Macromolecules **2008,** *41,* 614−622

New Well-Defined Polymeric Betaines: First Report Detailing the Synthesis and ROMP of Salt-Responsive Sulfopropylbetaine- and Carboxyethylbetaine-*exo*-7-oxanorbornene Monomers

David A. Rankin[†] and Andrew B. Lowe*[,‡]

Department of Chemistry & Biochemistry and School of Polymers and High Performance Materials, Department of Polymer Science, 118 College Drive #10076, The University of Southern Mississippi, Hattiesburg, Mississippi 39406-10076

Received August 29, 2007; Revised Manuscript Received November 2, 2007

ABSTRACT: We describe herein the synthesis and controlled ring-opening metathesis polymerization (ROMP) of highly functional zwitterionic sulfopropylbetaine- and carboxyethylbetaine-*exo*-7-oxanorbornene derivatives with the first-generation Grubbs' initiator $RuCl_2(PCy_3)_2CHPh$ in a 2,2,2-trifluoroethanol/methylene chloride solvent mixture. These are the first examples of such norbornene-based betaine substrates. Both species can be polymerized *directly* in a controlled manner in *organic media* as judged from the kinetic profiles and aqueous size exclusion chromatographic analysis. This represents the first time betaine monomers have been polymerized directly in a controlled fashion by a technique other than a controlled free radical polymerization process, and the first time it has been achieved in organic, as opposed to aqueous, media. Finally, preliminary results demonstrate that water-soluble, salt-responsive AB diblock copolymers can be prepared and that such materials are able to undergo supramolecular self-assembly in aqueous media to yield nanosized aggregates simply by controlling the aqueous electrolyte concentration.

Introduction

Polymeric betaines are a special class of zwitterionic polymer that bear both anionic and cationic functionality on the *same* monomer repeat unit.[1,2] Such materials may be further differentiated on the basis of the nature of the anionic functional group and include sulfo-,[3−5] carboxy-,[6−13] and phosphobetaines[14−19] as well as the less well-known alkoxydicyanoetheneolate species.[20−23] Materials containing such building blocks are interesting for various reasons, including the potential biocompatible/antimicrobial properties of such materials[24−30] as well as their anti-polyelectrolyte behavior in aqueous solution.[2] While synthetic polymeric betaines have been known since the 1950s,[31−33] there are, even today, very few examples of such materials prepared with well-defined molecular characteristics/architectures and even fewer in which such materials have been prepared directly. The vast majority of polymeric betaines have been synthesized via the direct conventional free radical solution polymerization of betaine monomers, as exemplified, for example, by the work of Salamone et al.,[4,34] Galin and coworkers,[35−37] and McCormick et al.[13,38] However, such a synthetic approach inevitably results in materials with broad molecular mass distributions and poorly defined microstructures. The ability to prepare polymeric betaines in a controlled fashion has proven to be significantly more challenging. This has been due, in part, to the limited solubility characteristics of many betaine monomers/polymers[39,40] and their incompatibility with controlled/living polymerization techniques/conditions. Well-defined polymeric betaines, i.e., those with predetermined molecular masses, narrow molecular mass distributions, and advanced architectures, were first reported by Lowe et al.[41−44] in the 1990s. These well-defined materials were prepared indirectly via the alkylation of tertiary amine-containing precursor (co)polymers with 1,3-propane sultone.[41] Specifically, (co)polymers containing 2-(dimethylamino)ethyl methacrylate were synthesized via group transfer polymerization (GTP) and subsequently modified via reaction at the tertiary amine residues with 1,3-propane sultone under facile conditions to yield the corresponding polysulfopropylbetaines. Such an approach, while effective, is not ideal since GTP is challenging, practically, to execute, and such postpolymerization modification reactions are rarely quantitative. In recent years several groups have reported the direct polymerization of betaine monomers in a controlled manner employing controlled free radical polymerization (CFRP) techniques and in particular atom transfer radical polymerization[16−18] and reversible addition−fragmentation chain transfer (RAFT) polymerization,[45−49] with RAFT proving to be the most versatile with respect to monomer choice. However, these techniques are limited to 1-substituted or 1,1-disubstituted substrates such as styrenic, (meth)acrylic, and (meth)acrylamido derivatives. What is evident, however, is that *only* CFRP techniques have been employed for the direct polymerization of betaine monomers in a controlled manner.

Ring-opening metathesis polymerization (ROMP) is a chain growth process that has undergone somewhat of a renaissance during the last couple of decades since the discovery and development of single-component initiators by the groups of Schrock[50−52] and Grubbs.[53−56] Of these initiators, the Grubbs Ru-based complexes have proven themselves to be particularly useful due their relative ease of synthesis, handling/storage, and their impressive functional group tolerance.[57,58] ROMP is applicable to monomers that cannot be polymerized by other, more common, chain growth techniques. In particular, strained cyclic monomers such as *exo/endo*-(7-oxa)norbornenes,[59−65] cyclooctenes,[62,66,67] and cyclooctatetraenes[68−70] are particularly useful substrates to name but a few. For example, we recently described the synthesis of a series of permanently cationic *exo*-7-oxanorbornene derivatives and evaluated their controlled polymerization in a novel 1:1 v/v 2,2,2-trifluoroethanol (TFE)/

---

* To whom correspondence should be addressed. E-mail: andrew@ablowe.com.

[†] Department of Chemistry & Biochemistry.

[‡] School of Polymers and High Performance Materials.

10.1021/ma701952c CCC: \$40.75

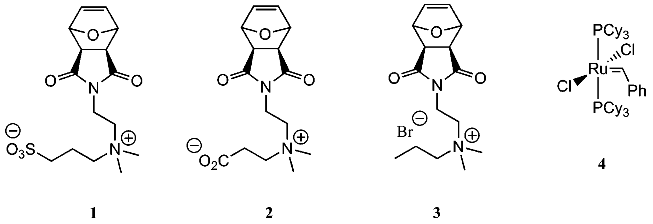


Figure 1. Chemical structures of the sulfopropylbetaine, **1**, carboxyethylbetaine, **2**, and propyl-quaternized cationic, **3**, *exo*-7-oxanorbornene monomers, and Grubbs' first-generation initiator, **4**.

methylene chloride solvent mixture.[59] The advantage of this route over other previously disclosed methods for the preparation of permanently cationic polymers via ROMP was the ability to use commercially available initiators in *organic* media as opposed to resorting to the synthesis of novel water-soluble initiators as described by Grubbs et al. and others[71−77] or the application of protection/deprotection protocols and/or post-polymerization modification as a route to similar polymeric structures.[78]

We describe herein the synthesis and direct ROMP of new sulfopropylbetaine and carboxyethylbetaine monomers, **1** and **2** (Figure 1), based on the *exo*-7-oxanorbornene structural motif. These are, to the best of our knowledge, the first examples of such 7-oxanorbornene-based betaine monomers. Monomers **1** and **2** were subsequently polymerized with the commercially available first-generation Grubbs' initiator $RuCl_2(PCy_3)_2CHPh$, **4** (Figure 1), in a 1:1 v/v solvent mixture of TFE/CH_2Cl_2—the same solvent mixture that we recently demonstrated to be an extremely effective medium for ROMP reactions with cationic *exo*-7-oxanorbornene substrates. Since such betaine substrates have never before been prepared/polymerized under ROMP conditions, this initial disclosure evaluates the basic polymerization characteristics and demonstrates the ability to prepare materials with advanced architectures and stimuli-responsive properties. These studies further highlight the functional group tolerance of Grubbs-type initiators and the applicability of the TFE/CH_2Cl_2 solvent mixture for preparing materials with high degrees of functionality under facile conditions without recourse to either novel catalyst synthesis or postpolymerization modification.

