on the β-carbon to the ω-haloalkyl functionalities observed at 2.43 ppm, although these resonances overlapped considerably with the backbone protons of **7** and their intensities could not be determined quantitatively.

Scheme 4



8 (M_1-M_2: St-MMA)
9 (M_1-M_2: St-*t*BMA)
10 (M_1-M_2: MMA-*t*BMA)

Synthesis of Statistical Copolymer-Based α-*exo*-Norbornenyl Macromonomers/ω-Bromoalkyl Macroinitiators. Our synthetic method based on ATRP can be readily extended to prepare a broad range of copolymer-based α-norbornenyl macromonomers. To verify this expectation, atom transfer radical copolymerizations initiated by **1** were investigated (Scheme 4), and the synthetic results are summarized in Table 2. Several comonomer pairs (M_1−M_2), including St−MMA, St−*t*BMA, and MMA−*t*BMA were chosen, because each individual monomer had exhibited well-controlled homopolymerizations in the presence of the norbornenyl unit under ATRP conditions. As a preliminary study, CuBr was used as the catalyst, PMDETA was used as the ligand, anisole was used as the solvent, no deactivator was used, the initial molar feed ratio was ($[M_1]_0$ + $[M_2]_0$/[**1**]$_0$/[CuBr]$_0$/[PMDETA]$_0$ = 200:1:1:2, and the polymerization temperature was set at 70 °C. For each trial, conversion of each comonomer was held below 80%, to avoid any considerable occurrence of norbornenyl polymerization by having a large excess of the highly reactive vinyl functionalities relative to that of the norbornenyl functionality.

A series of statistical copolymer-based α-*exo*-norbornenyl macromonomers/ω-bromoalkyl macroinitiators with well-defined linear structure was prepared. Their chemical structures were investigated by quantitative ^{1}H NMR analysis using a 600 MHz spectrometer with a long predelay of 30 s. The characteristic resonance of *exo*-norbornenyl alkene protons at 6.0−6.1 ppm was detected by ^{1}H NMR analysis for each of these macromonomers. Their experimental M_n values determined based on the ^{1}H NMR intensities at 6.0−6.1 ppm were in agreement with their experimental M_n values determined by GPC, indicating quantitatively the presence of one *exo*-norbornenyl group per polymer chain. Although the production process of atom transfer radical copolymerization provided these macromonomers with ω-bromoalkyl functionalities, only limited ^{1}H NMR evidence was found. For example, the resonance of the benzylic proton of the terminal styrene comonomer unit (on the α-carbon of the ω-bromoalkyl functionality) at 4.2−4.6 ppm was observed for macromonomer **8** and the methylene protons of the terminal MMA/*t*BMA comonomer unit (on the β-carbon of the ω-bromoalkyl functionality) resonating at 2.45 ppm were observed for macromonomer **10**, whereas some of the characteristic ^{1}H NMR resonances were not distinguishable because of overlap with resonances from other protons in the structures.

The molar fractions of comonomer units in macromonomers **8**−**10** were determined by ^{1}H NMR spectroscopy, and the good agreements between the experi-

Table 2. Synthesis of α-*exo*-Norbornenyl Statistical Copolymer-Based Macromonomers/ω-Bromoalkyl Macroinitiators[a]

sample	M_1	M_2	f_1[d]	anisole (vol %)	t (h)	conv (%)[b]		F_1[c]		M_n (kDa)			PDI
						M_1	M_2	calcd	^{1}H NMR	calcd	GPC	^{1}H NMR	
8a	St	MMA	0.25	50	20	68	76	0.23	0.28	14.7	18.0	18.6	1.19
8b	St	MMA	0.50	50	20	38	43	0.47	0.51	8.68	8.86	9.30	1.09
8c	St	MMA	0.75	50	20	27	35	0.70	0.68	6.47	6.33	7.00	1.06
9	St	*t*BMA	0.50	20	20	28	34	0.45	0.45	8.27	8.94	7.61	1.35
10	MMA	*t*BMA	0.50	50	2	66	69	0.49	0.49	16.8	22.4	19.5	1.25

[a] Copolymerization conditions: $([M_1]_0 + [M_2])_0/[\mathbf{1}]_0/[CuBr]_0/[PMDETA]_0 = 200:1:1:2$; 70 °C. [b] By ^{1}H NMR based on the vinyl protons of comonomer. [c] Mol fraction of M_1 in copolymer. [d] Mol fraction of M_1 in comonomer feed.

