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Photoresponsive Polymers Containing Nitrobenzyl Esters via Ring-Opening Metathesis Polymerization

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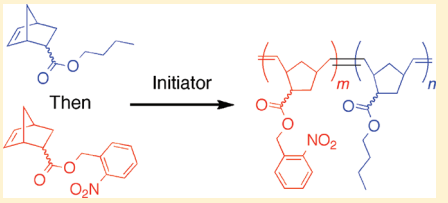
Supporting Information

ABSTRACT: This paper describes controlled ring-opening metathesis polymerizations (ROMP) of norbornene derivatives that bear photoreactive *o*-nitrobenzyl ester (NBE) moieties. Termination reactions have frustrated previous reported attempts to execute controlled radical polymerizations with nitrobenzyl ester-containing acrylate derivatives. We therefore prepared new NBE-containing norbornene derivatives, and found that polymerization with Grubbs's ruthenium carbene catalysts led to complete consumption of monomer in minutes to hours and yielded polymers with predictable molecular weights. We also demonstrate the preparation of NBE-containing block copolymers and show through UV irradiation of these polymers in solution and in thin film that the NBE moieties remain photoreactive.



INTRODUCTION

This paper describes new polymers, synthesized from norbornene-based monomers using ring-opening metathesis polymerization (ROMP), which contain photocleavable *o*-nitrobenzyl ester side chains. Polymers and other materials that irreversibly change their chemical structure upon irradiation with light are critical for technologies such as photolithography, optical storage, and actuation.[1] In addition to more traditional homopolymers and random copolymers, several block copolymers that have either one photoresponsive block or a photolabile linkage between two blocks have been reported.[2−9] Such strategies have taken advantage of block copolymer self-assembly properties to form light-degradable micelles for drug-delivery[10−12] or photoresponsive templates for nanoporous materials.[5]

In the general class of photolabile structural moieties, nitrobenzyl (NB) groups, including nitrobenzyl esters (NBEs), are among the most popular. Upon irradiation with UV light, an NBE undergoes a Norrish-type reaction, breaking its benzylic C−O bond to yield a carboxylic acid and *o*-nitrosobenzaldehyde.[13] In addition to the numerous applications in "photocaging" properties such as fluorescence[14−16] or biochemical activity,[17−19] the photolabile nature of NB groups and its relative ease of functionalization with other moieties has led to a number of materials-related applications such as polymer coatings for the micropatterning of proteins,[20] NBE-containing polymer brushes for phototunable wettability,[21] and photocleavable NBE linkers for combinatorial chemistry.[22,23]

Despite their vast utility, incorporation of NB groups into polymers is not necessarily readily achieved. Fustin, Gohy, and co-workers recently described the difficulty inherent in polymerizing monomers such as nitrobenzyl acrylate and methacrylate using popular techniques of controlled radical polymerization such as atom transfer radical polymerization (ATRP), because of the radical-terminating reactions of nitroaromatic groups.[24] Although there have been several reports of controlled ATRP of nitrobenzyl-containing vinyl monomers,[3,24,25] these reactions must be limited to low conversion or small percentage of NBE groups to prevent broadening of the polydispersity index (PDI) to values greater than 1.5. As a result, successful inclusion of photoresponsive NBE-functionalized monomers into well-defined polymer architectures has been limited.

Ring-opening metathesis polymerization (ROMP) is a class of polymerizations that, depending the monomer and initiator used, can result in the favorable initiation kinetics and slow termination reactions required for a controlled living polymerization.[26] In addition, the functional group compatibility of ROMP is excellent, with the exception of Lewis bases such as amines that can coordinate to the transition metal catalysts.[27,28] Although there are several examples of ROM polymers that contain nitrobenzyl groups—Meijer used NB ethers to photocage 2-ureido-pyrimidinone dimerization,[29] Zojer and co-workers used photodeprotection of a di-NBE homopolymer to tune grain sizes in a pentacene-based transistor[30,31]—and other photoreactive ROMP-derived polymers,[32] we are unaware of any studies of controlled polymerizations of nitrobenzyl-containing monomers using ROMP. Herein we report the use of ROMP to perform controlled polymerizations of NBE-substituted norbornyl monomers, including the preparation of block copolymers.

