Available online at www.sciencedirect.com
SCIENCE DIRECT®

ELSEVIER

Polymer 46 (2005) 2522–2530

polymer

www.elsevier.com/locate/polymer

Ring opening polymerization of 3-semifluoro- and 3-bromomethyloxetanes to poly(2,2-substituted-1,3-propylene oxide) telechelics for soft blocks in polyurethanes

Umit Makal, Janelle Uilk, Pinar Kurt, Robert S. Cooke, Kenneth J. Wynne*

Department of Chemical Engineering, Virginia Commonwealth University, 601 West Main Street, P.O. Box 843028 Room 444, Richmond, VA 23284-3028, USA

Received 10 November 2004; received in revised form 10 January 2005; accepted 13 January 2005

Abstract

The synthesis of hydroxy-terminated poly(2,2-substituted-1,3-propylene oxide) polyoxetane telechelics and co-telechelics bearing semifluorinated (–$CH_2OCH_2(CF_2)_nCF_3$) and functional bromomethyl pendant groups is reported. Characterization utilized ^{1}H NMR spectroscopy, temperature modulated DSC (MDCS), and gel permeation chromatography (GPC). Analysis of relative reactivity ratios for a 1:1 3FOx to BrOx feed indicates that in the early stages of reaction BrOx–BrOx dyad mole fraction is below the statistically predicted amount. However, a model suggests that the final telechelic dyad composition at complete reaction is not very different from a statistical copolymer. The co-telechelics have low T_gs (-33 to -39 °C) and molecular weight in a desirable range ($M_w \approx 3$–5 k). Telechelics were incorporated in polyurethanes (PUs) with isophorone diisocyanate (IPDI) and butanediol (BD) as the hard block. Characterization of polyurethane composition and bulk properties by ^{1}H NMR, MDSC, and GPC is described. The new polyurethanes hold promise for a ‘reaction on polymer’ approach to polyurethanes with functional soft blocks.

Keywords: Polyoxetanes; Polyurethanes; Ring-opening polymerization

1. Introduction

Incorporating a surface-modifying additive (SMA) during coating, forming, or similar process is an important method for controlling surface properties [1]. The SMA approach is simpler than plasma [2,3], plasma followed by grafting [4–6], or chemical processes [7–9] since in favorable cases there are no post-processing steps.

The potential value of SMAs in enhancing surface properties such as adhesion, diffusion control, biocompatibility, biofouling, and electromagnetic radiation absorption are readily apparent. Thus far, surface modifying additives have been employed principally to change wetting characteristics. Surfaces are made hydrophobic with poly(dimethylsiloxane) SMAs [10–15] or both hydrophobic and oleophobic with fluorinated SMAs [16–22].

Our goal is to provide a broader palette of SMA options such as hydrophilicity, photophysical behavior, biocompatibility, adhesion promotion, and antimicrobial properties. In working toward this goal we have incorporated functional groups into semifluorinated oxetane telechelics. Such functional telechelics are then precursors to functional polyurethane SMAs. This approach leverages the tendency of soft blocks to concentrate at the air-polymer interface [23–25].

In addition, surfacephilicity of fluorinated side chains is employed to surface concentrate functional groups. Semifluorinated groups have been used previously to surface-concentrate non-surfacephilic photostabilizers [26] and fullerenes [27]. Chaudhury has reported polyurethanes with multiple soft blocks that are hydrophobic (fluorinated, dimethylsiloxane) and hydrophilic (poly(ethylene glycol)). The presence of the fluorinated soft block acts to concentrate the hydrophilic block near the surface. These polyurethanes undergo reversible hydrophobic–hydrophilic

---

* Corresponding author. Tel.: +1 804 828 9303; fax: +1 804 828 3846.
E-mail address: kjwynne@vcu.edu (K.J. Wynne).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.01.069

wetting behavior in response to the polarity of the contacting medium.

In beginning to explore surfacephilic tendencies we reported amphiphilic polyoxetane telechelics with hydrophobic semifluorinated and hydrophilic alkyl ether (methoxyethoxyethoxy) pendant groups [28]. In order to obtain surface-active telechelics bearing reactive groups, we have now prepared co-telechelics containing semifluorinated and bromomethyl groups.

Oxetanes are typically polymerized under cationic ring-opening conditions [29,30]. Poly(2,2-substituted-1,3-propylene oxide)s with controllable molecular weights were prepared using BF_3-etherate and 1,4-butanediol as a co-catalyst [31]. Ring-opening of hydroxymethyloxetanes catalyzed using BF_3 complexes has been studied by Bednarek [32,33]. Oxetane telechelics with semifluorinated side chains were synthesized using cationic ring opening polymerization in several ways [16,17,34].