Experimental Section

All reagents were purchased from the Aldrich Chemical Co. at the highest available purity and used as received unless stated otherwise. $RuCl_2(PCy_3)_2CHPh$ was stored and handled in a PlasLabs nitrogen-filled glovebox. 2,2,2-Trifluoroethanol (TFE), CH_2Cl_2, and ethyl vinyl ether (EVE) were degassed by at least three freeze−pump thaw cycles using a high-vacuum Schlenk line, then blanketed in nitrogen, and stored in the glovebox until needed. *exo*-3,6-Epoxy-1,2,3,6-tetrahydrophthalic anhydride was recrystallized from 1:1 v/v ethyl acetate/hexane solvent mixture and then stored in a freezer until needed. *exo*-4-(2-(Dimethylamino)ethyl)-10-oxa-4-azatricyclo-[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (DMAETDD) was prepared by the reaction between *N*,*N*-dimethylethylenediamine and *exo*-3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride, as reported in the literature.[72] *exo*-[2-(3,5-Dioxo-10-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-8-en-4-yl)ethyl)dimethylpropylammonium bromide (Pr-quat-Br, **3**, Figure 1) was prepared according to the procedure we recently described.[59]

Synthesis of *exo*-[2-(3,5-Dioxo-10-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-8-en-4-yl)ethyl]dimethylpropylsulfobetaine, 1. The sulfopropylbetaine derivative **1** was prepared by a multistep procedure as follows: DMAETDD (5.11 g, 21.6 mmol) and THF (50 mL) were added to a 100 mL canonical flask equipped with a magnetic stir bar. 1,3-Propane sultone (3.16 g, 1.2 mol equiv) was then added to the flask in one portion. The reaction was heated at 50 °C for 48 h, during which time a white precipitate formed. The precipitate was isolated by Buchner filtration and dried in vacuo at ambient temperature, yielding the title compound as a white powder. Yield = 87%, mp = 188−190 °C. ^1H NMR (300 MHz, D_2O): δ (ppm) = 6.63 ($CH=$, 2H, m), 5.35 (OCH, 2H, m), 3.98 (imideN−CH_2, 2H, t), 3.56 (imideN−CH_2CH_2, 2H, t), 3.55 (−$N(CH_3)_2CH_2$, 2H, t), 3.20 ((C=O)CH, 2H, t), 3.18 ($N(CH_3)_2$, 6H, s), 2.99 (CH_2-SO_3, 2H, t), 2.22 ($CH_2CH_2CH_2$, 2H, m). ^{13}C NMR (75 MHz, H_2O): δ (ppm) 178.69 (N−C=O), 136.93 (HC=CH−CHO), 81.41 (HC−O), 63.07 (N−CH_2), 59.83 ($CH_2-N(CH_3)_2$), 51.46 ($N(CH_3)_2-CH_2$), 48.02 (($CH_3)_2-NCH_2$), 47.54 ($CH_2CH_2CH_2SO_3^-$), 32.78 ($CH-C$=O), 18.59 ($CH_2CH_2CH_2$).

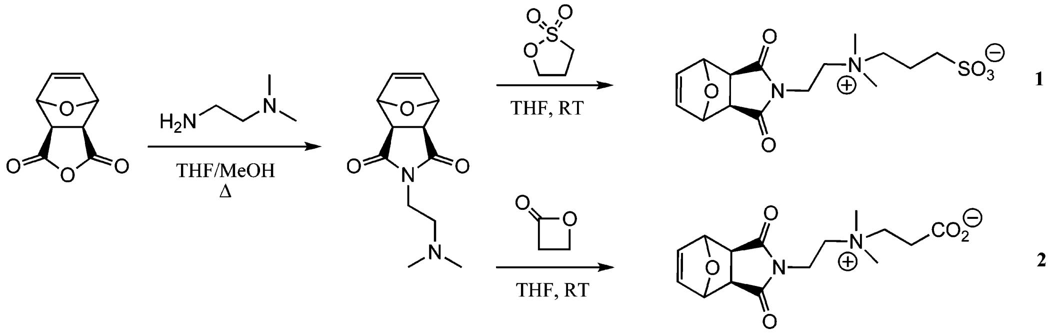
Synthesis of *exo*-[2-(3,5-Dioxo-10-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-8-en-4-yl)ethyl]dimethylpropylcarboxybetaine, 2. The title compound was prepared by a reaction between DMAETDD and β-propiolactone under a nitrogen atmosphere as follows: DMAETDD (5.07 g, 21.5 mmol) and THF (50 mL) were added to a 100 mL canonical flask equipped with a magnetic stir bar. Subsequently, β-propiolactone (1.86 g, 1.2 mol equiv) was added to the flask in one portion. The reaction was left at room temperature for 24 h, during which time a white precipitate formed. The precipitate was isolated by Buchner filtration and dried in vacuo at ambient temperature, yielding the title compound as a white powder. Yield = 90%, mp = 118−121 °C. ^1H NMR (300 MHz, D_2O): δ (ppm) = 6.48 ($CH=$, 2H, t), 5.20 (O−CH, 2H, t), 3.85 (imideN−CH_2, 2H, t), 3.51 ($N(CH_3)_2CH_2$, 2H, t), 3.40 (imideN−CH_2CH_2, 2H, m), 3.01 ($N(CH_3)_2$, 6H, s), 3.04 ((C=O)CH, 2H, m), 2.56 (CH_2-CO_2, 2H, t). ^{13}C NMR (75 MHz, H_2O): δ (ppm) 178.43 (N−C=O), 176.27 ($CH_2-CO_2^-$), 136.69 (HC=CH−CHO), 81.78 (HC−O), 62.12 (N−CH_2), 59.56 ($CH_2-N(CH_3)_2$), 51.59 ($N(CH_3)_2-CH_2$), 47.76 (($CH_3)_2-NCH_2$), 32.57 ($CH-C$=O), 30.73 ($CH_2CH_2CO_2^-$).

Protonation/Deprotonation of Carboxybetaine 2. Carboxybetaine **2** was protonated by stirring 1.00 g of monomer in 3.0 mL of 5.0 M solution of HCl for 30 min. The protonated monomer (**H-2**) was recovered by precipitation into a large volume of THF, followed by Buchner filtration and drying in vacuo. Protonation was confirmed by FT-IR spectroscopy.

Homopolymerization of Sulfopropylbetaine 1 and Carboxyethylbetaine 2. Below is a typical procedure for the homopolymerization of the betaine monomeric substrates: Protonated carboxybetaine **2** (0.5 g, 1.45 mmol) was added to a single-necked Schlenk flask (100 mL capacity) equipped with a magnetic stir bar. The flask was subsequently degassed/backfilled with N_2 three times using standard Schlenk line techniques prior to being transferred to a nitrogen-filled glovebox. TFE (2.0 mL) was then added to the flask. $RuCl_2(PCy_3)_2CHPh$ (20.6 mg, 0.025 mmol for a target M_n of 20 000) was weighed into a scintillation vial (20 mL capacity), and then CH_2Cl_2 (2.0 mL) was added. The catalyst solution was then added directly to the monomer solution with stirring. The polymerization was left for 8 min prior to quenching with EVE (0.5 mL). The solution was left to stir for 15 min prior to precipitation into a large excess of THF. The polymer was isolated by Buchner filtration, washed with THF, and dried in vacuo. Yield: 95%.

Self-Block Copolymerization. Below is a typical procedure for the self-block copolymerization of the betaine monomeric substrates: The sulfobetaine **1** (0.5 g, 1.30 mmol) was added to two separate Schlenk flasks (100 mL, 0.5 g in each) equipped with magnetic stir bars. Both flasks were simultaneously evacuated/backfilled with N_2 at least three times using standard Schlenk line techniques prior to transfer to a PlasLabs N_2-filled glovebox. TFE (5.0 mL) was then added to each flask. $RuCl_2(PCy_3)_2CHPh$ (0.041 g, 0.05 mmol, M_n(theory) = 10 000) was weighed out in a scintillation vial (20 mL capacity), and CH_2Cl_2 (5.0 mL) was then added. The catalyst solution was then added directly to one of the flasks containing monomer solution. The polymerization was allowed to proceed for 2 min prior to extracting an aliquot, which was quenched with EVE, for aqueous SEC analysis. The second monomer solution was then added directly to the homopolymer solution. The solution was left to stir for 5 min prior to quenching with EVE (0.5 mL). Homo- and diblock copolymers were recovered

Scheme 1. Outline for the Preparation of the Sulfopropylbetaine 1 and Carboxyethylbetaine 2[a]



[a] The intermediate tertiary amine, *exo*-4-(2-(dimethylamino)ethyl)-10-oxa-4-azatricyclo[5.2.1.$0^{2,6}$]dec-8-ene-3,5-dione (DMAETDD), was prepared from the reaction of *N*,*N*-dimethylethylendiamine with *exo*-3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride in a mixture of tetrahydrofuran (THF) and methanol. Subsequent reaction of DMAETDD with 1,3-propane sultone or β-propiolactone in THF yields **1** and **2**, respectively.

by precipitation in to a large excess of THF, isolated by Buchner filtration, and dried overnight in vacuo at ambient temperature.