EXPERIMENTAL SECTION

The following chemicals were purchased from commercial sources and used as received: *cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride, glycine, 2-nitrobenzyl alcohol, *N*,*N*′-dicyclohexylcarbodiimide, 4-(dimethylamino)pyridine, triethylamine, benzene, 1-(2-chloroethyl)piperidine

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hydrochloride, 5-hydroxy-2-nitrobenzaldehyde, 1-butanol, pyridine, extra dry DMF, potassium carbonate, sodium sulfate, sodium borohydride, iodomethane, oxalyl chloride, thionyl chloride, dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene](benzylidene)bis(3-bromopyridine)rutheniumII), Grubbs catalyst, second generation, Grubbs catalyst, first generation, and 5-norbornene-2-carboxylic acid. Dry tetrahydrofuran (THF) and dichloromethane (DCM) were obtained using a column purification system. The following compounds were prepared following literature procedures: *N*-(Glycine)-cis-5-norbornene-exocarboximide (**NB-Gly**),[33] and 5-norbornyl acid chloride (**NB-Cl**).[34] All synthetic procedures were carried out under standard air-free conditions unless otherwise indicated.

NMR spectra were acquired on either a Bruker Avance III 500 or a Bruker DPX-300 spectrometer. Chemical shifts are reported relative to the solvent (7.27 ppm for $CHCl_3$, 2.50 ppm for DMSO, and 77.23 ppm for $^{13}CHCl_3$). High-resolution mass spectra (HRMS) were obtained at the MIT Department of Chemistry Instrumentation Facility using a peak-matching protocol to determine the mass and error range of the molecular ion. Molecular weight distribution measurements of the polymers were conducted with a Shimadzu gel permeation chromatography (GPC) system equipped with a TOSOH TSKgel GMHh-M mixed-bed column and guard column (5 μm), equipped with both UV and refractive index detectors. The column was calibrated with low polydispersity poly(styrene) standards (TOSOH, PSt Quick Kit) with THF as the mobile phase eluting at 0.75 mL/min.

Silicon wafers were cleaned by rinsing with acetone and lint-free cleanroom cloths. Chlorobenzene solutions of polymer (5 mg/mL) were filtered with a 0.4 μm PTFE syringe filter and spun-cast on clean silicon wafers using a Laurell Technologies Corporation spin coater (Model WS-400-6NPP-Lite) and then dried in a vacuum oven at 60 °C at −14.7 psi (−30 in. Hg) for 1 h. Program for spin-coater: Spinning at 500 rpm for 3 s (acceleration of 330 rpm/s), followed by spinning at 1500 rpm for 20 s (acceleration of 1650 rpm/s). Irradiation of the films and solutions was performed with an ozone-free 200W Hg/Xe lamp (Newport-Oriel) equipped with recirculating water filter and manual shutter. The dynamic contact angles of sessile water droplets on the surfaces of polymer films were determined with a Ramé-Hart goniometer (Model 200-F1) at room temperature by measuring the advancing contact angles by adding water to the droplet with a 30-Gauge needle in stepwise fashion.

5-Norbornene-2-butyl Ester (1). To a solution of *n*-butanol (0.223 mL, 181 mg, 2.44 mmol) and pyridine (0.818 mL, 0.803 g, 10.2 mmol) in 5 mL of dry THF, a solution of **NB-Cl** (382 mg, 2.44 mmol) in 8 mL of dry THF was added dropwise under an atmosphere of argon. The reaction mixture was stirred overnight at room temperature. The solid white precipitate that had formed upon addition of **NB-Cl** was removed by vacuum filtration. The filtrate was then concentrated *in vacuo* to afford a yellow oil. The crude product was purified via flash chromatography using hexanes/EtOAc (12:1 v/v) to yield compound **1** as a mixture of the *endo* and *exo* stereoisomers. Yield: 341 mg (72%) ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.22−6.21 (1H, m), 5.96−5.94 (1H, m), 4.11−4.04 (2H, m), 3.23 (1H, s, br), 3.13−2.93 (2H, m), 1.92−1.91 (3H, m), 1.60−1.41 (8H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ 176.3, 174.8, 138.0, 137.7, 135.8, 132.4, 64.0, 49.6, 46.6, 46.3, 45.7, 43.4, 43.2, 42.5, 41.6, 30.7, 30.3, 29.2, 19.2, 13.7, 13.7. HRMS (m/z): calcd for $C_{12}H_{18}O_2$ (M+Na)$^+$, 217.1199; found, 217.1207.