The present paper describes the homo- and co-polymerization of 3-bromomethyl-3-methyloxetane (BrOx) with previously utilized 3FOx and 5FOx ($–OCH_2CF_2CF_3$) [28]. BF_3-etherate was chosen rather than BF_3-tetrahydrofuran since tetrahydrofuran (THF) ring-opens under cationic conditions and is incorporated in the polymer main chain [17]. Using the new P(FOx/BrOx) telechelics, where ‘P’ designates the monomer-in-telechelic, polyurethanes were prepared employing isophorone diisocyanate (IPDI)/butane diol (BD) hard blocks. Preliminary reports on the synthesis of P(BrOx:FOx) telechelics have appeared [35]. Separately, we report that the new telechelics prove useful for introducing surface concentrated functionality.

2. Experimental section

2.1. Materials

3-(2,2,2-trifluoroethoxymethyl)-3-methyloxetane (3FOx), 3-(2,2,3,3,3-pentafluoropropoxymethyl)-3-methyloxetane (5FOx), and 3-bromomethyl-3-methyloxetane (BrOx) were synthesized following published procedures [17] or were generously provided by Gencorp Aerojet (Sacramento, CA) or OMNOVA Solutions (Akron OH). Monomers were distilled under vacuum before use: 3FOx and 5FOx at 100 °C/5 mmHg and BrOx at 85 °C/5 mmHg. Boron trifluoride dietherate ($BF_3O(C_2H_5)_2$), was used as received. Methylene chloride and other organic solvents were either used as received or dried and stored over 4 Å molecular sieves. Isophorone diisocyanate (IPDI, 98%) and dibutyltin dilaurate catalyst (T-12) were obtained from Aldrich. 1,4-butanediol (BD) was purchased from Acros chemicals and used as received. Poly(tetramethylene oxide) (PTMO-2000) was purchased from Aldrich and used as received.

2.2. Telechelic synthesis

Homo and copolymerization of BrOx and FOx monomers were carried out by a modification of the procedure reported by Malik [17]. Cationic ring opening polymerization was employed with BF_3 etherate and 1,4-butanediol as catalyst and co-catalyst, respectively. A typical procedure follows.

2.2.1. Poly(2-bromomethyl-2-methyl-1,3-propylene oxide) P(BrOx)

Methylene chloride (5.06 g) was poured into a round bottom flask under nitrogen followed by 1,4-butanediol (1.08 g, 11.98 mmol). BF_3-OEt_2 (3.05 ml, 24.17 mmol) was then added followed by stirring under nitrogen for 45 min. The solution was cooled to between −25 and −20 °C with a dry ice/ethanol bath, and 3-bromomethyl-3-methyloxetane (39.5 g, 239.2 mmol) in methylene chloride (59.4 g) was added dropwise (0.5 ml/min). The mixture was kept at this temperature for 4 h with stirring, brought to room temperature, and quenched with deionized water. The organic phase was separated, washed with 2 wt% HCl (aq) and then with 10% NaCl (aq). Phase separation of the desired product was effected by addition of (3:1) methanol:deionized water. The product was placed in a vacuum oven (50 °C/5 mmHg) overnight to give a clear, viscous oil (36.4 g, >90% yield). ^1H NMR ($CDCl_3$) δ 1.05 ($–CH_3$, 3H, s), δ 3.20–3.38 (backbone $–CH_2–C–CH_2–$, 4H, s), δ 3.40–3.44 (sidechain $CH_2–Br$, 2H, s).

2.2.2. Poly(2-trifluoroethoxymethyl-2-methyl-1,3-propylene oxide) P(3FOx)

P(3FOx) and P(FOx:BrOx) co- telechelics were prepared in a similar manner. P(3FOx) ^1H NMR ($CDCl_3$): δ 0.92 ($–CH_3$, 3H, s), δ 3.15–3.22 (backbone $–CH_2–C–CH_2–$, 4H, m), δ 3.41–3.48 (sidechain $CH_2–O$, 2H, s), δ 3.70–3.81 ($O–CH_2–CF_3$, 2H, q). Typical ^1H NMR spectrum for co-telechelic P(3FOx:BrOx-1:1) ($CDCl_3$): δ 0.90–0.98 (FOx $–CH_3$, 3H, s), δ 1.05 (BrOx $–CH_3$, 3H, s), δ 3.15–3.30 (backbone $–CH_2–C–CH_2–$, 8H, m), δ 3.40–3.45 (sidechain $CH_2–Br$, 2H, s), δ 3.40–3.45 (sidechain $CH_2–O$, 2H, s), δ 3.75–3.85 ($O–CH_2$, 2H, m).

