# Synthesis and Functionalization of ROMP-Based Gradient Copolymers of 5-Substituted Norbornenes

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ABSTRACT: Gradient copolymers of exo-5-(benzyloxy)norbornene and exo-5-[(4-tert-butyl)benzyloxy]norbornene were synthesized via ring-opening metathesis polymerization (ROMP). Kinetic studies revealed that the reactivity ratios of both monomers were close to unity. As predicted, this monomer pair did not result in copolymers with significant gradients under batch polymerization conditions. However, semibatch conditions resulted in copolymers with sizable gradients whose shape was independent of the rate of addition. Addition of the monomers simultaneously via a dual and opposite ramping strategy led to a 50/50 copolymer with an exceptionally linear gradient. These gradient copolymers were further functionalized via hydrogenation, bromination, and bromoalkoxylation.

## Introduction

In recent years, there has been a growing interest in the synthesis of gradient copolymers.  $^{1-\widetilde{2}2}$  Gradient copolymers from two monomers A and B constitute a new class of copolymer where the monomer composition changes continuously along the backbone from predominantly A to predominantly B. The composition of an A-B gradient copolymer is best described as being between two extremes: those of the corresponding diblock copolymer and the random copolymer. Several theoretical studies have been conducted regarding the properties and applications of gradient copolymers.<sup>23–27</sup> Modeling studies by Pakula and Matyjaszewski<sup>24</sup> demonstrated that dynamic<sup>28</sup> and thermodynamic properties of gradient copolymers could be shifted continuously along a temperature regime by synthetically modulating the composition and shape<sup>29</sup> of the gradient.<sup>18</sup> The order-disorder transition and microphase separation morphology have also been examined in bulk gradient copolymers.<sup>23,24</sup> Hence, one can, in theory, access a wide range of new polymer materials with programmable thermal properties from only two monomers simply by varying the synthetic conditions. A-B gradient copolymers are also of interest because their unusual architecture could potentially make them excellent compatibilizers in blends of homopolymers A and B.<sup>30</sup> Gradient copolymers are also being applied as the backbone in usual polymer brushes  $^{7,10,21,22,31}$  so that the density of grafted side chains varies smoothly along the chain.

Theoretically, monodisperse gradient copolymers can be synthesized from any controlled/"living" polymerization technique which exhibits simultaneous initiation of all growing chains with negligible chain transfer and easy cross-propagation.<sup>1</sup> To date, gradient copolymers have been successfully synthesized by nitroxide-mediated controlled radical polymerization (NM-CRP),9,13,15,16 atomtransfer radical polymerization (ATRP), 6,7,10,12-14,17-19,21,22

and reversible addition-fragmentation transfer polymerization (RAFT).<sup>5</sup> Herein, we report the first synthesis of gradient copolymers by ring-opening metathesis polymerization (ROMP). exo-5-(Benzyloxy)norbornene (**3a**) and *exo*-5-[(4-*tert*-butyl)benzyloxy]norbornene (**3b**) have been homopolymerized successfully with Grubbs catalyst 1, and their copolymerization under controlled addition rates yielded polymers with highly linear gradients.



When used with the "living" catalyst  $1,^{32,33}$  ROMP meets all of the requirements for successful gradient copolymer synthesis and can provide several advantages over radical polymerization systems. First, modern single-component catalysts allow ROMP to be carried out at room temperature (or below), with significantly faster rates than those observed for NM-CRP, which often requires higher temperature for successful initiation. Hence, using ROMP would eliminate undesirable thermal polymerization and the consequent broadening of the polydispersity of the resulting polymer.<sup>34</sup> Second, the C-C double bonds in the backbone of the resulting ROMP polymer can be further derivatized to provide a facile route to several new functionalized polymers.

Gradient copolymers can be produced under either batch or semibatch conditions. In batch polymerization, both monomers are added at the same time to the reaction flask, and the gradient produced is highly dependent on the reactivity ratio of the monomer pair and the monomer feed ratio.<sup>1</sup> While gradient copolymers have been formed under batch conditions for monomer pairs with very different reactivity ratios, only moderate changes in chain composition were observed.<sup>6,12,14,18,35</sup> In semibatch polymerization, a forced gradient is formed through the continuous addition of one monomer into a reaction flask containing the second monomer.<sup>1</sup> Semibatch polymerization of monomers even with reactivity ratios close to unity, as in the case for **3a** and **3b**, has

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resulted in gradient copolymers with significant changes in chain composition.  $^{7,13,14,16-18,20}$ 

To carry out a comprehensive study of the properties of A–B gradient copolymers, a variety of such copolymers, ranging from a 50/50 copolymer with a linear gradient to those with less significant gradients or nonlinear gradients, are needed. To date, only a few examples of A–B copolymers with cumulative compositions of 50% A and linear gradients have been reported.<sup>14,17,18</sup> In fact, the gradient shape for gradient copolymers of styrene and either acrylonitrile, methyl acrylate, or *n*-butyl acrylate was shown to change from S-like to linear with increasing addition rate. Herein we report the synthesis of 50/50 A-B copolymers with linear gradients whose significance can be changed with increasing addition rate. We also formed A-B gradient copolymers of **3a** and **3b** via the use of a forced gradient, where the two monomers are added at opposite ramping speeds.

## **Experimental Section**

**Materials.** HPLC-grade tetrahydrofuran (THF) was purified using the Dow-Grubbs purification system,<sup>36</sup> collected under argon, degassed under vacuum, and stored under nitrogen in a Strauss flask prior to use. Ethyl vinyl ether was dried over CaH<sub>2</sub>, vacuum-transferred into an airtight solvent bulb prior to transfer into an inert-atmosphere glovebox, and stored at 0 °C. All monomers were synthesized and stored under nitrogen at 0 °C. Deuterated solvents (Cambridge Isotope Laboratories), all other solvents, and reagents were purchased from commercial sources and used without further purification.