NBE−Norbornyl Monomer (2). To a solution of 2-nitrobenzyl alcohol (1.36 g, 8.89 mmol) and pyridine (2.98 mL, 2.93 g, 37.0 mmol) in 15 mL of dry THF, a solution of **NB-Cl** (1.39 g, 8.89 mmol) in 15 mL of dry THF was added dropwise under an atmosphere of argon. The reaction mixture was stirred overnight at room temperature. The solid yellow precipitate formed upon addition of **NB-Cl** was removed by vacuum filtration. The filtrate was concentrated *in vacuo* to afford a yellow oil. The crude product was purified via flash chromatography using hexanes/EtOAc (6:1 v/v) to yield **2** as a mixture of the *endo* and *exo* stereoisomers. Yield: 2.13 g (88%) ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.12−8.08 (1H, m), 7.68−7.57 (2H, m), 7.52−7.47 (1H, t), 6.16−6.14 (1H, m), 5.93−5.92 (1H, m) 5.53−5.46 (2H, m), 3.10 (1H, br s), 3.08−3.05 (1H, m), 3.07 (1H, br s), 1.99−1.91 (2H, m), 1.32−1.26 (2H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.1, 147.7, 138.0, 135.7, 133.6, 129.2, 128.8, 125.0, 62.9, 49.7, 46.6, 46.4, 45.9, 43.3, 43.1, 42.6, 41.7, 30.4, 29.2. HRMS (m/z): calcd for $C_{15}H_{15}NO_4$ (M + Na)$^+$, 296.0893; found, 296.0903.

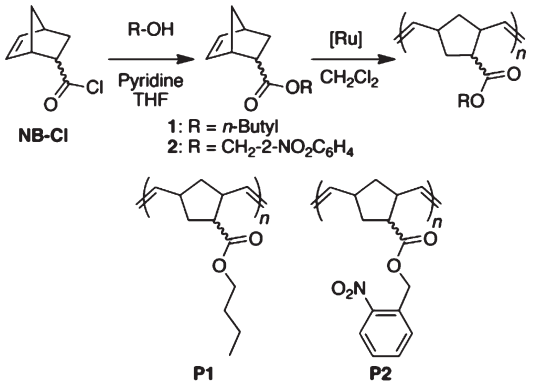
NBE-Substituted Imide Monomer (3). A three-neck round-bottom flask was charged with *N*-(glycine)-*cis*-5-norbornene-*exo*-carboximide (1.0 g, 4.5 mmol), 2-nitrobenzyl alcohol (1.16 g, 7.6 mmol), DCC (1.57 g, 7.6 mmol), and DMAP (0.92 g, 7.6 mmol). Upon addition of 35 mL of CH_2Cl_2, the reaction was stirred at room temperature under argon overnight. The reaction mixture was filtered to remove the precipitate formed during the reaction, and the filtrate was concentrated to dryness to yield a yellow liquid. The residue was dissolved in EtOAc, washed with 10% HCl (3 × 30 mL) and then dried over $MgSO_4$. Recrystallization of the residue from ethyl acetate/hexanes gave 0.83 g (56%) of compound **3** as a pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.11 (d, J = 8.1 Hz, 1H), 7.68 (t, J = 7.4 Hz, 1H), 7.58 (d, J = 7.0 Hz, 1H), 7.50 (t, J = 7.3 Hz, 1H), 6.28 (s, 2H), 5.59 (s, 2H), 4.34 (s, 2H), 3.30 (s, 2H), 2.76 (s, 2H), 1.61 (d, J = 9.8 Hz, 1H), 1.49 (d, J = 9.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 177.1, 166.5, 147.3, 138.0, 134.0, 131.2, 129.1, 129.0, 125.2, 64.1, 48.1, 45.4, 42.8, 39.4. HRMS (m/z): calcd for $C_{18}H_{16}N_2O_6$ (M + Na)$^+$, 379.0901; found, 379.0918.

2-Nitro-5-(2-piperidin-1-ylethoxy)benzaldehyde (4). **4** was synthesized as previously reported.[35] ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.43 (1H, s), 8.12−8.22 (1H, d), 7.30−7.29 (1H, d), 7.15−7.12 (1H, dd), 4.22−4.20 (2H, t), 2.79−2.77 (2H, t), 2.48 (4H, br s), 1.60−1.55 (4H, m), 1.44−1.42 (2H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ 188.5, 163.4, 142.1, 134.3, 127.2, 118.9, 114.0, 67.4, 55.5, 55.1, 25.9, 24.1. HRMS (m/z): calcd for $C_{14}H_{18}N_2O_4$ (M + H)$^+$, 279.1339; found, 279.1362.