2.3. Reactivity ratios

Copolymerization of 3FOx and BrOx was carried out in methylene chloride at 0 °C and terminated below 10% monomer conversion to minimize errors due to changes in feed ratio [36]. Copolymer compositions were calculated from integration of $C–CH_3$ peaks in the ^1H NMR spectra.

2.4. Polyurethane synthesis

Polyurethanes (PUs) were synthesized in two steps [24]. First, a calculated amount of telechelic and excess diisocyanate (IPDI) was introduced into a three-neck round-bottomed flask equipped with a mechanical stirrer, nitrogen inlet, and condenser. The reaction was started in DMF with an initial 85–90 wt% concentration of reactants. After addition of dibutyltin dilaurate catalyst (0.15–0.20 wt% of the total reaction mixture in THF), the reactants were kept at 65–70 °C for 3 h. The preparation of diisocyanate-terminated prepolymer was confirmed by FT-IR spectroscopy (urethane carbonyl, 1724 cm^{-1}, and N–H, 3346 cm^{-1}, absorbances).

In the second stage, BD was added and heating was continued (65 °C) until all isocyanate groups were consumed (ca. 4 h). The course of the chain extension reaction was monitored with FT-IR by following the disappearance of sharp isocyanate band at 2267 cm^{-1}. As the viscosity increased during the chain extension reaction, DMF or DMF/THF was added to dilute the reaction mixture. The final solids content of the polymer solution was 30–40%. The product was precipitated into methanol or methanol/water for purification. The final polyurethane compositions were verified with ^1H NMR.

Reactions were run in DMF or DMF/THF because phase separation was observed using THF alone. However, once prepared all polyurethanes were soluble in THF which was the only solvent used for coating deposition.

2.5. Hard block synthesis

Hard block was synthesized in one step. A calculated amount of diisocyanate (IPDI) was mixed with BD, so that the NCO/OH ratio equalled 1. THF was employed as the reaction solvent. Dibutyltin dilaurate catalyst was added and the reaction mixture was held at 55–60 °C. FTIR was used to monitor the reaction completion. The product was precipitated into methanol/water mixture for purification. The final hard block composition was verified by ^1H NMR spectroscopy.

3. Characterization

Telechelic ($CDCl_3$) and polyurethane (D_6-DMSO) ^1H NMR spectra were recorded using a Varian Spectrometer (Inova 400 MHz) operating at 400 MHz. FT-IR spectra were obtained using a Nicolet 400 FT-IR spectrometer using neat liquids (telechelics) or solution cast films on KBr discs. Differential scanning calorimetry (DSC) was done with a TA-Q 1000 Series™ instrument (TA Instruments). Unless otherwise noted, measurements were carried out at a heating rate of 10 °C/min from −75 °C. Indium metal was used for calibration. In addition to standard DSC, temperature modulated DSC (MDSC) with modulation amplitude of ±0.5 °C, modulation period of 60 s, and heating rate of 3 °C/min was also carried out for telechelics and polyurethanes. DSC samples of telechelics and polyurethanes were directly deposited on the DSC pan, while physical mixtures were first generated in homogeneous solution ($CHCl_3$) followed by deposition through solvent evaporation.

3.1. Molecular weight determination

3.1.1. Gel permeation chromatography (GPC)

Polyurethane molecular weights were measured using a Viscotek TriSEC triple detector GPC system (THF) with sample concentrations of 10–15 mg/ml and a flow rate of 1 ml/min. Universal calibration by polystyrene standards was used for calculation of molecular weight (M_n, M_w) and polydispersity.

3.1.2. End group analysis

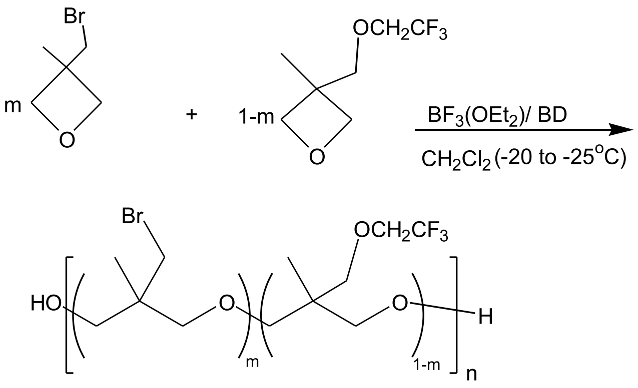
The degree of polymerization (D_p) and M_n are determined by end group analysis, which utilizes the reaction of trifluoroacetic anhydride (TFA) with telechelic hydroxyl end groups [28]. An estimated 2–4 fold molar TFA excess was added to the telechelic solution in $CDCl_3$. The solution was stirred at room temperature for 1 h before determining the ^1H NMR spectrum. The ratio of signals of methylene protons next to the fluoroacetyl group compared to the methyl of the repeat unit was used for calculation of D_p for the telechelics.