**Methods.** All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques or in an inert-atmosphere glovebox, unless otherwise noted. Conversion of the copolymerizations was determined on a Hewlett-Packard 5890A gas chromatograph equipped with a FID detector and a 30 m HP-5 capillary column (0.32 mm inner diameter, 0.25 mm film thickness; method: initial time = 0min, initial temperature = 50 °C, rate = 10 °C/min, final temperature = 250 °C, final time = 5 min) using undecane as an internal standard. Molecular weights relative to polystyrene standards were measured on a Waters gel-permeation chromatograph (GPC) equipped with Breeze software, a 717 autosampler, Shodex KF-G guard column, KF-803L and KF-806L columns in series, a Waters 2440 UV detector, and a 410 RI detector. HPLC-grade THF was used as the eluent at a flow rate of 1.0 mL/min, and the instrument was calibrated using polystyrene standards (Aldrich, 15 standards, 760-1 800 000 Da). <sup>1</sup>H spectra were recorded on a Varian Mercury 400 FT-NMR spectrometer (400.178 MHz for <sup>1</sup>H). <sup>13</sup>C NMR spectra were recorded on a Varian Inova 500 FT-NMR spectrometer (125.669 MHz for <sup>13</sup>C). <sup>1</sup>H NMR data are reported as follows: chemical shift (multiplicity: br = broad, s = singlet, d =doublet, t = triplet, q = quartet, and m = multiplet), peak assignments, and integration. <sup>1</sup>H and <sup>13</sup>C chemical shifts are reported in ppm downfield from tetramethylsilane (TMS,  $\delta$ scale) with the residual solvent resonances as internal standards, while peak assignments were made using ACD/Labs software packages (Advanced Chemistry Development, Inc.). GC-MS experiments were recorded on a Hewlett-Packard 6890 series instrument equipped with a HP-5 column (initial time = 2 min, initial temperature = 50 °C, rate = 10 °C/min, final temperature = 280 °C, final time = 5 min). All flash column chromatography was performed under a positive pressure of nitrogen using 230-400 mesh silica gel (56 mm i.d.  $\times$  200 mm L), unless otherwise noted. Monomer addition was carried out via either a Kd Scientific KDS100 syringe pump or a Sage Instruments syringe pump model 341B.

*exo*-5-(Benzyloxy)norbornene (3a). This compound was prepared using a modified literature procedure.<sup>37</sup> In an inert-atmosphere glovebox, a 100 mL Schlenk flask equipped with

a magnetic stir bar was charged with exo-5-norbornene-2-ol<sup>38,39</sup> (2 g, 18 mmol), THF (25 mL), and oil-free sodium hydride (500 mg, 21 mmol). The flask was capped with a rubber septum, removed from the glovebox, attached to a water-cooled condenser and a nitrogen bubbler, heated to reflux for 12 h while stirring, and then cooled to room temperature. Under nitrogen, benzyl bromide (2 mL, 17 mmol) in a THF solution (20 mL) was then added to the reaction mixture via cannula. The reaction mixture was again brought to reflux and was stirred for an additional 12 h. After cooling to room temperature, the reaction mixture was poured into diethyl ether (100 mL) and washed with water (3  $\times$  100 mL). The organic layer was collected, dried over anhydrous sodium sulfate, and filtered. The solvent was removed from the filtrate on a rotary evaporator to afford the crude product as a yellow oil. Flash column chromatography with methylene chloride:hexanes (20: 80) as the eluent gave the desired product as colorless oil (2.54 g, 69.8%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.58 (m, 7-norbornenyl-H<sub>2</sub>, 2H), 1.78 (d, 6-norbornenyl-H<sub>2</sub>, 2H), 2.96 (m, 4-norbornenyl-H and 1-norbornenyl-H, 2H), 3.62 (d, 5-norbornenyl-H, 1H), 4.56 (q, benzyl- $H_2$ , 2H), 5.94 (m, 3-norbornenyl-H, 1H), 6.21 (m, 2-norbornenyl-H, 1H), 7.30 (m, o- and p-aromatics, 3H), 7.35 (d, m-aromatics, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  34.7 (6-norbornenyl-C), 40.6 (1-norbornenyl-C), 46.3 (7-norbornenyl-C), 46.7 (4norbornenyl-C), 71.4 (benzyl-C), 80.2 (5-norbornenyl-C), 127.8 (o- and p-aromatics-3C), 128.6 (m-aromatics-2C), 133.4 (3norbornenyl-C), 139.1 (1-phenyl-C), 140.92 (2-norbornenyl-C). GC-MS: calcd for C<sub>14</sub>H<sub>16</sub>O: 200.28; found: 200.

*exo*-5-[(4-*tert*-Butyl)benzyloxy]norbornene (3b). This compound was synthesized by the same procedure used for **3a**. A colorless oil was obtained (3.61 g, 77.6%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.35 (s, *tert*-butyl- $H_9$ , 9H), 1.58 (m, 7-norbornenyl- $H_2$ , 2H), 1.78 (d, 6-norbornenyl- $H_2$ , 2H), 2.85 (d, 1,4-norbornenyl-H, 2H), 3.65 (d, 5-norbornenyl-H, 1H), 4.54 (q, benzyl- $H_2$ , 2H), 5.96 (m, 3-norbornenyl-H, 1H), 6.21 (m, 2-norbornenyl-H, 1H), 7.31 (m, o- and p-aromatics, 3H), 7.40 (d, *m*-aromatics, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  31.6 (*tert*-butyl-3C), 34.7 (6-norbornenyl-C), 40.6 (1-norbornenyl-C), 46.3 (7-norbornenyl-C), 46.7 (4-norbornenyl-C), 71.2 (benzyl-C), 80.2 (5-norbornenyl-C), 125.5 (*m*-aromatics-2C), 127.7 (*o*-aromatics-2C), 133.4 (1-phenyl-C), 136.1 (3-norbornenyl-C), 140.9 (2-norbornenyl-C), 50.5 (*p*-aromatics-1C). EIMS: calcd for C<sub>18</sub>H<sub>24</sub>O: 256.38; found: 256.1.