2-Nitro-5-(2-piperidin-1-ylethoxy)benzyl Alcohol (5). Sodium borohydride (232 mg, 6.13 mmol) was added to a solution of **4** (1.11 g, 3.96 mmol) in 18 mL of MeOH at 0 °C. The ice bath was removed and the reaction was stirred at room temperature overnight. The reaction mixture was concentrated *in vacuo*. The yellow solid was then redissolved in ethyl acetate, washed with water and brine, and dried over sodium sulfate to yield **5**. Yield: 0.68 g (62%) ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10−8.07 (1H, d, J = 9.3 Hz), 7.29 (1H, d, J = 2.7 Hz), 6.82−6.78 (1H, m), 4.98 (2H, s), 4.21−4.17 (2H, t), 2.82−2.78 (2H, t), 2.54 (4H, br s), 1.66−1.59 (4H, m), 1.48−1.46 (2H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.4, 141.1, 140.0, 127.7, 113.9, 113.4, 66.7, 62.0, 57.6, 55.2, 25.7, 24.0. HRMS (m/z) calcd for $C_{14}H_{20}N_2O_4$ (M+H)$^+$, 281.1496; found, 281.1501.

Cationic Monomer 6. First, 0.500 g (1.79 mmol) of compound **5** was dissolved in 5 mL of dry THF. Pyridine (0.173 mL, 0.170 g, 2.14 mmol) was then added to the solution. **NB-Cl** (0.290 g, 1.79 mmol) in 8 mL of dry THF was subsequently added dropwise to the reaction mixture, which was then stirred overnight at room temperature. The gray precipitate that formed upon addition of **NB-Cl** was removed by vacuum filtration. The filtrate was then concentrated *in vacuo* to yield a brown solid. The crude product was purified via flash chromatography (95% DCM/5% MeOH) to yield the expected ester product as a mixture of *endo* and *exo* isomers. Yield: 160 mg (22%) ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.19−8.15 (1H, m), 7.05−7.02 (1H, m), 6.91−6.87 (1H, m), 6.23−6.11 (1H, m), 5.96−5.93 (1H, m), 5.53−5.47 (2H, m), 4.24−4.20 (2H, t), 3.28 (1H, br s), 3.11−3.05 (1H, m), 2.94 (1H, br s), 2.88−2.84 (2H, m), 2.57 (4H, br s), 2.00−1.81 (2H, m), 1.66−1.59 (4H, m), 1.53−1.33 (2H, m), 1.32−1.25 (2H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 178.5, 174.0, 162.9, 140.3, 138.2, 138.0, 137.5, 135.7, 135.6, 132.6, 132.3, 127.9, 114.6, 114.5, 113.2, 113.0, 66.5, 63.1, 57.2, 54.8, 49.8, 49.7, 46.7, 46.4, 45.9, 45.8, 43.8, 43.3, 43.1, 42.6, 42.5, 41.7, 30.5, 29.3,

Scheme 1. Synthesis of Monomers 1 and 2 and Structures of Corresponding Polymers P1 and P2



25.5, 23.9. HRMS (m/z): calcd for $C_{22}H_{28}N_2O_5$ $(M+H)^+$, 401.2071; found, 401.2080.

The unmethylated ester (701 mg, 1.75 mmol) was dissolved in 50 mL of dry CH_2Cl_2. Iodomethane (4.80 mL, 10.9 g, 77.1 mmol) was added to the reaction mixture and stirred overnight at room temperature. The solvent was removed *in vacuo* to yield **6**, a yellow solid, as a mixture of *endo* and *exo* isomers. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18−8.15 (1H, m), 7.11−7.10 (2H, m), 6.21−5.89 (2H, m), 5.48−5.42 (2H, m), 4.74 (2H, br s), 4.34 (2H, br s), 3.87−3.79 (4H, m), 3.51 (3H, s), 3.26 (1H, br s), 3.13−3.11 (1H, m), 2.93 (1H, br s), 2.04−2.02 (4H, m), 1.84 (4H, br s), 1.51−1.25 (2H, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.2, 160.9, 141.5, 138.2, 137.9, 135.7, 132.4, 132.1, 128.2, 115.5, 113.6, 63.0, 62.9, 62.7, 62.2, 49.8, 49.5, 46.6, 46.4, 46.0, 45.7, 43.3, 43.1, 42.9, 42.6, 41.7, 30.5, 29.3, 29.2, 20.6, 20.3. HRMS (m/z): calcd for $C_{23}H_{31}N_2O_5$ (M^+), 415.2227; found, 415.2237.

General Polymerization Procedure. Dry dichloromethane was sparged with argon for ~20 min. Initiator **I**, **II**, or **III** was then added to a solution of monomer at a concentration between 50 and 125 mg/mL in CH_2Cl_2. The reaction mixture was stirred until all monomer was consumed as shown by TLC. The polymerization was then terminated by the addition of 5 equiv of ethyl vinyl ether.