Block Polymerization of the Sulfopropylbetaine 1 with the Propylquat 3. The sulfobetaine **1** (0.5 g, 1.39 mmol) was added to a single-neck Schlenk flask (100 mL capacity) equipped with a magnetic stir bar. The cationic monomer **3** (1.17 g, 3.24 mmol) was added to a second identical flask. Both flasks were degassed/backfilled with N_2 three times using standard Schlenk line techniques, after which they were transferred to a PlasLabs N_2-filled glovebox. TFE (2.50 mL) was subsequently added to each flask and allowed to stir until each monomer was completely dissolved. Grubbs initiator **4** (41.0 mg, 0.05 mmol) was added to a scintillation vial (20.0 mL capacity). To this vial was then added CH_2Cl_2 (2.50 mL). After complete dissolution of **4**, the catalyst solution was added directly to the flask containing the TFE solution of **1**. The homopolymerization of **1** was allowed to proceed for 1.5 min prior to the extraction of an aliquot, which was immediately quenched with EVE. The TFE solution of **3** was immediately added to the poly**1** solution. The block copolymerization was allowed to proceed for 20 min prior to quenching with EVE. The **1**−**3** AB diblock copolymer was recovered by precipitation into a large excess of THF, followed by isolation via Buchner filtration and drying in vacuo overnight at ambient temperature. Target molar composition 30:70 **1**:**3**, experimentally determined composition via ^{1}H NMR spectroscopy recorded in D_20 + NaCl: 31:69. M_n determined by aqueous size exclusion chromatography: 14 300 with $M_w/M_n = 1.34$.

Characterization Techniques. ^{1}H (300.1 MHz) and ^{13}C (75.9 MHz) NMR spectra were recorded on a Bruker 300 53 mm spectrometer in appropriate deuterated solvents or deuterated solvent mixtures. Melting points of the new monomers were determined using an electrothermal digital melting point apparatus.

Aqueous Size Exclusion Chromatography (ASEC). Polymer molecular masses, molecular mass distributions, and polydispersity indices were determined by aqueous size exclusion chromatography (aqueous SEC) in 0.25 M NaBr at a flow rate of 1.00 mL min^{-1} at ambient temperature. The system was comprised of a Viscotek VE1122 pump, a Viscotek VE3580 RI detector, and a Viscotek $PW_{X L}$ guard column followed by a series of two Viscotek columns (ViscoGEL G5000$PW_{X L}$ 7.8 mm (i.d) × 30.0 cm (*L*) + G4000$PW_{X L}$ 7.8 mm × 30.0 cm (*L*)) with a theoretical linear molecular mass range of 200−1 000 000 g/mol poly(ethylene oxide) (PEO). The system was calibrated with a series of narrow molecular mass distribution PEO/poly(ethylene glycol) (PEG) standards (MW range: 620−460 000). Data were analyzed with the Omnisec Interactive SEC software package.

Mass Spectrometry. Mass spectra were acquired on a Thermo Finnigan LXQ electrospray ionization-mass spectrometry (ESI-MS) ion-trap instrument using Xcalibur 2.0 for data acquisition and processing. The spectrometer was optimized using the Autotune feature of Xcalibur for the ions if interest. The spectrometer was used in ESI full scan mode from 150 to 2000 amu. Samples were introduced into the MS using the direct liquid infusion (DLI) method, and at least 50 scans were overlaid for each sample. Samples were prepared by dissolving 1.00 mg of monomer in 1.00 mL of MeOH/H_2O (1:1) 0.5% acetic acid solution. Pipetted 1.00 μL of this solution and diluted with an additional 1.00 mL of MeOH/H_2O (1:1) 0.5% acetic acid. Injected 300 μL by of sample solution by DLI using a Hamilton syringe.

Dynamic Light Scattering. Dynamic light scattering (DLS) experiments were performed on a Malvern Instruments Zetasizer Nano ZS instrument equipped with a 4 mW He−Ne laser operating at $\lambda = 633$ nm, an avalanche photodiode detector with high quantum efficiency, and an ALV/LSE-5003 multiple tau digital correlator electronics system. The data were collected and processed using the Dispersion Technology Software Version 5. Samples were prepared as 0.5 wt % solutions in DI H_2O and 0.1 M NaCl.

Results and Discussion

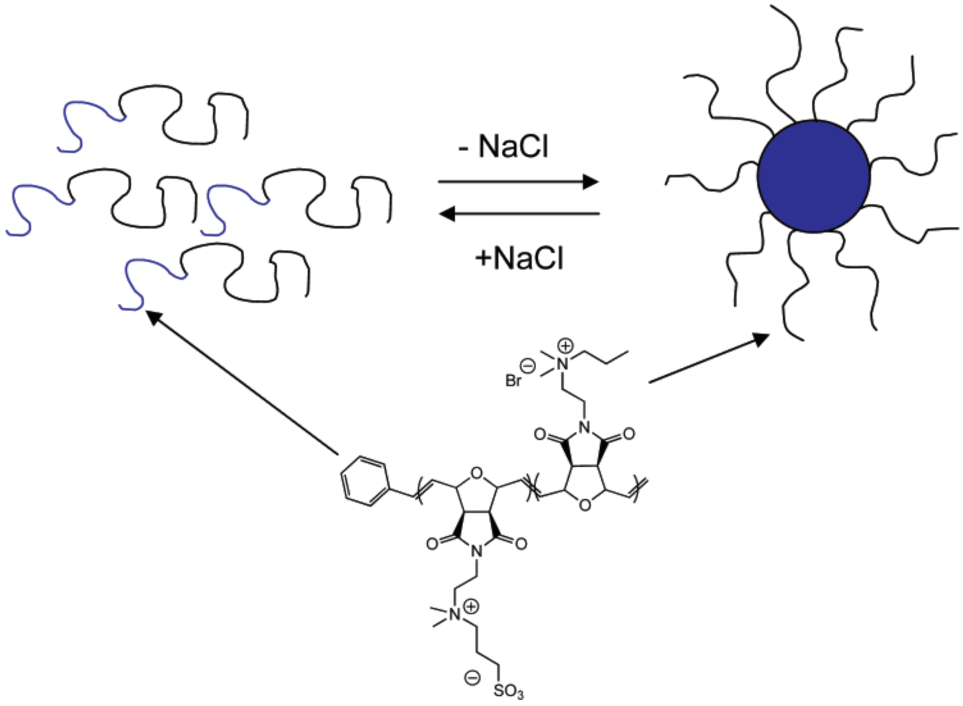
Both **1** and **2** were prepared by a multistep procedure involving initial reaction of *exo*-3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride with *N*,*N*-dimethylethylenediamine, yielding the intermediate tertiary amine functional imide derivative (DMAETDD) which was subsequently modified with 1,3-propane sultone to yield **1** or β-propiolactone to yield **2** (Scheme 1). Monomers were characterized using a combination of ^{1}H/^{13}C NMR spectroscopy and mass spectrometry. Figure 2 shows the ^{13}C NMR spectra of **1** recorded in D_2O and **2** recorded in d_6-DMSO with all relevant peak assignments. The structure of **1** and **2** was also confirmed by mass spectrometry with *m*/*z* for **1** and **2** determined to be 359.08 (*m*/*z* theory: 358.12) and 309.17 (*m*/*z* theory: 308.14), respectively.

In this particular study we have intentionally limited ourselves exclusively to the *exo*-monomer derivatives since *exo*-norbornene substrates are well-known to be more readily polymerized than the corresponding *endo*-stereoisomers, especially in the case of polymerizations initiated by first-generation Grubbs' catalysts such as **4**.

With the new betaine monomers **1** and **2** in hand, we next examined their homo- and copolymerization behavior with **4** in 1:1 v/v TFE/CH_2Cl_2. We will present and discuss the results from the studies with **1** followed by those observed for **2** and conclude with some preliminary aqueous solution studies.