**Determination of Reactivity Ratios.** In an inert-atmosphere glovebox, THF (25 mL) and a mixture of **3a** and **3b** (10, 30, 50, 70, or 90% of **3a**, with a total of 7 mmol in each round-bottom) were added to a series of 100 mL round-bottom flasks equipped with magnetic stir bars. To a series of 5 scintillation vials, Grubbs catalyst **1** (8.0 mg,  $9.7 \times 10^{-3}$  mmol, 0.0014 equiv) and THF (1 mL) were added. While each monomer mixture was stirred rapidly, the catalyst solution was injected. The reaction was quenched after 3 min with ethyl vinyl ether (1 mL).<sup>40</sup> Conversion of the monomer into copolymer was determined by GC, and the reactivity ratios were detained as averages of four runs.

**Synthesis of Homopolymers of 3a and 3b.** In a typical polymerization, a scintillation vial equipped with a stir bar was charged with either **3a** or **3b** (2.5 mmol) and diluted with THF (10 mL). Another scintillation vial was charged with Grubbs catalyst **1** (5.1 mg,  $6.2 \times 10^{-3}$  mmol) and diluted with THF (1 mL). The catalyst solution was injected into the stirring monomer solution, and the vial was capped. The vial was removed from the glovebox, and after 40 min the polymerization was quenched with ethyl vinyl ether (2 mL). 2,6-Di-*tert*-butyl-4-methylphenol (BHT) (30 mg) was added, and the polymer was precipitated in swirling methanol. The final polymer was dried for 2 days under vacuum.

**Synthesis of Block Copolymers of 3a and 3b.** In a typical polymerization, a scintillation vial equipped with a stir bar was charged with **3a** (0.50 g, 2.50 mmol) and diluted with THF (7 mL). Another scintillation vial was charged with Grubbs catalyst **1** (13.7 mg,  $1.7 \times 10^{-2}$  mmol) and diluted with THF (1 mL). The catalyst solution was injected into the stirring monomer solution, and the vial was capped. Another scintil-

lation vial was charged with **3b** (0.65 g, 2.55 mmol) and diluted with THF (2 mL). After 40 min of polymerization, the **3b** solution was injected into the reaction mixture. The vial was rinsed with THF (1 mL  $\times$  3) and added to the reaction mixture. The reaction vial was removed from the glovebox, and after 40 min the polymerization was quenched with ethyl vinyl ether (2 mL). BHT (30 mg) was added, and the polymer was precipitated in swirling methanol. The final polymer was dried for 2 days under vacuum.

**Synthesis of Random Copolymers of 3a and 3b.** In a typical polymerization a scintillation vial equipped with a stir bar was charged with **3a** (0.25 g, 1.25 mmol) and **3b** (0.32 g, 1.25 mmol) and diluted with THF (7 mL). Another scintillation vial was charged with Grubbs catalyst **1** (8.3 mg,  $1.0 \times 10^{-2}$  mmol) and diluted with THF (1 mL). The catalyst solution was injected into the stirring monomer solution, and the vial was capped. The vial was removed from the glovebox, and after 40 min the polymerization was quenched with ethyl vinyl ether (2 mL). BHT (30 mg) was added, and the polymer was precipitated in swirling methanol. The final polymer was dried for 2 days under vacuum.

Synthesis of Gradient Copolymers: Semibatch. In an inert-atmosphere glovebox, compounds **3a** (25  $\mu$ L, 1.2  $\times$  10<sup>-1</sup> mmol) and **3b** (570  $\mu$ L, 2.2 mmol), undecane (70  $\mu$ L, 3.3  $\times$  10<sup>-1</sup> mmol), and THF (152 mL) were added to a 500 mL roundbottom flask containing a magnetic stir bar. The flask was capped with a rubber septum and attached to a syringe pump loaded with neat 3a (1 mL) in a 1 mL gastight syringe. Grubbs catalyst 1 (8.3 mg,  $1.0 \times 10^{-2}$  mmol) was dissolved in THF (2 mL) in a scintillation vial and loaded into a 3 mL disposable syringe. The catalyst solution was injected into the rapidly stirring monomer solution, and the syringe pump was started simultaneously to add **3a** at a set rate. During the polymerization, 2 mL aliquots were removed from the reaction flask and quenched with ethyl vinyl ether (1 mL).<sup>40</sup> BHT (5 mg) and triphenylphosphine oxide (20 mg) were then added to each aliquot to prevent cross-linking and ease the removal of the catalyst.<sup>41</sup> A portion of each aliquot (0.3 mL) was loaded on a plug of silica gel (3.55 cm L  $\times$  0.55 cm i.d.), eluted with CH<sub>2</sub>-Cl<sub>2</sub> (8 mL), and analyzed by GC. The amount of monomer incorporated into the polymer was calculated from the amount of remaining monomer.<sup>1</sup> The remaining portion of each aliquot was concentrated on a rotary evaporator to about 0.1 mL. Methanol (2 mL) was then added to the residue to precipitate the polymer, the mother liquor was decanted, and the polymer was dried under vacuum overnight before being analyzed by GPC.

Typical reaction times were 30 min to 1 h, depending on the rate of addition of 3a. The polymerization was allowed to proceed until the feed ratio<sup>42</sup> was 90% **3a** (as determined by GC) and then was quenched with ethyl vinyl ether (5 mL).<sup>40</sup> (At this point, the gradient composition is approximately **3a**: **3b** 1:1, and the resulting polymer is designated as **3a**<sub>1</sub>-g-**3b**<sub>1</sub>. To achieve a gradient composition of  $3a:3b 2:1 (3a_2-g-3b_1)$ , the polymerization is carried out for about 15-20 min beyond the initial point of 90% 3a feed ratio.) BHT (125 mg) and triphenylphosphine oxide (300 mg) were then added to the flask. The reaction solution was concentrated on a rotary evaporator to about 5 mL and precipitated in rapidly stirred methanol (250 mL). The precipitated polymer was collected and precipitated a second time if necessary. The final polymer sample was collected and dried under vacuum before analysis by GPC. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.22 (s, *tert*-butyl-H<sub>9</sub>), 1.56 (br s, cyclopentyl-Hs), 2.06 (br s, cyclopentyl-Hs), 2.82 (br s, cyclopentyl-Hs), 3.30 (br d, cyclopentyl-Hs), 3.71 (br s, cyclopentyl-H), 4.45 (br d, benzyl-H<sub>2</sub>), 5.49 (m, olefin-Hs), 7.14-7.37 (m, aromatic-Hs).