P1. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.49−5.27 (2H), 4.10−3.91 (2H), 3.2−2.4 (3H), 2.04−1.66 (2H), 1.63−1.50 (2H), 1.45−1.19 (4H), 0.98−0.85 (3H).

P2. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.11−7.99 (1H), 7.69−7.54 (2H), 7.53−7.39 (1H), 5.56−5.12 (4H), 3.30−2.55 (3H), 2.17−1.86 (2H), 1.37−1.26 (2H).

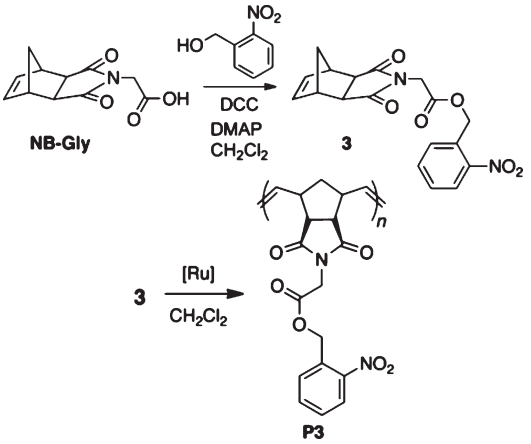
P3. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.12−8.07 (1H), 7.67−7.45 (3H), 5.69−5.50 (4H), 4.26−4.12 (2H), 3.50−2.60 (4H), 2.36−2.03 (1H), 1.65−1.40 (1H).

P6. ^{1}H NMR (500 MHz, $(CD_3)_2SO$): δ 8.27−8.07 (1H), 7.30−7.03 (2H), 5.55−5.03 (4H), 4.72−4.54 (2H), 3.98−3.81 (2H), 3.58−3.39 (4H), 3.22−3.13 (3H), 3.12−2.97 (1H), 2.95−2.61 (2H), 2.09−1.75 (6H), 1.67−1.46 (4H).

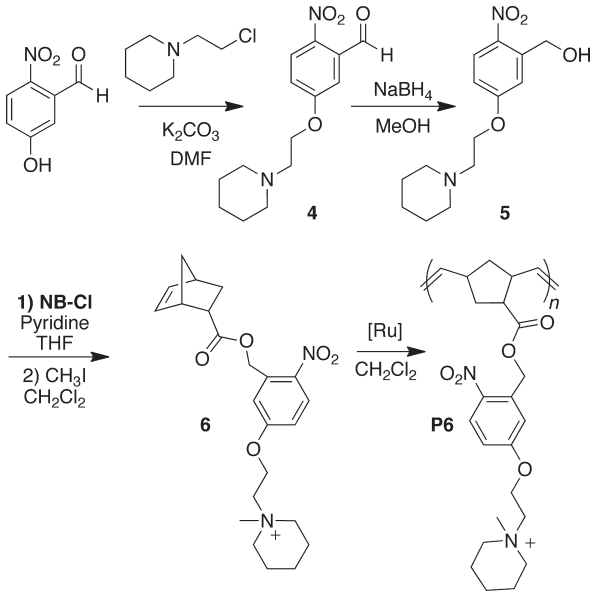
Block copolymers were prepared with an identical procedure, except that upon consumption of the first monomer, an aliquot of another monomer was added. An example follows:

P2-*b*-P1. To a solution of monomer **2** (50 mg, 0.18 mmol) in CH_2Cl_2 was added a solution of catalyst **III** (6.3 mg, 0.0071 mmol) in CH_2Cl_2 such that the final concentration of monomer was 50 mg/mL (total solvent was 1.0 mL). The reaction was stirred at ambient temperature under argon for 30 min, at which time TLC analysis showed no monomer remained in solution. A small aliquot was then removed for GPC analysis, followed by addition of a solution of monomer **1** (36 mg, 0.18 mmol) dissolved in 0.7 mL of CH_2Cl_2. TLC analysis after 25 min indicated no monomer remained, so the reaction was terminated with a drop of ethyl vinyl ether. NMR analysis of each block copolymer showed the ratio of incorporation of the monomers was approximately 1:1.

Scheme 2. Synthesis of Imide-Based Monomer 3 and of Corresponding Polymer P3



Scheme 3. Synthesis of photocleavable cationic polymer P6



RESULTS AND DISCUSSION

We prepared two types of ester-containing norbornene monomers. The first (Schemes 1 and 3, monomers **1**, **2**, and **6**) were mixtures of *endo* and *exo* (80:20) stereoisomers of 5-norbornene-2-carboxylic acid esters. Our generally applicable synthetic scheme was to first prepare the acid chloride **NB-Cl** from the commercially available mixture of stereoisomeric carboxylic acids, followed by esterification with the appropriate alcohol in the presence of pyridine. The second (Scheme 2, monomer **3**) was a norbornene-*exo*-imide substituted with a carboxylic ester, prepared from norbornene-*exo*-anhydride and glycine,[33] followed by DCC-mediated esterification with *o*-nitrobenzyl alcohol.