Homopolymerizations of **1** were conducted at 7.38 wt % in a 1:1 TFE/CH_2Cl_2 solvent mixture at ambient temperature. TFE was chosen as a cosolvent for several reasons. First, we recently demonstrated it to be a suitable cosolvent for the direct homogeneous polymerization of permanently cationic substrates;[59] second, in the same report, we demonstrated that **4** is stable in the presence of TFE, at least on the time scale of polymerization, and finally, TFE is known to be a thermodynamically excellent solvent for sulfopropylbetaine monomers and (co)polymers.[79]

Scheme 2. Cartoon Demonstrating the Salt-Induced Assembly/disassembly of the 1−3 AB Diblock Copolymer



Polymerizations were conducted in a nitrogen-filled glovebox and monitored by extracting aliquots at various time intervals that were immediately terminated by the addition of EVE. The polymer/monomer was isolated by precipitation into a large excess of THF and then analyzed by a combination of techniques. Conversions were determined by NMR spectroscopy by monitoring the disappearance of the monomer vinylic resonance and the appearance of the polymer vinylic resonances associated with the unsaturated backbone. For example, Figure 3 shows the NMR spectra, between $\delta = 8.0$ and 5.5 ppm, of several aliquots extracted from the homopolymerization of **1** and clearly demonstrates the distinct difference in chemical shift between the different vinylic hydrogens. Additionally, the phenyl end group associated with the original carbene moiety in **4** is visible at ca. $\delta \sim 7.25-7.50$ ppm. The importance/utility of this will be further highlighted below. Clearly, a direct ratio of the integrals associated with the monomer and polymer vinylic species is a quick and convenient method for determining the conversion. The two different resonances associated with the polymeric vinylic hydrogens is a consequence of the stereochemistry associated with the backbone vinylic groups. The

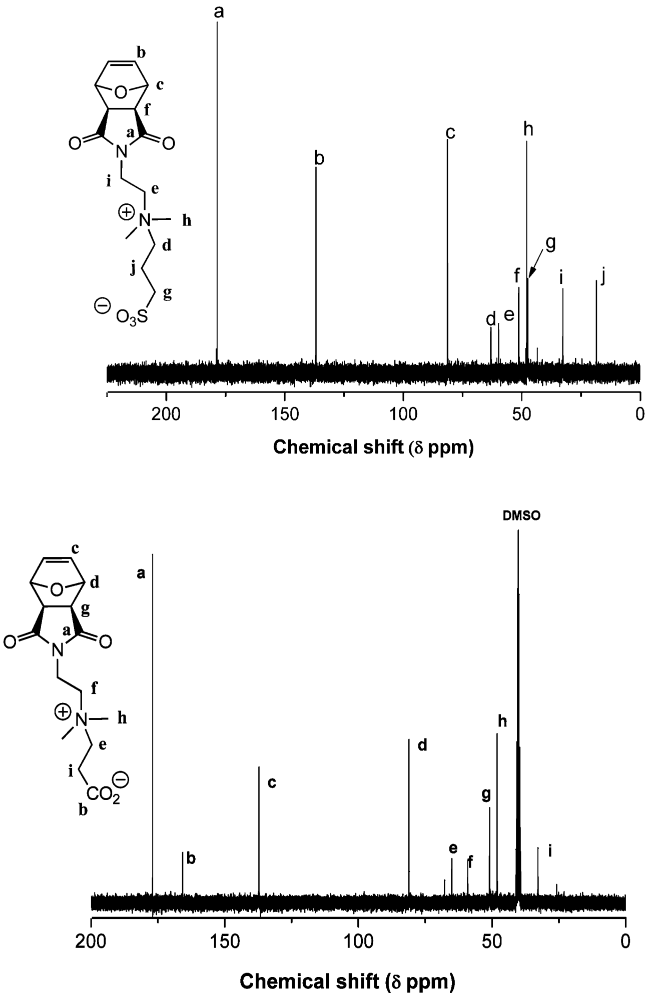


Figure 2. ^{13}C NMR spectra of **1** recorded in D_2O/NaCl and **2** recorded in d_6-DMSO.

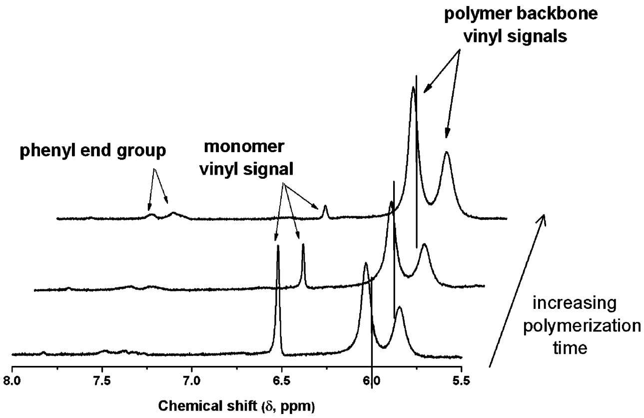


Figure 3. Series of ^{1}H NMR spectra from the homopolymerization of **1** with **4**, recorded in D_2O/NaCl, demonstrating conversion of monomer to polymer as well as the resulting stereochemistry in the polymer backbone. The polymerization was conducted in 1:1 v/v 2,2,2-trifluoroethanol (TFE)/CH_2Cl_2 at ambient temperature with $RuCl_2(PCy_3)_2$-CHPh.

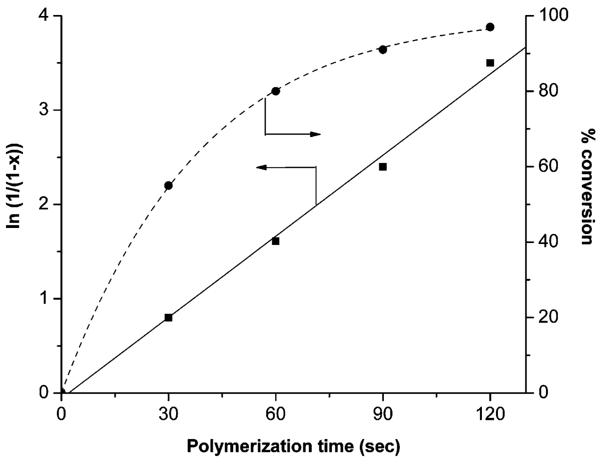


Figure 4. Conversion vs time and pseudo-first-order rate plot for the homopolymerization of the sulfopropylbetaine **1** with $RuCl_2(PCy_3)_2$-CHPh at 7.38 wt % and ambient temperature.

formation of polymer containing unsaturation in the backbone leads to the possibility of both cis and trans stereochemistry. A direct ratio of these two signals yields the relative cis/trans ratio, and we find that the resulting homopolymer of **1** contains ~60–70% trans residues. This is consistent with our previous observations for homopolymers derived from permanently cationic *exo*-7-oxanorbornene substrates prepared with **4** in TFE/CH_2Cl_2 as well as reports from other research groups.[59]

With the conversion data readily available, the pseudo-first-order kinetic plots are easily generated. For example, Figure 4 shows a typical kinetic profile for the homopolymerization of **1**. Several points are particularly noteworthy. First, even under these relatively dilute conditions, the homopolymerization of **1** proceeds extremely rapidly with essentially quantitative conversion being reached in 2 min. This is significantly more rapid than similar cationic substrates we recently reported even though the monomer concentration is ~3 times lower. This is also considerably faster than the homogeneous aqueous systems with cationic substrates reported by Grubbs and co-workers mediated by water-soluble first-generation catalyst derivatives.[73] Knowing the conversion profile, it is straightforward to generate the first-order kinetic plot (Figure 4). The rate expression for a ROMP polymerization is given by $R_p = k_p[\mathrm{Ru}][\mathrm{M}]$, where R_p is the rate of polymerization, k_p is the rate constant of propagation, [Ru] is the initial initiator concentration, and [M] is the starting monomer concentration. This formally second-order rate expression can be forced to a first-order expression since [Ru] is assumed to be constant, i.e., $R_p = k_{comp}[\mathrm{M}]$ where $k_{comp} = k_p[\mathrm{Ru}]$. As such, the first-order rate plot, $\ln(1/(1 - x))$ vs time, where x is the fractional conversion, should be linear (if the polymerization is first order in monomer and there is no discernible chain length dependence of k_p) and pass through the origin, which is observed to be the case. The slope of the kinetic plot is equal to $k_p[\mathrm{Ru}]$, and since [Ru] is known, k_p is readily obtained and for the homopolymerization of **1** was determined to be 2.87 L mol^{-1} s^{-1}.

This value of k_p is an order of magnitude larger than the k_p values recently determined for analogous cationic derivatives in our group and also those reported for an *exo*-7-oxanorbornene derivative polymerized with **4** reported by Holland et al.[60] This difference in k_p may be due to the fact that in our earlier study the cationic substrates all had bromide counterions, although this was not the case in the study by Holland. The nature of the halide ligand is known to have a significant kinetic effect with, for example, $RuBr_2(PCy_3)_2CHPh$ being a faster initiator than **4** but at the expense of lower overall activity (lower k_p).[80] Indeed, we recently demonstrated that monomers with a bromide counterion may serve as a convenient source of bromide and lead to the in situ generation of the mixed, $RuClBr(PCy_3)_2CHPh$, species or the dibromo analogue noted above.[81] However, a contributing factor to the generally fast rate of polymerization may also be the nature of the cosolvent mixture, although this does not account for the observed difference between the cationic substrates. Sanford et al. have reported that the dielectric constant (ϵ) of a solvent can have a significant effect on polymerization rate with solvents with higher ϵ leading to faster polymerizations.[80] This was rationalized in terms of enhanced stabilization of the active unsaturated intermediate in more polar solvents. The TFE cosolvent employed in these studies may likewise be imparting a rate-enhancing effect given its high ϵ of 27.7. However, it is not entirely clear why the polymerization of **1** is so rapid.