**Synthesis of Gradient Copolymers: Dual Ramping.** In an inert-atmosphere glovebox, compounds **3a** (0.808 g, 4.040 mmol) and **3b** (0.517 g, 2.020 mmol) were weighed into a 10 and 50 mL volumetric flask, respectively, and diluted with THF. Both solutions were taken up into gastight syringes and loaded onto two different syringe pumps. In a scintillation vial, Grubbs catalyst **1** (8.3 mg, 0.010 mmol) was dissolved in THF (2 mL) and loaded into a 3 mL disposable syringe.

 Table 1. Monomer Addition Rates (mmol/h) of 3a and 3b

 throughout the Reaction for Dual-Ramping Experiments

		time (min)							
run	monomer	0	3	6	12	18	24	30	36
1	3a	1.8		2.8	3.4	4.0	6.0	10.0	18.0
	3b	27.0		17.0	10.0	6.8	5.0	3.4	2.3
2	3a	0.82	1.2	2.9	3.3	3.7	6.2	9.4	12.0
	3b	9.3	7.1	5.0	2.9	1.7	1.3	0.84	0.84
3	3a	1.2	2.1	2.9	3.3	3.7	5.8	9.9	1.2
	3b	9.4	7.1	5.0	2.9	1.7	1.3	0.85	0.85

Table 2. Monomer Addition Rates (mmol/h) of 3a and 3b for Synthesis of an Unusual Gradient Shape during the Dual-Ramping Method

			time (min)							
run	monomer	0	2	6	12	18	24	30	36	
4	3a 3b	0.00 4.02	1.80 4.02	2.80 2.54	3.60 1.54	6.00 0.76	8.00 0.50	12.00 0.35	18.00 0.20	

Next, a 500 mL round-bottom flask equipped with a magnetic stir bar was charged with **3a** (9  $\mu$ L, 4.3 × 10<sup>-3</sup> mmol), **3b** (100  $\mu$ L, 3.8  $\times$  10<sup>-1</sup> mmol), undecane (100  $\mu$ L, 8.6  $\times$  10<sup>-1</sup> mmol), and THF (102 mL). The monomer solution flask was capped with a rubber septum, attached to the loaded syringe pumps, and allowed to stir rapidly. The catalyst solution was injected into the reaction flask, and the solutions of 3a and **3b** were simultaneously added via syringe pumps. The addition rate of the 3a solution was ramped up while the 3b solution was ramped down every 3-6 min (Table 1). Aliquots (2 mL) were taken 1 min after each change in addition rate and quenched with ethyl vinyl ether (1 mL).<sup>40</sup> BHT (5 mg) and triphenylphosphine oxide (20 mg) were then added to each aliquot. A portion of each aliquot (0.3 mL) was loaded on a plug of silica gel (3.55 cm L  $\times$  0.55 cm i.d.), eluted with CH<sub>2</sub>- $Cl_2$  (8 mL), and analyzed by GC. The amount of monomer incorporated into the polymer was calculated from the amount of remaining monomer. The remaining portion of each aliquot was concentrated on a rotary evaporator to about 0.1 mL. Methanol (2 mL) was then added to the residue to precipitate the polymer, the mother liquor was decanted, and the polymer was dried under vacuum overnight before being analyzed by GPC.

The reaction was quenched at 42 min with ethyl vinyl ether (5 mL). BHT (125 mg) and triphenylphosphine oxide (300 mg) were then added to the flask. The reaction solution was concentrated on a rotary evaporator to about 5 mL and precipitated in rapidly stirred methanol (250 mL). The precipitated polymer was collected and precipitated a second time if necessary. The final polymer sample was collected and dried under vacuum before analysis by GPC.

**Synthesis of Gradient Copolymers with Unusual Gradient Shapes: Dual Ramping.** The same dual-ramping procedure described above was used. The rates of addition (Table 2) were adjusted every 6 min, and the reaction was allowed to polymerize for a total of 42 min.

Polymer Hydrogenation. This experiment was a modification of a literature procedure.43 In an inert nitrogen atmosphere glovebox, the ROMP polymer (630 mg) was dissolved in THF (9 mL) and methylene chloride (3 mL) and loaded into a 125 mL Parr reactor equipped with a magnetic stir bar and a glass liner. To this solution, Grubbs catalyst 1 (25 mg, 0.030 mmol) was added. The reactor was sealed, removed from the box, pressurized with hydrogen (1000 psi), and allowed to stir for 1 week at room temperature. The reaction was monitored by <sup>1</sup>H NMR spectroscopy though opening the Parr reactor in the glovebox, removing an aliquot, and precipitating the polymer. If the reaction was not complete, the Parr reactor was repressurized with H<sub>2</sub> and the reaction was allowed to continue. Once hydrogenation was complete, the reaction was transferred into a 500 mL roundbottom flask, and the reactor was rinsed with methylene chloride (3  $\times$  2 mL). BHT (50 mg) was then added to the flask. The combined organics were concentrated on a rotary evapora-