We used three different alcohols for esterification of the norbornene carboxylic acids. Two were commercially available:

Chart 1. Ruthenium Carbene Initiators Used in ROMP Reactions

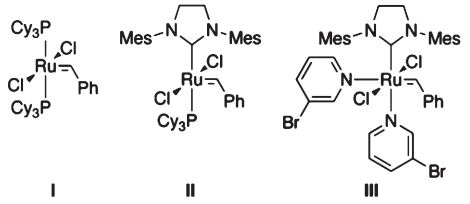


Table 1. Comparison of Initiators I, II, and III for Polymerization of 2 at [M]/[I] = 20

	I	II	III
time (min)[a]	120	20	25
M_n (g/mol)	7100	68 000	8300
PDI	1.14	2.16	1.28

[a] Approximate time to reach 100% conversion as determined by thin-layer chromatography.

n-butanol and 2-nitrobenzyl alcohol, which gave monomers **1** and **2**, respectively. Scheme 3 shows the synthesis of photocleavable cationic monomer **6**, which we prepared by alkylating the phenol group of 2-nitro-5-hydroxybenzaldehyde with *N*-(2-chloroethyl)piperdine hydrochloride, followed by reduction with sodium borohydride in methanol to give the benzylic alcohol. Esterification as described above yielded the amine-substituted photocleavable norbornene, which we methylated with CH_3I before polymerization because of the known inhibitory effect that amines have on ROMP reactions initiated with ruthenium carbene complexes.[27,36]

Upon completing the successful synthesis of NBE-containing norbornene monomers, our next goal was to determine if they were amenable to metathesis polymerization, and to determine whether these polymerizations showed characteristics of living polymerizations. We therefore initiated polymerizations of **2** in CH_2Cl_2 using Grubbs's catalysts **I**, **II**, and **III** (Chart 1) at a monomer:initiator molar ratio of 20:1. As Table 1 shows, under these conditions all three initiators resulted in complete monomer conversion as determined by both TLC and NMR in times ranging from minutes to hours. NMR spectra of the crude reaction mixtures were consistent with the expected structure of **P2**. Initiator **I** required at least 4x more time than initiators **II** or **III** to consume all monomer, which is consistent with the more active nature of second- and third-generation Grubbs initiators.

Samples of **P2** prepared with initiators **I** and **III** did show characteristics of controlled polymerizations. Number-average molecular weights (M_n) of **P2** prepared with initiator **I** depended linearly on the ratio of monomer to initiator (Figure 1) as determined by gel permeation chromatography referenced with low-PDI poly(styrene) standards. These polymers generally had polydispersity indices (PDIs) generally between 1.2 and 1.3, although high molecular-weight shoulders on the GPC traces of **P2** tended to broaden the PDI values of these polymers at [M]/[I] ratios greater than 100. These highest molecular weight polymers of those we prepared therefore had PDI values that ranged between 1.2 and 1.8. Others have reported similar high molecular weight shoulders on GPC traces of ROM polymers initiated by ruthenium carbene complexes, and have attributed them to coupling between two growing chain ends.[37,38]

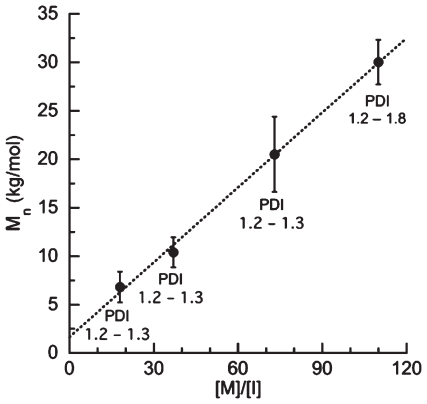


Figure 1. Linear dependence (R = 0.998) of M_n of **P2**, prepared with initiator **I**, on the molar ratio of monomer to initiator, [M]/[I]. $[M]_0$ = 125 mg/mL.