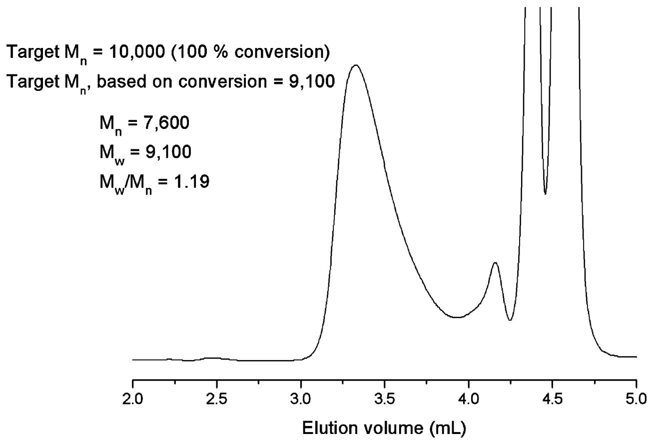


Figure 5. Aqueous size exclusion chromatographic trace (RI signal) for a poly**1** homopolymer with a theoretical M_n of 9100. Analysis was conducted in 0.25 M NaBr at a flow rate of 1.0 mL/min. The system was calibrated with a series of narrow molecular weight distribution poly(ethylene oxide) standards.

Regardless of the precise cause of the observed high rate of polymerization, the kinetic data for the homopolymerization of **1** with **4** is consistent with a controlled polymerization. However, the ability to control the molecular mass is also an important feature associated with such controlled polymerizations. Figure 5 shows the aqueous size exclusion chromatogram (RI signal) for a homopolymer of **1** with a theoretical M_n of 9100. While the trace is unimodal and near symmetric, the chromatogram has an ill-defined baseline, presumably due to its low molecular mass approaching the lower limits of the column set. However, the measured M_n of 7600 is in close agreement with the theoretical M_n of 9100. Additionally, the measured polydispersity index (M_w/M_n) is low at 1.19 and is consistent with (co)-polymers prepared in a controlled manner.

While this measured M_n is close to the theoretical value, it must be borne in mind that the aqueous SEC instrument was calibrated with a series of narrow molecular mass distribution poly(ethylene oxide) standards which may be considered to be poor equivalents for the highly functional zwitterionic, betaine (co)polymers. A complementary method to SEC for determining the *absolute* molecular mass, at least for materials with relatively low molecular masses and appropriate chain-end functionality, is end-group analysis using ^{1}H NMR spectroscopy. Figure 6, for example, shows the ^{1}H NMR spectrum of a poly**1** homopolymer polymerized to ca. 91% conversion. For these lower molecular mass polymers, as noted above, the phenyl end group derived from the original carbene moiety in **4** is visible at $\delta \sim$

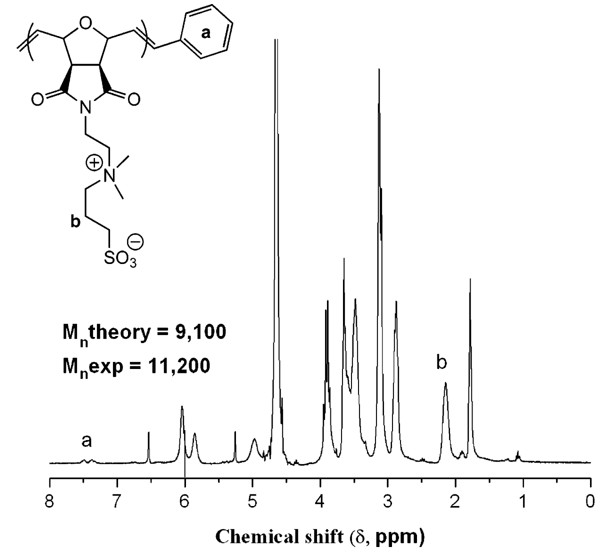


Figure 6. ^{1}H NMR spectrum of a poly**1** homopolymer recorded in D_2O/NaCl with a theoretical M_n of 9100.

7.4−7.5 ppm, labeled **a** in Figure 6, and serves as a convenient tag for absolute molecular mass determination since every polymer chain should contain one such group at one chain terminus. A direct ratio of this signal with a clear resonance signal associated with the polymer facilitates a determination of the absolute molecular mass. For example, the methylene unit labeled **b** can be employed as such a comparative signal. A direct ratio of **a** and **b** yields a calculated absolute M_n of 11 200. Again, this value is close to the theoretical value which given the low sensitivity of NMR and the low intensity of the phenyl end group is gratifying and would indicate that initiation by **4** is essentially quantitative.

The ability to prepare (co)polymers with predetermined molecular masses simply by varying the [Ru]:[M] is another important feature associated with a controlled polymerization. As such, we conducted three different homopolymerizations of **1** targeting homopolymers with molecular masses of 10K, 20K, and 40K (Table 1). In all instances the aqueous SEC traces (RI signal, not shown) were symmetric and unimodal and exhibited a clear shift to lower retention volume with increasing targeted molecular mass. However, the measured molecular masses of 7600, 12 600, and 17 400 did not coincide with the theoretical values, for the reason noted earlier. However, the measured polydispersity indices were low and in the range M_w/M_n = 1.19−1.21. Unfortunately, in the case of the poly**1** homopolymers with targeted molecular masses of 20K and 40K, end-group analysis could not be performed since the phenyl end group was not visible in the ^{1}H NMR spectra.

The ultimate test for a controlled polymerization is an evaluation of retention of chain-end activity upon the complete conversion of monomer. This is most readily demonstrated via block copolymer synthesis. Figure 7 shows the aqueous SEC traces (RI signal) obtained from a self-blocking experiment conducted with **1**. The trace at higher retention volume (lower molecular mass) represents the homopolymer with a targeted M_n of 10 000 obtained from **1** polymerized to near-quantitative conversion. The trace at lower retention volume (higher molecular mass) represents the "block" copolymer obtained after the addition of a second batch of **1**. The "block" copolymer trace is symmetric and unimodal with little, if any, indication of any low molecular mass impurity due to the loss of active chain ends after the quantitative conversion of the first batch of **1**. The experimentally determined polydispersity also falls from M_w/M_n = 1.25 for the first batch of **1** to 1.15 for the "block" copolymer. These observations are entirely consistent with a controlled polymerization and demonstrate the ability, at least in principle, to be able to prepare novel AB diblock copolymers with **1** as a highly functional comonomer.

Having demonstrated the controlled nature of the homopolymerization of **1**, we next evaluated the ROMP of **2** under the same general conditions. In preliminary experiments we examined the direct polymerization of **2**. However, we observed little/no conversion presumably due to catalyst deactivation via the competitive complexation of the carboxylate functional group associated with **2** to the Ru metal center. To circumvent this problem, we first protonated **2** by treating it with HCl thus converting it to a substrate (**H-2**) bearing only a formal positive charge while simultaneously introducing a chloride counterion. The polymerization of **H-2** was then evaluated. Figure 8 shows the conversion and kinetic profile for the homopolymerization of **H-2** (target M_n = 20 000), at 20 wt % with **4** at ambient temperature. The linear kinetic profile is consistent with the observations for **1** and with the polymerization proceeding in a controlled manner. However, the homopolymerization of **H-2** is significantly slower than for **1**. Whereas near-quantitative conversion of **1** was observed within 2 min, it takes 6 min for **H-2** to reach ca. 95% conversion. This is also evident from the calculated k_p value which was determined to be 0.289 L/(mol s)—a significantly lower value than for the homopolymerization of **1** although it is consistent with the permanently cationic *exo*-7-oxanorbornene substrates we recently described.[59]

As with **1**, we next proceeded to demonstrate the ability to control the M_n of the target **H-2** homopolymers by simply varying [Ru]:[M]. Three **H-2** homopolymers with M_n's of 10K, 20K, and 40K were targeted, and the results are summarized in Table 1.