Table 3. Number-Average Molecular Weight, Weight-Average Molecular Weight, Polydispersity Index, and  $T_{g,(1/2)\Delta C_p}$  Datafor Hydrogenated, Brominated, and Bromoalkoxylated Gradient Copolymers of 3a and 3b

polymer	$M_{ m n}  imes 10^{-3}$ (g/mol)	$M_{ m w}  imes 10^{-3}$ (g/mol)	PDI	$T_{\mathrm{g},(1/2)\Delta C_p}$ (°C)	% <b>3a</b>
original 1:1 gradient poly( <b>3a</b> 1-g- <b>3b</b> 1)	171	192	1.12	32.8	54.1
original 2:1 gradient poly(3a <sub>2</sub> -g-3b <sub>1</sub> )	164	197	1.20	30.4	68.3
brominated 2:1 gradient poly(3a <sub>2</sub> -g-3b <sub>1</sub> )	168	210	1.25	decomp	68.3
bromomethoxylated 2:1 gradient poly(3a <sub>2</sub> -g-3b <sub>1</sub> )	203	242	1.19	decomp	68.3
hydrogenated 1:1 gradient poly( <b>3a</b> <sub>1</sub> -g- <b>3b</b> <sub>1</sub> )	177	202	1.14	21.2	54.1

tor to 5 mL and precipitated into rapidly stirred methanol (200 mL). The precipitated polymer was collected and precipitated a second time. The final polymer sample was collected and dried under vacuum before analysis by GPC. GPC analysis was performed on both the hydrogenated and original polymer to verify that no degradation of the polymer had occurred. <sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta$  0.72 (br s, cyclopentyl-*Hs*), 1.22 (s, *tert*-butyl- $H_9$ ), 1.33 (br s, backbone-*Hs*), 1.65 (br s, cyclopentyl-*Hs*), 2.17 (br s, cyclopentyl-*Hs*), 3.63 (br d, cyclopentyl-*H*), 4.47 (br m, benzyl-H<sub>2</sub>), 7.10–7.39 (m, aromatic-*Hs*).

**Polymer Bromination.** In a typical experiment, ROMP gradient polymer (314 mg) was dissolved in methylene chloride (100 mL) in a 500 mL round-bottom flask equipped with a magnetic stir bar. 2,6-Lutidine (0.30 mL, 2.6 mmol) was added via syringe, and the reaction flask was attached to a 25 mL addition funnel. Bromine (0.10 mL, 1.9 mmol) was then dissolved in methylene chloride (10 mL) and loaded into the addition funnel. The bromine solution was added to the rapidly stirring reaction over 15 min, and the resulting red solution was allowed to stir for 1 h. The reaction mixture was concentrated to dryness on a rotary evaporator, redissolved in a minimal amount of methylene chloride (<5 mL), and precipitated into rapidly stirring methanol (250 mL). The precipitated polymer was collected and dried under vacuum overnight. GPC analysis was performed on both the brominated and original polymer to ensure that no randomization of the polymer had occurred (Table 3). <sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta$  1.24 (s, cyclopentyl-Hs), 1.38 (s, tert-butyl-H<sub>9</sub>), 1.88 (br s, cyclopentyl-Hs), 3.11 (br s, backbone-H2), 4.27 (br s, cyclopentyl-H), 4.44 (br s, benzyl-H<sub>2</sub>), 7.23–7.39 (m, aromatic-Hs). EA: Theoretical wt % Br = 42.5% for full bromination, actual wt % Br = 40.46%, indicating that 95% of the polymer double bond has been brominated.

Polymer Bromoalkoxylation. In a typical experiment, ROMP gradient copolymer (0.393 g) was dissolved in methylene chloride (125 mL) and methanol (70 mL) in a 500 mL round-bottom flask equipped with a magnetic stir bar. 2,6-Lutidine (0.30 mL, 2.6 mmol) was added via syringe, and the reaction flask was attached to a 25 mL addition funnel. Bromine (0.11 mL, 2.1 mmol) was then dissolved in methylene chloride (10 mL) and loaded into the addition funnel. The bromine solution was added to the rapidly stirring reaction over 15 min, and the resulting red solution was allowed to stir for 1 h. The reaction mixture was concentrated to dryness on a rotary evaporator, redissolved in a minimal amount of methylene chloride (<5 mL), and precipitated into rapidly stirring methanol (250 mL). The precipitated powder polymer was collected via vacuum filtration and dried under vacuum overnight. GPC analysis was performed on both the bromoalkoxylated and original polymer to verify that no randomization of the polymer had occurred. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.24 (s, tert-butyl-H<sub>9</sub>), 1.88 (br s, cyclopentyl-Hs), 2.78 (br s, methoxy-H<sub>3</sub>), 3.28 (br s, backbone ether-H), 4.27 (br s, benzyl-H<sub>2</sub>), 4.45 (br s, brominated backbone-H), 7.22–7.35 (m, aromatic-Hs). EA: theoretical wt % Br = 17.5% for completely selective bromomethoxylation, actual wt % Br = 34.31%, indicating that 57% of the polymer double bond has been brominated and 43% of the double bonds have been bromomethoxylated.

**Sample Preparation for DSC Analysis.** The unsaturated ROMP polymers and copolymers described above often contain a small amount of residual monomers, which plasticize the polymers and influence their thermal properties. Hence, the residual monomers must be removed before accurate thermal data for these materials can be obtained. To accomplish this objective, a small quantity (270 mg) of the ROMP copolymer

Scheme 1. Synthesis of Monomers



was dissolved in  $CH_2Cl_2$  (2 mL) and precipitated into stirring methanol (100 mL). The precipitated polymer was collected and dried under vacuum. The mother liquor was evaporated on a rotary evaporator and resuspended in  $CH_2Cl_2$  (3 mL). A portion of this solution (1 mL) was then eluted through a plug of slica gel with  $CH_2Cl_2$  (8 mL) and checked by GC for sign of residual monomers. When residual monomer was detected, the precipitated polymers were again redissolved and reprecipitated and the mother liquor was reanalyzed. This process was repeated until no monomer could be detected in the mother liquor by GC and required an average of six cycles. The clean polymer was then dried under vacuum for 2 days.

**Thermal Property Characterization.** The glass transition temperature,  $T_{\rm g}$ , of each as-precipitated polymer, prepared in the manner described above, was obtained via differential scanning calorimetry (DSC) on a Mettler-Toledo DSC 822 instrument. Dry nitrogen was purged through the cell at a flow rate between 45 and 55 mL/min, and an external refrigeration unit was used to cool. In a typical experiment, 1-10 mg of sample in an aluminum pan was heated from -50 to 100 °C at a rate of 10 °C/min, held at 100 °C for 10 min, quenched at a rate of 40 °C/min, and then reheated to 100 °C at 10 °C/min, unless otherwise noted. The  $T_{\rm g}$ 's are reported as the onset temperature,  $T_{\rm g,onset}$ , and the temperature at half the change in heat capacity,  $T_{\rm g,(1/2)\Delta C_{p'}}$  for the second heating cycle. All reported  $T_{\rm g}$ 's have a  $\pm 0.3$  K experimental error.