Table 2. Molecular weight distributions of diblock copolymers with NBE groups with initiator III

		1st block		Diblock	
1st/2nd block	[M]/[I] per block	M_n	PDI	M_n	PDI
P2/P1	26/26	9900	1.11	16 600	1.18
P1/P2	36/36	11 500	1.08	25 800	1.16
P2/P3	30/30	11 500	1.10	26 700	1.10

Although initiator **II** polymerized **2** efficiently, it did so in an uncontrolled fashion, with the resulting **P2** having an M_n ten-times higher than expected for a controlled polymerization, and a PDI of 2.16. Such a result is characteristic of a chain reaction that has a high ratio of rate of propagation to rate of initiation. Our overall results in comparing these three initiators are consistent with their previously reported kinetics of initiation and propagation.[39,40] Monomer **3** was also amenable to homopolymerization using initiator **I** or **III**, each of which yielded a similarly narrow molecular weight distribution at molecular weights below 20 000 g/mol: M_n = 11 200 ± 2300 (expected M_n = 7100 for [M]/[I] = 20), PDI = 1.14 ± 0.06. Although we were able to purify these polymers by precipitation into nonsolvents (methanol for **P2** and **P3**, diethyl ether for **P6**), we acquired all GPC data for these polymers from crude terminated reaction mixtures to prevent any fractionation of the polymer samples and subsequent skewing of molecular weight distributions.

As we were able to demonstrate some characteristics of controlled polymerizations with NBE-containing monomers, we proceeded to synthesize block copolymers using monomers **1**, **2**, and **3** in CH_2Cl_2 with initiator **III**, which consistently gave polymers with low PDIs. Addition of a second monomer after TLC analysis indicated the consumption of the first monomer (30 min after combining monomer with initiator **III**) resulted in A-B diblock copolymers. In all cases, the second monomer was consumed within 30 min. Table 2 summarizes the molecular weight distributions (via GPC) of A−B diblock copolymers that have at least one NBE-containing block, as well as the homopolymers resulting from quenching a small aliquot of each polymerization after the first monomer was consumed but before addition of the second monomer. In each combination listed in Table 2, the M_n of the sample increased upon addition of the

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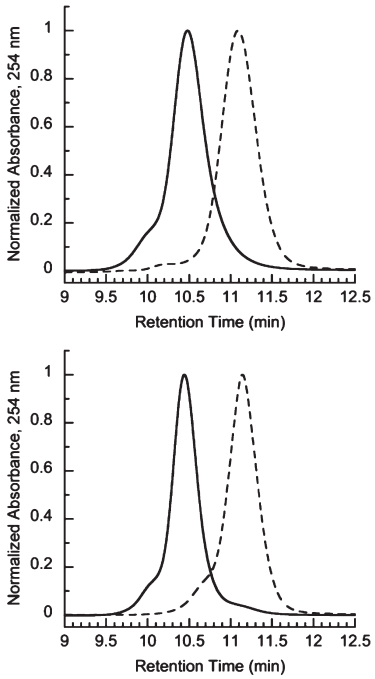

Figure 2. GPC chromatograms. Top: **P1**-*b*-**P2** Bottom: **P2**-*b*-**P3**. In each case, the dashed line is the chromatogram of a terminated aliquot of the reaction upon consumption of the first monomer; the solid line is the chromatogram upon consumption of the second monomer.

second monomer while the PDI remained less than 1.3. When **3** was the first monomer used in an attempt to make a block copolymer, however, not all of the chain ends of **P3** added to the second monomer; a low molecular weight peak that corresponded to unreacted **P3** homopolymer remained after consumption of the second monomer. Therefore, although the ROM polymerization of **3** does show predictable M_n values up to M_n = 20 000 g/mol with relatively narrow PDI values, it is not completely living due to termination of some active chain ends. Nevertheless, we were able to prepare a diblock copolymer of the two different NBE-containing monomers **2** and **3** with initiator **III** when monomer **3** was the second monomer added (Figure 2, bottom). This strategy of adding a monomer that shows nonliving behavior as the second monomer in a ROMP-derived diblock copolymer has been used in previous reports.[40,41]

The NBE-containing polymers we prepared were photoreactive upon irradiation with UV light. After irradiation of colorless solutions of **P2** or **P3** in $CDCl_3$ with a 200 W Hg/Xe lamp for 20 min at wavelengths higher than 295 nm, the solutions became deeply yellow in color and polymeric material precipitated. NMR spectra of the $CDCl_3$ supernatant showed no polymer remaining dissolved and contained a mixture of aromatic products. An identical experiment in DMSO-d_6, in which **P2** is soluble both before and after irradiation, showed that the polymeric NBE groups were cleaved from the polymer after 60 min of irradiation, while the poly(norbornene) backbone remained intact (see Supporting Information, Figure S1). In addition, relative to the rest of the polymeric backbone, the integration of the signals between 5.0 and 5.5 ppm, which comprised both the benzylic and olefinic protons of **P2**, decreased by a factor of 2. This observation is consistent with loss of the benzylic methylene protons upon irradiation. **P3**, which was insoluble in DMSO before irradiation,