Consistent with the results described above for the poly**1** homopolymers, the M_n as determined by aqueous SEC is significantly different from the theoretical value and is again due to the calibration with poly(ethylene oxide) standards. However, it is apparent that the targeted molecular mass can be tuned by varying the reaction stoichiometry—consistent with the results presented earlier for **1**. The measured polydispersity indices are, likewise, consistent with a well-controlled polymerization although were found to be slightly higher (M_w/M_n = 1.21−1.28) than those determined for the poly**1** homopolymers.

As with the low molecular mass poly**1** homopolymer, we were able to determine the absolute molecular mass by end-group analysis. In contrast, however, to the poly**1** homopolymers, we were able to determine the values for all three homopolymers, presumably due to the enhanced dissolution of the poly**H-2** homopolymers in the NMR solvent. As with the poly**1** homopolymer, it is clear from Table 1 that the absolute molecular masses are more consistent with the targeted values vs those determined by aqueous SEC. For example, in the case of the poly**H-2** homopolymer with a theoretical M_n of 38 000 (based on the degree of conversion), the measured absolute molecular mass by end-group analysis is 32 100.

Having demonstrated the ability to prepare homo- and copolymers of **1** and **H-2** in a controlled manner, we next examined the synthesis of an AB diblock copolymer of **1** with the permanently cationic monomer **3** (Figure 1) achieved via sequential monomer addition of **1** followed by **3**. Figure 9 shows the aqueous SEC traces (RI signal) for a poly**1** homopolymer and the corresponding poly(**1**−**3**) block copolymer. The trace at higher retention volume represents the homopolymer and has a measured M_n of 11 500 (M_n(theory) = =20 000) and M_w/M_n

Table 1. Summary of the Theoretical M_n, Measured M_n and M_w/M_n, and Experimentally Determined k_p Values from Homopolymerizations of the Sulfopropylbetaine 1 and the Protonated Carboxyethylbetaine H-2

monomer	M_n(theory)[a]	% conv[b]	M_n(ASEC)[c]	M_w/M_n[c]	M_n(NMR)	k_p[d] (L/(mol s))[e]
1	10 000	96	7 600	1.19	11 200	2.87
1	20 000	97	12 600	1.19		
1	40 000	95	17 400	1.21		
H-2	10 000	96	3 600	1.25	11 400	0.289
H-2	20 000	95	7 400	1.21	24 700	
H-2	40 000	95	12 600	1.28	32 100	

[a] M_n(theory) = mass of monomer (g)/mol of initiator. [b] As determined by ^{1}H NMR spectroscopy. [c] As determined by aqueous size exclusion chromatography in 0.25 M NaBr. System was calibrated with narrow molecular mass poly(ethylene oxide) standards. [d] k_p = rate constant for propagation. [e] As determined from the pseudo-first-order kinetic plots.

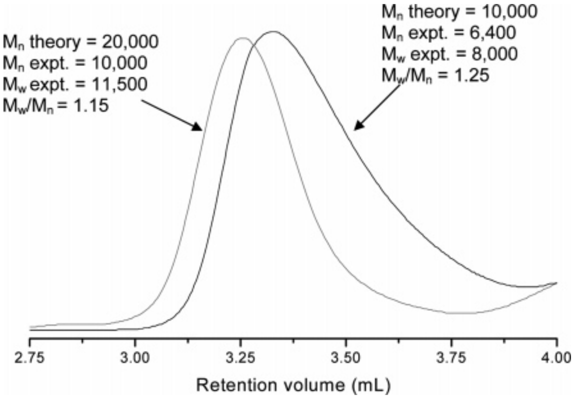


Figure 7. Aqueous size exclusion chromatographic traces (RI signal) for the self-blocking experiment with the sulfopropylbetaine **1**. Analysis was conducted in 0.25 M NaBr at a flow rate of 1.0 mL/min. The system was calibrated with a series of narrow molecular weight distribution poly(ethylene oxide) standards.

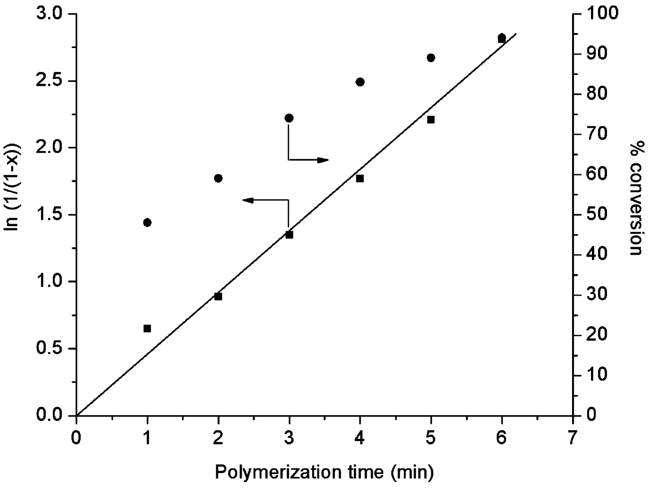


Figure 8. Conversion and kinetic profile for the homopolymerization of the protonated carboxyethylbetaine **H-2** with RuCl$_2$(PCy$_3$)$_2$CHPh in 2,2,2-trifluoroethanol (TFE)/CH$_2$Cl$_2$ at ambient temperature.

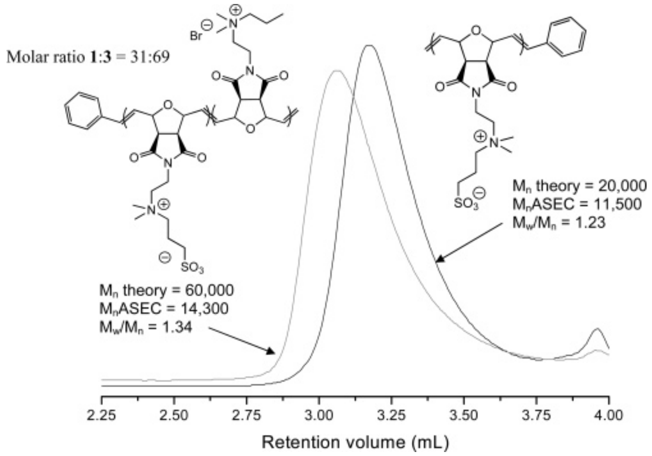


Figure 9. Aqueous size exclusion chromatographic traces (RI signal) for the block copolymerization of the sulfopropylbetaine **1** with the propylquat **3**. Analysis was conducted in 0.25 M NaBr at a flow rate of 1.0 mL/min. The system was calibrated with a series of narrow molecular weight distribution poly(ethylene oxide) standards.

of 1.23. Based on the kinetics determined earlier, the polymerization of **1** was allowed to run for 2 min prior to the subsequent addition of **3**. The trace at lower retention volume represents the **1**−**3** AB diblock copolymer. The trace is unimodal although there is some evidence of tailing to lower molecular mass, which may indicate less than quantitative crossover efficiency. The measured molecular mass is 14 300 and the $M_w/M_n = 1.34$. Given the targeted molecular mass for the block copolymer of 60 000, this value may seem surprisingly low. Aside from the inherent discrepancy associated with the system calibration with linear nonionic poly(ethylene oxide) standards, such a low measured M_n might also be rationalized when the behavior of the zwitterionic−cationic block copolymer in the SEC eluent (0.25 M NaBr) is considered. Such conditions are required to solubilize the polybetaine component, and as such, under these conditions the poly**1** block is likely somewhat expanded. In contrast, the cationic block will be highly collapsed under these conditions due to the polyelectrolyte effect. As such, the AB diblock copolymer could easily have a hydrodynamic volume not significantly greater than the poly**1** homopolymer and certainly would result in a much lower measured M_n than the true value. However, aqueous SEC clearly demonstrates successful block copolymer formation. The copolymer was intentionally targeted to be rich in **3** residues (30:70 molar ratio of **1**:**3**) given the planned aqueous solution studies described below. The actual copolymer composition was determined by ^{1}H NMR spectroscopy and was found to be 31:69 **1**:**3** at 94% conversion.