# **Results and Discussion**

Monomers **3a** and **3b** were synthesized in three steps from norbornadiene (Scheme 1). Their reactivity ratios for ROMP using catalyst **1** were measured to be  $0.99 \pm$ 0.06 and  $1.13 \pm 0.09$ , respectively. Since the reactivities of ROMP monomers toward well-defined ROMP catalysts are known to be influenced by the ring strain of the monomer,<sup>44-46</sup> the stability of the propagating carbene,<sup>47</sup> and steric effects,<sup>44,48-51</sup> similar reactivities for **3a** and **3b** are expected: the discriminating substituents are simply too far from the olefin moiety to have a large effect. We are aware of only one other example where reactivity ratios for 5-subsituted norbornenes are found to be similar and close to unity.<sup>52</sup>

To date, differences in the reactivities between ROMP monomers toward a specific catalyst system are typically framed in terms of the differences in their homopolymerization rates and the observed differences in monomer conversion during copolymerization;<sup>53–58</sup> measured reactivity ratios are rare. Ilker and Coughlin determined the reactivity ratios for *endo-N*-ethyl-7-oxanobornene-2,3-dicarboxylimide and cyclooctene (COE)



Figure 1.  $F_{\text{cum}}$  of **3a** vs normalized chain length for different addition rates of **3a**.



Figure 2.  $F_{inst}$  of **3a** vs normalized chain length for different addition rates of **3a**.

in the presence of **1** to be 0.04 and 0.08, respectively, allowing for the formation of an almost perfectly alternating copolymer.<sup>59</sup> Balcar and Dosedlová found the reactivity ratios for 5-norbornene-2-yl acetate and COE and norbornene (NBE) to be  $r_1 = 1$  and  $r_2 = 132$  and  $r_1 = r_2 = 1$ , respectively, using WCl<sub>6</sub>/(CH<sub>3</sub>)<sub>4</sub>Sn.<sup>52</sup> Reactivity ratios for NBE and COE were determined to be 8.9 and 0.51, respectively, using WCl<sub>6</sub>/Ph<sub>4</sub>Sn.<sup>60</sup> Monakov et al. also measured reactivity ratios for NBE with various 7-oxonorbornenes in the presence of RuCl<sub>3</sub>·3H<sub>2</sub>O.<sup>61</sup>

As expected for monomers with similar reactivity ratios, mixtures of **3a** and **3b** gave no gradients in batch polymerization. However, semibatch polymerizations, with the addition of **3a** to a 1:9 mixture of **3a**:**3b** at different rates, did produce significant gradients (Figure 1). From the monomer conversion data, cumulative ( $F_{cum}$ ) and instantaneous compositions ( $F_{inst}$ )<sup>1</sup> were calculated from eqs 1 and 2, where X and Y are the quantities (mol) of monomers x and y in the polymer, respectively, and  $\rho$  is conversion.

$$F_{\rm cum,1} = \frac{X}{X+Y} \tag{1}$$

$$F_{\text{inst},1} = F_{\text{cum},1} + \rho \, \frac{\Delta F_{\text{cum},1}}{\Delta \rho} \tag{2}$$

As seen in Figure 1, 50/50 copolymers of **3a** and **3b** with linear gradients were produced at three different addition rates of **3a**. The significance of the gradient, as expressed by either  $F_{\text{cum},3a}$  (Figure 1) or  $F_{\text{inst},3a}$  (Figure 2), decreases with increasing addition rate of **3a**. The shape of the gradient for **3a** and **3b** ROMP copolymers does not change with addition rate as is does in ATRP polymerization with *n*-butyl acrylate/styrene<sup>14</sup> ( $r_{\text{S}} = 0.70$ ,  $r_{\text{nBA}} = 0.16$ ), methyl acrylate/styrene,<sup>17</sup> and styrene/acrylonitrile<sup>18</sup> ( $r_{\text{S}} = 0.29$ ,  $r_{\text{AN}} = 0.02$ ) where the reactivity ratios of the polymer pairs are less than 1.



**Figure 3.**  $M_n$  and PDI of a  $3a_1$ -*g*- $3b_1$  copolymer as a function of polymerization time.



**Figure 4.** Comparison of percentage of **3a** incorporated into the copolymer as determined by GC and <sup>1</sup>H NMR.

These latter monomer pairs have some tendency to alternate while 3a and 3b tend toward random copolymers. Gradient copolymers of styrene and 4-acetoxystyrene, whose reactivity ratios in radical polymerization are also close to unity ( $r_{\rm S} = 0.887$  and  $r_{\rm AS} = 1.128$ ),<sup>62</sup> have been made via NM-CRP.13,15,16 However, significant gradients were only achieved for copolymer compositions that are well over 50% styrene<sup>16</sup> or 50% 4-acetoxystyrene.<sup>13</sup> Our work suggested that, for ROMP monomer pairs that favor statistical tendencies, consistent linear gradient shape could be obtained over a range of appropriate addition rates. This is significant because a plethora of gradient copolymer compositions can be achieved via semibatch polymerization for a single pair of monomers simply by changing the addition rates and times for one monomer.

Figure 3 shows the  $M_n$  and polydispersity index of a  $3a_1$ -g- $3b_1$  copolymer as a function of polymerization time. The linear increase in  $M_n$  and the steady low PDI demonstrate the living nature of catalyst 1 toward 3a and 3b and the formation of a "controlled" copolymer. For ease of experiment, we determined the extent of polymerization and monomer incorporation via GC quantification of unreacted monomer, an indirect but facile method. However, the percentage of monomer incorporated into the copolymer can also be followed by NMR spectroscopy at long reaction times when sufficient amounts of polymer can be recovered for analysis. Increasing incorporation of 3a into the copolymer can be observed, and this data corresponded well with the GC conversion data (Figure 4).