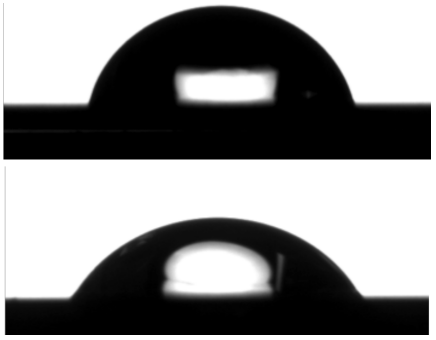

Figure 3. Decrease of contact angle of water on a spun-cast thin film of **P2** from before irradiation (top) to after irradiation (bottom).

became soluble after UV irradiation for 30 min, and showed similar results. Solutions of **P1** in $CDCl_3$, which lacks any NBE groups, showed no change in either NMR spectra or physical appearance upon exposure to UV irradiation under identical conditions.

Films of the NBE-containing polymers were also photoreactive. We prepared thin films of **P2** with $M_n \sim 10\,000$ g/mol by spin-casting from chlorobenzene. Before irradiation with UV light, sessile drops of water on these films had an average advancing contact angle of 74 ± 2° (Figure 3, top). After irradiation of films of **P2** with the unfiltered output of an ozone-free 200 W Hg/Xe lamp for 30 min, the advancing contact angle of water was 64 ± 2° (Figure 3, bottom). In comparison, butyl-ester containing polymer **P1** showed no change in advancing contact angle (76 ± 1°) after identical conditions of irradiation. Other NBE-substituted materials have shown significant decreases in water contact angles upon photolysis.[42−44] This observed decrease in hydrophobicity of **P2**, along with the observations of change in solubility and NMR spectra, is consistent with the photoconversion of hydrophobic NBEs to more hydrophilic carboxylic acids.

In addition, we were able to synthesize homopolymers of monomer **6** in high yield using ROMP. Polymerization of **6** in dichloromethane using initiator **II** or **III** gave **P6** with complete conversion of monomer within 30 min as determined by NMR analysis. Although we were unable to obtain GPC data for cationic **P6** because of the known interactions between cationic polymers and GPC columns,[28,45] we made two observations consistent with a successful polymerization: (i) during the reaction in CH_2Cl_2, a solid which was soluble in dipolar aprotic solvents such as DMF and DMSO precipitated from the reaction, (ii) the NMR spectrum of the crude reaction mixture in DMSO-d_6 (Figure S2 in the Supporting Information) showed no observable peaks associated with the monomer and was consistent with the expected structure. This successful polymerization stands in strong contrast to our earlier attempts to polymerize an methacrylate monomer with functionality similar to that of monomer **6** through a variety of radical-initiated methods (AIBN, ATRP, RAFT), all of which gave low conversion and low molecular weight polymers even after long reaction times and at high concentrations of monomer. Photocleavable cationic groups have been used in several applications that take advantage of the ability to control formal charge of a material with light,[46,47] but we are unaware of any such structure in a polymeric material with nitrobenzyl groups. Polymerization of the unmethylated precursor of **6** with initiator **III** remained incomplete after 3 h, which suggests inhibition of the polymerization by the Lewis basic amine.

CONCLUSION

We have demonstrated controlled polymerization of several nitrobenzyl ester-containing monomers using ROMP. These reactions give polymers with predictable molecular weights and PDI values less than 1.3 at up to 75 monomers per initiator, which has been shown to be a sufficient degree of polymerization for preparing block copolymer micelles with polymers derived from ROMP reactions.[48] They also allow the synthesis of diblock copolymers that contain these photoreactive monomers. Our experiments also show that with ROMP it is unnecessary to limit the conversion of monomer in order to achieve controlled polymerizations with predictable molecular weights. This contribution represents an important advance in photoreactive materials because controlled polymerizations of nitrobenzyl acrylate or nitrobenzyl methacrylate require: (i) concentrations of monomer over 3 M and (ii) limiting conversion of monomer to no more than 35−40%.[24] These disadvantages, which the ROMP approach alleviates, complicate synthesis of block copolymers and would be problematic for polymerizing structurally elaborated monomers of high value. We therefore conclude that the use of ROMP is an important improvement in the preparation of well-defined nitrobenzyl ester-containing photoreactive polymers.

ASSOCIATED CONTENT

Supporting Information. NMR spectra of **P2** before and after irradiation and NMR spectrum of **P6**. This material is available free of charge via the Internet at http://pubs.acs.org/.

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