The aqueous solution properties of the **1**−**3** AB diblock copolymer were anticipated to be complex and to elicit measurable changes in response to the presence/absence of low molecular weight electrolytes. The stimulus responsive behavior of both ionic and zwitterionic (co)polymers toward salts is well documented. Whereas cationic (or anionic) polymers exhibit the well-known polyelectrolyte effect, i.e., chain contraction, upon the addition of low molecular weight salts, a conformational change in response to a stimulus, polymeric betaines exhibit so-called anti-polyelectrolyte behavior. Indeed, the response of polymeric betaines is somewhat more complex than for polyelectrolytes. Polymeric betaines, as a general rule, are insoluble in pure water or at best sparingly soluble. This is due to the formation of a 3D ionic network due to the net attractive ionic interactions between the betaine residues which occurs both inter- and intramolecularly.[40] Addition of a critical amount of salt[39]—sufficient to screen these inter- and intramolecular ionic interactions—will result in dissolution. This represents a mac-

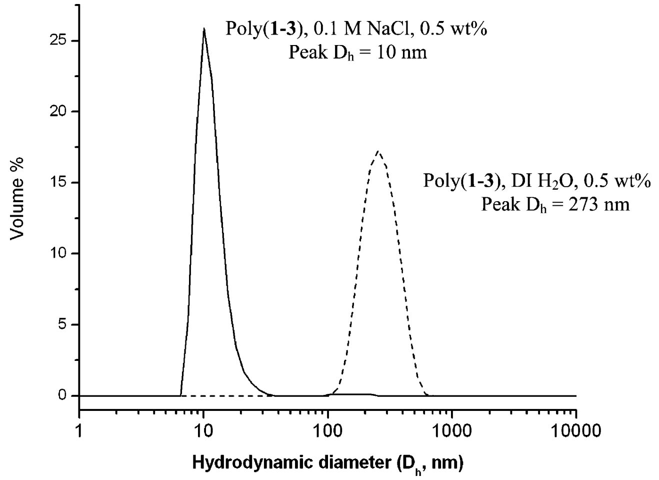


Figure 10. Hydrodynamic diameter size distributions, as determined by dynamic light scattering, for the **1**−**3** AB diblock copolymer in the presence and absence of NaCl. Measurements were made on 0.5 wt % polymer solutions.

roscopic phase response to the applied environmental change, i.e., change in electrolyte concentration. Further addition of low molecular weight salt will result in an additional conformational response by the polymeric betaine as more ionic interactions are screened, resulting in chain expansion—opposite to that observed for polyelectrolytes. Such anticipated stimulus-responsive behavior can be conveniently examined using a variety of techniques including NMR spectroscopy and dynamic light scattering (DLS). Figure 10 shows the experimentally determined hydrodynamic diameter (D_h) size distributions for the **1**−**3** AB diblock copolymer in the presence (0.1 M NaCl) and absence of NaCl. In the presence of salt we see that the block copolymer has an average D_h of ca. 10 nm. Under these conditions both blocks are expected to be hydrophilic, and the copolymer would be anticipated to exist as single molecularly dissolved chains or unimers. Indeed, for a block copolymer of the given molecular mass, the measured D_h of ca. 10 nm is entirely consistent with it existing in the unimeric state. In contrast, when the **1**−**3** AB diblock copolymer is initially molecularly dissolved in a small volume of TFE, a nonselective solvent, and subsequently diluted with deionized water, a selective solvent for the cationic block, we observe aggregates with an average hydrodynamic diameter of 273 nm. These results are entirely consistent with the predicted hydrophilic (**3**)/hydrophobic (**1**) nature of the block copolymer under these solvent conditions and the self-assembly of the block copolymer into multimeric aggregates consisting of a hydrophobic core stabilized by a hydrophilic corona.

Summary/Conclusions

We have described herein the synthesis and controlled ring-opening metathesis polymerization of the first examples of sulfopropylbetaine and carboxyethylbetaine monomers based on the *exo*-7-oxanorbornene structural motif. We have demonstrated that both monomers can be polymerized in a controlled manner, as judged from the kinetic profiles and aqueous SEC analysis, in *organic media* using $RuCl_2(PCy_3)_2CHPh$. In the case of the sulfopropylbetaine derivative, homopolymerization proceeded extremely rapidly with essentially quantitative conversion being obtained in 2 min. In contrast, the carboxyethylbetaine monomer needed to be first protonated to facilitate controlled polymerization, presumably to prevent competitive complexation via the carboxylate functional group of the Ru metal center. The ability to prepare materials with advanced architectures, i.e., block copolymers, was demonstrated by both a self-blocking experiment as well as in the synthesis of an AB diblock copolymer of the sulfopropylbetaine with a permanently cationic comonomer. This represents the first time such betaine monomers have been (co)polymerized directly in a *controlled* fashion by a technique other than a controlled/living free radical process and also the first time it has been achieved in a solvent other than water and/or salt solution. Finally, in a preliminary experiment we demonstrated the stimulus-responsive behavior of the betaine−cationic block copolymer with the material being able to form polymeric self-assemblies simply by controlling the aqueous solution electrolyte concentration.

Acknowledgment. A.B.L. thanks the Department of Education GAANN grant (Award P200A060323) funded through the Department of Chemistry & Biochemistry at USM for financial support of this research in the form of a stipend for D.A.R. Additionally, the NSF-funded Materials Research Science and Engineering Center (MRSEC) (Award DMR-0213883) is acknowledge for partial funds enabling the purchase of the aqueous SEC. Prof. Gordon Cannon is thanked for the use of his DLS instrument.

References and Notes

(1) Lowe, A. B.; McCormick, C. L. *Chem. Rev.* **2002**, *102*, 4177−4190.
(2) Kudaibergenov, S.; Jaeher, W.; Laschewsky, A. *Adv. Polym. Sci.* **2006**, *201*, 157−224.
(3) Monroy, Soto, V. M.; Galin, J. C. *Polymer* **1984**, *25*, 121−128.
(4) Salamone, J. C.; Volksen, W.; Israel, S. C.; Olson, A. P.; Raia, D. C. *Polymer* **1977**, *18*, 1058−1062.
(5) Ehrmann, M.; Galin, J. C. *Polymer* **1992**, *33*, 859−865.
(6) Nagaya, J.; Uzawa, H.; Minoura, N. *Macromol. Rapid Commun.* **1999**, *20*, 573−576.
(7) Bonte, N.; Laschewsky, A. *Polymer* **1996**, *37*, 2011−2019.
(8) Favresse, P.; Laschewsky, A. *Polymer* **2001**, *42*, 2755−2766.
(9) Kathmann, E. E.; White, L. A.; McCormick, C. L. *Polymer* **1997**, *38*, 871−878.
(10) Kathmann, E. E.; White, L. A.; McCormick, C. L. *Polymer* **1997**, *38*, 879−886.
(11) Kathmann, E. E.; McCormick, C. L. *J. Polym. Sci., Polym. Chem.* **1997**, *35*, 231−242.
(12) Kathmann, E. E.; McCormick, C. L. *J. Polym. Sci., Polym. Chem.* **1997**, *35*, 243−253.
(13) Kathmann, E. E.; McCormick, C. L. *Macromolecules* **1997**, *30*, 5297−5304.
(14) Nakaya, T.; Li, Y. J. *Prog. Polym. Sci.* **1999**, *24*, 143−181.
(15) Lewis, A. L.; Cumming, Z. L.; Goreush, H. H.; Kirkwood, L. C.; Tolhurst, L. A.; Stratford, P. W. *Biomaterials* **2001**, *22*, 99−111.
(16) Ma, Y.; Tang, Y.; Billingham, N. C.; Armes, S. P.; Lewis, A. L.; Lloyd, A. W.; Salvage, J. P. *Macromolecules* **2003**, *36*, 3475−3484.
(17) Lobb, E. J.; Ma, I.; Billingham, N. C.; Armes, S. P.; Lewis, A. L. *J. Am. Chem. Soc.* **2001**, *123*, 7913−7914.
(18) Ma, I.; Lobb, E. J.; Billingham, N. C.; Armes, S. P.; Lewis, A. L.; Lloyd, A. W.; Salvage, J. P. *Macromolecules* **2002**, *35*, 9306−9314.
(19) Umeda, T.; Nakaya, T.; Imoto, M. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 457−459.
(20) Gingreau, C.; Galin, J.-C. *Polymer* **1994**, *35*, 4669−4677.
(21) Pujol-Fortin, M. L.; Galin, M.; Galin, J. C. *Macromolecules* **1991**, *24*, 6443−6451.
(22) Pujol-Fortin, M. L.; Galin, J. C. *Polymer* **1994**, *35*, 1462−1472.
(23) Galin, M.; Galin, J. C. *Macromol. Chem. Phys.* **1997**, *198*, 1021−1034.
(24) Ward, M.; Sanchez, M.; Elasri, M. O.; Lowe, A. B. *J. Appl. Polym. Sci.* **2006**, *101*, 1036−1041.
(25) Lowe, A. B.; Vamvakaki, M.; Wassall, M. A.; Wong, L.; Billingham, N. C.; Armes, S. P.; Lloyd, A. W. *J. Biomed. Mater. Res.* **2000**, *52*, 88−94.
(26) West, S. L.; Salvage, J. P.; Lobb, E. J.; Armes, S. P.; Billingham, N. C.; Lewis, A. L.; Hanlon, G. W.; Lloyd, A. W. *Biomaterials* **2004**, *25*, 1195−1204.
(27) Lewis, A. L.; Hughes, P. D.; Kirkwood, L. C.; Leppard, S. W.; Redman, R. P.; Tolhurst, L. A.; Stratford, P. W. *Biomaterials* **2000**, *21*, 1847−1859.
(28) Ishihara, K.; Aragaki, R.; Ueda, T.; Watenabe, A.; Nakabayashi, N. *J. Biomed. Mater. Res.* **1990**, *24*, 1069−1077.