Ideally, for a monomer pair with similar and closeto-unity reactivity ratios, such as 3a and 3b, the feed ratio for the monomers should be changed linearly from 0 to 1 during the polymerization to achieve the best gradient (Figure 5). In our case, because of the high



**Figure 5.** Idealized relationship between feed ratio of **3a** and time. The solid line represents the perfectly ideal gradient polymerization where the feedstock begins with no **3a**. The dotted line represents the desired change in the feed ratio for a polymerization setup that begins with a feedstock of 10% **3a**.



**Figure 6.** Experimental observation of the change in the feed ratio of **3a** during polymerization at three different addition rates. The solid lines represent the ideal change in the feed ratio for the polymerization time span.

activity of the ROMP catalyst and the limitation of our addition equipment, the initial feed ratio needs to be kept at about 0.1 to avoid making a homopolymer block at one end of the desired gradient copolymer.

While the gradient shapes shown in Figures 1 and 2 are fairly linear, they begin to deviate near the end of the polymerization. This is a mathematical consequence of the change in feed ratio toward the end of the polymerization for monomer pairs with reactivity ratios near unity. The feed ratio of 3a is the mole fraction of **3a** in the feedstock. At a constant addition rate, the feed ratio of **3a** ceases to be linear and begins to taper off near 70% (Figure 6) because the relationship between the change in the feed ratio with respect to time is "hyperbolic", asymptotically approaching 100%. To maintain a linear change in the feed ratio for the entire polymerization time span, an increasingly large excess of 3a would need to be added toward the end of the polymerization. However, such large and rapid additions of neat 3a near the end of the polymerization would result in local concentration gradient problems and may give rise to a block of **3a** at the end of the gradient copolymer. We hypothesized that a dual-ramping method where the addition rate of both monomers can be varied semicontinuously in opposite directions would allow us to compensate for this problem. This strategy would allow us to fine-tune the feed ratio as the polymerization occurred by adjusting the addition rate of both monomers over time.

To this end, we set up a copolymerization with two syringe pumps, each loaded with a solution of one monomer. The concentration of monomer **3a** in the reaction mixture was gradually increased by raising the



**Figure 7.** Experimental observation of the change in the feed ratio of **3a** during a dual-ramping polymerization. The solid line represents the ideal change in the feed ratio for the polymerization time span.



**Figure 8.**  $F_{\text{inst}}$  and  $F_{\text{cum}}$  of **3a** vs normalized chain length for several different dual-ramping runs. The rates for the runs are listed in Table 1.



**Figure 9.**  $F_{\text{inst}}$  of **3a** vs normalized chain length for an unusually shaped gradient copolymer synthesized via a dual-ramping strategy.

addition rate of **3a** (ramp up) while the concentration of **3b** in the reaction mixture was decreased by reducing the addition rate of **3b** (ramp down). This dual-ramping strategy allowed us to achieve a near-ideal feed ratio (Figure 7) and resulted in copolymers with ideal linear gradients containing about 55% **3a** (Figure 8). It also allowed for the design of novel gradient shapes such as that shown in Figure 9. The gradient copolymer with this S-shape<sup>19</sup> can be considered as having three blocks. The first and last blocks have steep gradients while the middle block has a gradual gradient, with a composition that is close to that of a random copolymer (Figure 9).

**Functionalization of the ROMP Copolymer.** While NM-CRP can be utilized to make gradient copolymers of a variety of vinyl monomers, the final polymer chains are capped with dormant radicals. Unless chemically deactivated, these radicals can become active upon heating and the polymer chains may recombine<sup>63</sup> which could limit their application and processing potential.

 Table 4. Thermal Properties of ROMP Gradient, Block, and Random Copolymers of 3a and 3b as Well as the Respective Homopolymers

polymer	$T_{g,onset}$ (°C)	$T_{\mathrm{g},(1/2)\Delta C_p}$ (°C)	$M_{ m n}  imes$ 10 $^{-3}$ (g/mol)	$M_{ m w}  imes 10^{-3}$ (g/mol)	PDI	% <b>3a</b>
poly( <b>3a</b> )	18.1	20.7	87	120	1.38	100
poly( <b>3b</b> )	45.0	48.6	65	72	1.10	0
poly( <b>3a</b> - <i>b</i> - <b>3b</b> )	17.9	20.8	110	148	1.35	46.4
	40.7	45.3				
poly( <b>3a</b> - <i>r</i> - <b>3b</b> )	23.9	28.0	67	79	1.18	50.1
1.1 gradient poly( <b>3a</b> <sub>1</sub> - <i>g</i> - <b>3b</b> <sub>1</sub> ) 1	26.1	29.5	161	184	1.14	58.4
1:1 gradient poly(3a1-g-3b1) 2	29.4	34.8	165	191	1.15	52.9
1:1 gradient poly( <b>3a</b> <sub>1</sub> -g- <b>3b</b> <sub>1</sub> ) 3	28.9	32.8	163	184	1.13	54.0
1.1 gradient poly( <b>3a</b> <sub>1</sub> - <i>g</i> - <b>3b</b> <sub>1</sub> ) 4	29.9	36.0	151	186	1.23	46.3

 Table 5. Thermal Properties of the Hydrogenated ROMP Gradient, Block, and Random Copolymers of 3a and 3b as Well as the Respective Homopolymers

polymer	$T_{\rm g,onset}$ (°C)	$T_{g,(1/2)\Delta C_p}$ (°C)	$M_{ m n}  imes 10^{-3}$ (g/mol)	$M_{ m w}  imes 10^{-3}$ (g/mol)	PDI	% <b>3a</b>			
hydrogenated poly( <b>3a</b> )	6.4	9.2	125	156	1.24	100			
hydrogenated poly(3b)	36.4	40.0	105	119	1.13	0			
hydrogenated poly(3a-b-3b)	6.1	9.8	179	196	1.10	49.5			
	28.6	35.7							
hydrogenated poly( <b>3a</b> - <i>r</i> - <b>3b</b> )	16.9	20.1	74	86	1.16	61.9			
hydrogenated 1:1 gradient poly( <b>3a</b> <sub>1</sub> -g- <b>3b</b> <sub>1</sub> ) 2	18.9	23.8	136	177	1.30	52.9			
hydrogenated 1:1 gradient poly(3a <sub>1</sub> -g-3b <sub>1</sub> ) 3	16.6	20.7	177	202	1.14	54.0			