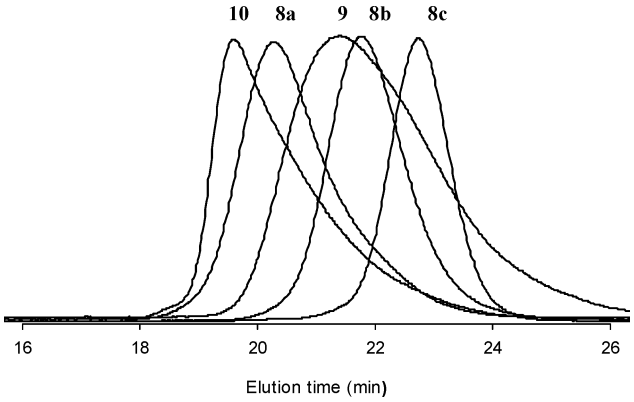


Figure 6. GPC chromatograms of statistical copolymer-based α-*exo*-norbornenyl macromonomers **8**−**10**.

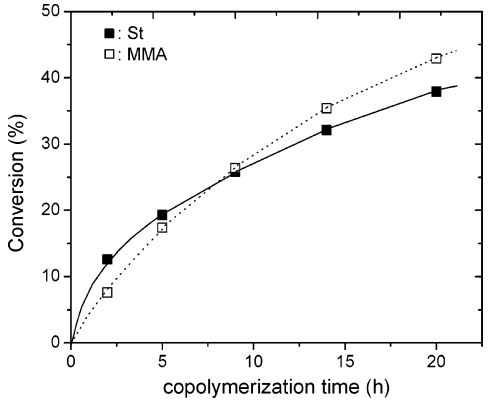


Figure 7. Time dependence of conversions of styrene and MMA for their atom transfer radical copolymerization initiated by **1** (copolymerization conditions: $[St]_0/[MMA]_0/[\mathbf{1}]_0/[CuBr]_0/[PMDETA]_0 = 100:100:1:1:2$; 70 °C).

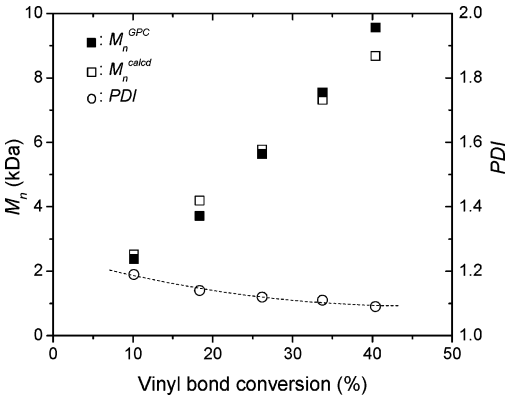


Figure 8. M_n and PDI values for macromonomers vs vinyl bond conversions during atom transfer radical copolymerization of styrene and MMA initiated by **1** (copolymerization conditions: $[St]_0/[MMA]_0/[\mathbf{1}]_0/[CuBr]_0/[PMDETA]_0 = 100:100:1:1:2$; 70 °C).

mental and calculated values suggested well-controlled copolymerization behaviors in each synthetic system. Furthermore, as indicated by the synthesis of a series of poly(St-*stat*-MMA)-based macromonomers **8a**−**c**, the molar fractions of comonomer units in the macromonomers could be manipulated by changing the feed ratios.

Additionally, ^{1}H NMR analysis also provided useful evidence for the statistical copolymer structures of macromonomers **8**−**10**. For instance, in contrast to PMMA homopolymer or PMMA-*b*-PSt block copolymers with a single ^{1}H NMR resonance for the methoxy protons of MMA units at 3.58 ppm, poly(St-*stat*-MMA)-based macromonomers **8a**−**c** exhibit multimodal ^{1}H NMR resonances of methoxy protons of MMA comonomer units at 2.6−3.6 ppm, reflecting very diverse chemical environments for their MMA comonomer units resulting from statistical copolymerization.

GPC analysis illustrated that each statistical copolymer-based macromonomer had a monomodal molecular weight distribution (Figure 6), suggesting that the norbornenyl functionality was not involved in the copolymerization process. Macromonomers **8** and **10** had also relatively low PDI values (1.06−1.25). Poly(St-*stat*-*t*BMA)-based macromonomer **9** has a PDI of 1.35, and it is possible that the reaction conditions for the copolymerization can be refined to yield a product having narrowed molecular weight distribution.

To study the typical copolymerization behavior for atom transfer radical copolymerization initiated by **1**, copolymerization of St−MMA was chosen as an exemplary system, for which the copolymerization process for the synthesis of poly(St-*stat*-MMA)-based macromonomer **8b** was investigated by the analyses of aliquots withdrawn from the corresponding copolymerization solutions at time intervals. A portion of each aliquot was analyzed by ^{1}H NMR spectroscopy to determine the conversions of styrene and MMA. As shown in Figure 7 for the synthetic trial for **8b**, in a qualitative agreement with the conventional radical copolymerization of styrene with MMA, the conversions of both styrene and MMA increased steadily, suggesting their comparable reactivities in atom transfer radical copolymerization. A portion of each aliquot was analyzed by GPC, and the well-controlled copolymerization behavior was established for the system based on the GPC analytic results. As shown in Figure 8, the experimental and theoretical M_n values were in excellent agreement, and the PDI values were not only relatively low (1.09−1.19) but also decreased with increasing conversions of vinyl bonds.