(29) Ishihara, K.; Ziats, N. P.; Tierney, B. P.; Nakabayashi, N.; Anderson, J. M. *J. Biomed. Mater. Res.* **1991**, *25*, 1397−1407.

(30) Ueda, T.; Oshida, H.; Kurita, K.; Ishihara, K.; Nakabayashi, N. *Polym. J.* **1992**, *24*, 1259−1269.

(31) Ladenheim, H.; Morawetz, H. *J. Polym. Sci.* **1957**, *36*, 251−254.

(32) Hart, R.; Timmerman, D. *J. Polym. Sci.* **1958**, *28*, 638−640.

(33) Rosenheck, K.; Katchalsky, A. *J. Polym. Sci.* **1958**, *32*, 511−514.

(34) Salamone, J. C.; Volksen, W.; Olson, A. P.; Israel, S. C. *Polymer* **1978**, *19*, 1157−1162.

(35) Galin, M.; Galin, J. C. *Makromol. Chem.* **1993**, *194*, 3479−3491.

(36) Galin, J. C.; Galin, M. *J. Polym. Sci., Polym. Phys.* **1992**, *30*, 1103−1111.

(37) Galin, M.; Mathis, A.; Galin, J.-C. *Polym. Adv. Technol.* **2001**, *12*, 574−582.

(38) Armentrout, R. S.; McCormick, C. L. *Macromolecules* **2000**, *33*, 419−424.

(39) Monroy, Soto, V. M.; Galin, J. C. *Polymer* **1984**, *25*, 254−262.

(40) Schulz, D. N.; Peiffer, D. G.; Agarwal, P. K.; Larabee, J.; Kaladas, J. J.; Soni, L.; Handwerker, B.; Garner, R. T. *Polymer* **1986**, *27*, 1734−1742.

(41) Lowe, A. B.; Billingham, N. C.; Armes, S. P. *Chem. Commun.* **1996**, 1555−1556.

(42) Bütün, V.; Bennett, C. E.; Vamvakaki, M.; Lowe, A. B.; Billingham, N. C.; Armes, S. P. *J. Mater. Chem.* **1997**, *7*, 1693−1695.

(43) Tuzar, Z.; Pospisil, H.; Plestil, J.; Lowe, A. B.; Baines, F. L.; Billingham, N. C.; Armes, S. P. *Macromolecules* **1997**, *30*, 2509−2512.

(44) Lowe, A. B.; Billingham, N. C.; Armes, S. P. *Macromolecules* **1999**, *32*, 2141−2148.

(45) McCormick, C. L.; Lowe, A. B. *Acc. Chem. Res.* **2004**, *37*, 312−325.

(46) Lowe, A. B.; McCormick, C. L. *Prog. Polym. Sci.* **2007**, *32*, 283−351.

(47) Donovan, M. S.; Sumerlin, B. S.; Lowe, A. B.; McCormick, C. L. *Macromolecules* **2002**, *35*, 8663−8666.

(48) Lowe, A. B.; McCormick, C. L. *Aust. J. Chem.* **2002**, *55*, 367−379.

(49) Donovan, M. S.; Lowe, A. B.; Sanford, T. A.; McCormick, C. L. *J. Polym. Sci., Polym. Chem.* **2003**, *41*, 1262−1281.

(50) Schrock, R. R.; Krouse, S. A.; Knoll, K.; Feldman, J.; Murdzek, J. S.; Yang, D. C. *J. Mol. Catal.* **1988**, *46*, 243−253.

(51) McConville, D. H.; Wolf, J. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 4413−4414.

(52) Totland, K. M.; Boyd, T. J.; Lavoie, G. G.; Davis, W. M.; Schrock, R. R. *Macromolecules* **1996**, *29*, 6114−6125.

(53) *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, 2003.

(54) Slugovc, C. *Macromol. Rapid Commun.* **2004**, *25*, 1283−1297.

(55) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **1995**, *34*, 2039−2041.

(56) Bielawski, C. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 2903−2906.

(57) Amir-Ebrahimi, V.; Corry, D. A.; Hamilton, J. G.; Thompson, J. M.; Rooney, J. J. *Macromolecules* **2000**, *33*, 717−724.

(58) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18−29.

(59) Rankin, D. A.; P'Pool, S. J.; Schanz, H.-J.; Lowe, A. B. *J. Polym. Sci., Polym. Chem.* **2007**, *45*, 2113−2128.

(60) Holland, M. G.; Griffith, V. E.; France, M. B.; Desjardins, S. G. *J. Polym. Sci., Polym. Chem.* **2003**, *41*, 2125−2131.

(61) Maynard, H. D.; Okada, S. Y.; Grubbs, R. H. *Macromolecules* **2000**, *33*, 6239−6248.

(62) Melis, K.; de Vos, D.; Jacobs, P.; Verpoort, F. *NATO Sci., Ser. II: Math., Phys. Chem.* **2003**, *122* (Novel Metathesis Chemistry), 237−242.

(63) Weck, M.; Schwab, P.; Grubbs, R. H. *Macromolecules* **1996**, *29*, 1789−1793.

(64) Clark, M. B.; Lee, T. R. *Polym. Prepr.* **1998**, *39* (1), 416−417.

(65) Christian, Kluger, W. H. B. *J. Polym. Sci., Polym. Chem.* **2007**, *45*, 485−499.

(66) Breitenkamp, K.; Simeone, J.; Jin, E.; Emrick, T. *Macromolecules* **2002**, *35*, 9249−9252.

(67) Bandari, R.; Prager-Duschke, A.; Kuhnel, C.; Decker, U.; Schlemmer, B.; Buchmeiser, M. R. *Macromolecules* **2006**, *39*, 5222−5229.

(68) Langsdorf, B. L.; Zhou, X.; Lonergan, M. C. *Macromolecules* **2001**, *34*, 2450−2458.

(69) Langsdorf, B. L.; Zhou, X.; Lonergan, M. C. *Book of Abstracts*, 218th ACS National Meeting, New Orleans, Aug 22−26, 1999; INOR-610.

(70) Scherman Oren, A.; Rutenberg Isaac, M.; Grubbs Robert, H. *J. Am. Chem. Soc.* **2003**, *125*, 8515−22.

(71) Lynn, D. M.; Kanaoka, S.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 784−790.

(72) Mohr, B.; Lynn, D. M.; Grubbs, R. H. *Organometallics* **1996**, *15*, 4317−4325.

(73) Lynn, D. M.; Mohr, B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 1627−1628.

(74) Lynn, D. M.; Mohr, B.; Grubbs, R. H.; Henling, L. M.; Day, M. W. *J. Am. Chem. Soc.* **2000**, *122*, 6601−6609.

(75) Gallivan, J. P.; Jordan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **2005**, *46*, 2577−2580.

(76) Hong, S. H.; Grubbs, R. H. *J. Am. Chem. Soc.* **2006**, *128*, 3508−3509.

(77) Quemener, D.; Heroguez, V.; Gnanou, Y. *J. Polym. Sci., Polym. Chem.* **2006**, *44*, 2784−2793.

(78) Ilker, M. F.; Schule, H.; Coughlin, E. B. *Macromolecules* **2004**, *37*, 694−700.

(79) Huglin, M. B.; Radwan, M. A. *Makromol. Chem.* **1991**, *192*, 2433−2445.

(80) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543−6554.

(81) Rankin, D. A.; Schanz, H.-J.; Lowe, A. B. *Macromol. Chem. Phys.* **2007**, *208*, 2389−2395.

MA701952C