The same problem could potentially occur with gradient copolymers made from ATRP if the metal catalyst is not completely removed at the end of the polymerization. In contrast, gradient copolymers synthesized via ROMP would not be plagued by such problems as the catalyst can be cleaved from the end of the polymer via a quenching agent. Furthermore, the olefins in the backbone of ROMP polymers provide the opportunity for postpolymerization modification. For example, we have demonstrated that the gradient copolymers of **3a** and **3b** can be hydrogenated, brominated, and bromomethoxylated (Scheme 2).

In our hands, chemical hydrogenation of our **3a**and **3b**-based polymers with toluenesulfonylhydrazine (TSH)<sup>64,65</sup> in the presence of tributylamine led to an increase in polymer dispersity and polymer degradation due to the high temperatures required for the formation of the diimide hydrogenation agent. Established polymer hydrogenation catalysts such as Crabtree's catalyst<sup>66</sup> resulted only in limited success: 39.2% of the olefins remained even after 24 h under 50 psi of H<sub>2</sub>. An additional 25.8% of the olefins were hydrogenated at 66 h after an addition of more catalyst (2 mg,  $2.5 \times 10^{-6}$ mol). Our best strategy took advantage of a procedure by Drouin et al. where Grubbs catalyst 1 was used in a tandem ROMP-hydrogenation cycle for the synthesis of ROMP polymers and hydrogenated ROMP polymers.<sup>43</sup> Under moderate hydrogen pressure, Grubbs catalyst 1 can be converted into a hydrogenation catalyst, which allowed us to carry out polymer synthesis and the subsequent polymer hydrogenation in a onepot manner. Drouin and co-workers reported complete hydrogenation of poly(cyclooctene) in 24 h; however, our hydrogenation experiments required up to a week for complete conversion. The increased reaction time may result from the more sterically hindered double bond present in norbornene-based ROMP polymers as well as the increased chain lengths of our gradient copolymers: on average, our gradient copolymers were 700-800 repeating units long while Drouin et al. used polymers with DP of about 200-300.

Electrophilic addition of a halogen to unsaturated polymers is another well-known method for polymer modification. For example, chlorination of elastomers such as butyl rubber is a commercially important strategy to improve cure properties.<sup>67–69</sup> Bromination of unsaturated polymers is also straightforward but has been less extensively studied.<sup>67,69–73</sup> In our hands, the gradient copolymers of 3a and 3b were easily brominated in methylene chloride using a bulky base (2,6-lutidine) in conjunction with liquid Br<sub>2</sub>. The resulting fully brominated polymer was soluble in most organic solvents. We also synthesized a soluble bromomethoxylated polymer through the controlled bromination of the **3a** and **3b** gradient copolymers in methanol. Other reactive cosolvents such as THF can potentially be incorporated into this bromination chemistry as demonstrated by Dreyfuss and co-workers for polybutadiene.<sup>70</sup> Table 3 lists the characterization data for our brominated and hydrogenated polymers.

While there is a growing number of reports on the synthesis of gradient copolymers, there have been few

studies that report on the thermal properties of gradient copolymers. Farcet and Charleux detected only one  $T_{g}$ in their styrene/*n*-butyl acrylate copolymers with weak gradients. Matyjaszewski et al. demonstrated microphase separation of copolymers with a much stronger gradient through both thermal and rheological analysis for styrene/methyl acrylate gradient copolymers and by small-angle X-ray scattering (SAXS) in styrene/acrylonitrile gradient copolymers. These workers observed a single  $T_{\rm g}$  in a thermally quenched gradient copolymer and two  $T_{g}$ 's in an annealed gradient copolymer.

The thermal properties for our norbornene-based ROMP polymers are shown in Table 4 and the corresponding hydrogenated polymers in Table 5. The benzyl ether substituents on norbornene raised the  $T_{g}$ 's of poly3a and poly3b to near and above room temperature, respectively. Hydrogenation lowered the  $T_g$ 's due to increased freedom of rotation in the backbone. This decrease was also observed by Hillmyer et al. in their carboximide-functionalized 7-oxanorbornene polymers.<sup>66</sup> The brominated and bromomethoxylated gradient copolymers were not thermally stable and decomposed above 100 °C.

In our studies, the linear gradient copolymers synthesized by the dual-ramping method exhibit only one  $T_{\rm g}$ , and no microphase separation is detected by preliminary SAXS experiments. This is not surprising since  $\chi$  (the Flory–Huggins interaction parameter) is estimated to be low for these copolymers.<sup>74</sup> Interestingly, the monomers are substantial plasticizers, and a combined 5 wt % can depress the  $T_g$  by 13–19 °C. The ROMP gradient, block, and random copolymers of 3a and **3b** as well as the respective homopolymers were all high molecular weight  $(M_n = 80 - 170 \times 10^3)$  with narrow PDI's, most within 1.11-1.20.

#### Conclusion

In conclusion, we have synthesized the first gradient copolymers via ROMP. These norbornene-based gradient copolymers are among a very few gradient copolymers reported to date where a linear gradient shape can be obtained in conjunction with a 50/50 monomer cumulative composition. Furthermore, through a dualramping strategy, we can fine-tune the monomer feed ratio to produce an exceptionally linear gradient copolymer and manipulate the gradient shape. Our ROMP gradient polymers can be easily functionalized further via hydrogenation, bromination, or bromoalkoxylation. Interfacial segregation studies are being carried in our laboratory to evaluate the use of these gradient copolymers as compatibilization agents and as model for systems of copolymers having a low  $\chi$  parameter.

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