Thermal Analysis. The thermal stability and glass transition temperature, T_g, were determined by TGA and DSC under nitrogen atmosphere, respectively, for each of the α-exo-norbornenyl ω-haloalkyl macromolecules **2**−**10**.

As a surprising experimental result by TGA, the presence of α-norbornenyl functionalities in these samples appreciably improved the stability of the macromono-

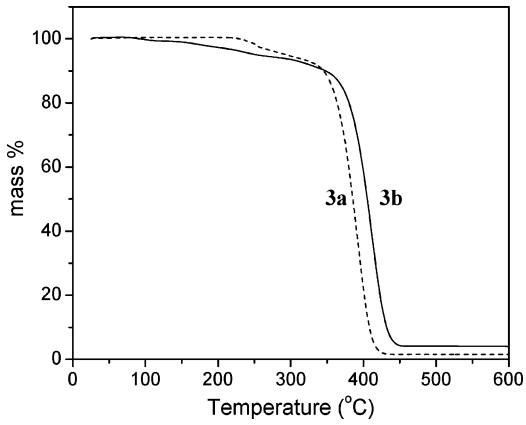


Figure 9. Thermolytic profiles of α-exo-norbornenyl PMMA-based macromonomers **3a** (M_n^{GPC} = 13.8 kDa; 0.9 wt % norbornenyl functionality) and **3b** (M_n^{GPC} = 3.60 kDa; 3.4 wt % norbornenyl functionality).

mers for major thermal degradations, presumably because certain extents of radical polymerization of norbornenyl functionalities can be activated under elevated temperatures to resist a fast degradation. As evidence (Figure 9), in contrast to the fact that polymers with higher molecular weights typically have better thermal stability than their analogues with lower molecular weights, PMMA-based macromonomer **3b** (M_n^{GPC} = 3.60 kDa; 3.4 wt % norbornenyl functionality; 50% mass loss at 405 °C) exhibited a lag of ca. 20 °C for major thermal degradation relative to its high-molecular-weight analogue **3a** (M_n^{GPC} = 13.8 kDa; 0.9 wt % norbornenyl functionality; 50% mass loss at 385 °C), and both samples are more thermally stable than typical commercially available PMMA with inert chain ends (50% mass loss at 371 °C).[71] Similarly, PMA-based macromonomer **5b** (M_n^{GPC} = 9.03 kDa; 1.4 wt % norbornenyl functionality; 50% mass loss at 414 °C) exhibited a lag of ca. 4 °C for major thermal degradation relative to its high-molecular-weight analogue **5a** (M_n^{GPC} = 14.3 kDa; 0.9 wt % norbornenyl functionality; 50% mass loss at 410 °C). On the other hand, all macromonomers exhibited relatively low onset temperatures of initial thermal degradations (<230 °C), and their presence of thermally instable ω-haloalkyl functionalities presumably promoted these initial thermal degradations.[72,73]

Each of the homopolymer-based macromonomers **2**−**6** exhibited one T_g value very close to the reference T_g value of its base polymer,[63] suggesting no significant influence of the terminal functionalities. The homopolymer-based macromonomers having the same monomer units (**3a** vs **3b**; **5a** vs **5b**) showed increased T_g values with increased molecular weights, as expected. The PMMA-*b*-P*t*BMA-based diblock macromonomer **7** exhibited two T_g values (98 °C for PMMA block and 118 °C for P*t*BMA block), supporting its block copolymer structure. Each of the statistical copolymer-based macromonomers **8**−**10** showed only one T_g value, in an agreement of its statistical copolymer structure.

Conclusions

A new and versatile synthetic method for the preparation of α-norbornenyl macromonomers by atom transfer radical (co)polymerization using a norbornenyl-functionalized initiator has been developed, and a variety of homopolymer and statistical copolymer-based macromonomers with quantitative α-norbornenyl functionality have been prepared. By using (co)monomers with high reactivity, such as St, MMA, and *t*BMA, the resulting macromonomers have well-defined linear structure, narrow molecular weight distribution, and controlled molecular weight and composition. By using less reactive monomers such as MA and *t*BA, the norbornenyl functionality can have considerable reactivity under the reaction conditions, and the resulting macromonomers may have a mixed linear and branched structure. All of these α-norbornenyl macromonomers have also ω-haloalkyl termini and, therefore, can serve as ATRP macroinitiators to further prepare macromonomers with block copolymer structures. Because, relative to ionic polymerization, ATRP does not require stringent reaction conditions, but has a wide range of applicable vinyl monomers and can be broadly used in various types of copolymerizations, this method can be considered as a generalized approach for the preparation of a broad variety of α-norbornenyl macromonomers from many types of vinyl monomers. The preparation of novel polymeric nanostructures from these α-*exo*-norbornenyl macromonomers is now in progress.

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