4. Results and discussion

4.1. Telechelics

4.1.1. Synthesis

Scheme 1 shows the ring-opening polymerization for BrOx and 3FOx monomers using BF_3-etherate catalyst and 1,4-butanediol as co-catalyst. Reactions were carried out at −20 to −25 °C under slow nitrogen purge with a BF_3-etherate/1,4-butanediol ratio of 2.02:1. It is important to run the reaction at low temperature (ca. −20 °C or less) because higher reaction temperatures often give rise to products with carbonyl IR absorbance and M_n different from anticipated values. Table 1 contains telechelic compositions, catalyst



Scheme 1. Synthesis of P(3FOx:BrOx) co-telechelics by cationic ring-opening polymerization.

Table 1
Compositions and molecular weights of telechelic poly(oxetanes)

Telechelic	Monomer feed ratio[a,b]			Poly(oxetane) telechelics		
	3FOx	5FOx	BrOx	P(FOx:BrOx)[c]	D_p[c]	$M_n \times 10^{-3}$[c,d,e]
P(3FOx)	1.0	–	–	–	18.5	3.40
P(5FOx)	–	1.0	–	–	24.2	5.66
P(BrOx)	–	–	1.0	–	17.1	2.82
P(3FOx:BrOx-1:1)	1.0	–	1.0	1.2:1.0	27.0	4.71
P(3FOx:BrOx-2:1)	2.0	–	1.0	2.2:1.0	26.5	4.70
P(3FOx:BrOx-1:2)	1.0	–	2.0	1.0:1.7	19.6	3.36
P(5FOx:BrOx-1:1)	–	1.0	1.0	1.2:1.0	20.5	4.09
P(5FOx:BrOx-2:1)	–	2.0	1.0	1.9:1.0	11.9	2.50
P(5FOx:BrOx-1:2)	–	1.0	2.0	1.0:1.8	18.1	3.40

[a] Monomer/catalyst (BF_3-OEt_2) mole ratio = 10.

[b] Catalyst (BF_3-OEt_2)/ co-catalyst (1,4-butanediol) mole ratio = 2.02.

[c] Determined by ^{1}H NMR end group analysis; Equivalent molecular weight = $M_n/2$.

[d] M_w by GPC with PS standards (universal calibration): P(BrOx); 2.6×10^3, P(5FOx:BrOx-1:2); 5.8×10^3, P(3FOx:BrOx-1:2); 4.1×10^3.

[e] Polydispersities for these three telechelics by GPC were: P(BrOx) 1.58, P(5FOx:BrOx-1:2); 1.35, P(3FOx:BrOx-1:2); 2.04.

ratios and molecular weights. Compositions are designated by the molar repeat ratio, e.g. P(3FOx:BrOx-1:1).

4.1.2. ^{1}H NMR

Fig. 1D shows the ^{1}H NMR spectrum of P(3FOx:BrOx-1:1). The ratio of 3FOx:BrOx segments is easily determined by integration of methyl peaks at 0.92 ppm (CH_3, FOx) and 1.05 ppm (CH_3, BrOx). Composition is further validated by integral ratios of CH_2–Br (3.45 ppm, BrOx) to CH_2–O–CH_2CF_3 (3.49 ppm, 3FOx) or CH_2–O–$CH_2CF_2CF_3$ (3.44 ppm, 5FOx). The observed compositions for the telechelics are close to the feed ratios (Table 1).

While the 2-methyl groups and 2-methylene groups are useful for co-telechelic composition, the ^{1}H chemical shifts of these groups are almost identical to those observed for homo-telechelics. The question of homo-telechelic mixtures vs. co-telechelics is also addressed in Fig. 1. The ^{1}H NMR spectra of P(BrOx) and P(3FOx) homo-telechelics (Fig. 1A and B, respectively) are shown along with a spectrum of a physical mixture of homo-telechelics (Fig. 1C).

Unlike the previously studied P(FOx:Me2Ox) telechelics [28], the main chain –CH_2–C–CH_2–O– protons have markedly different chemical shifts in the putative co-telechelic compared to the physical mixture and

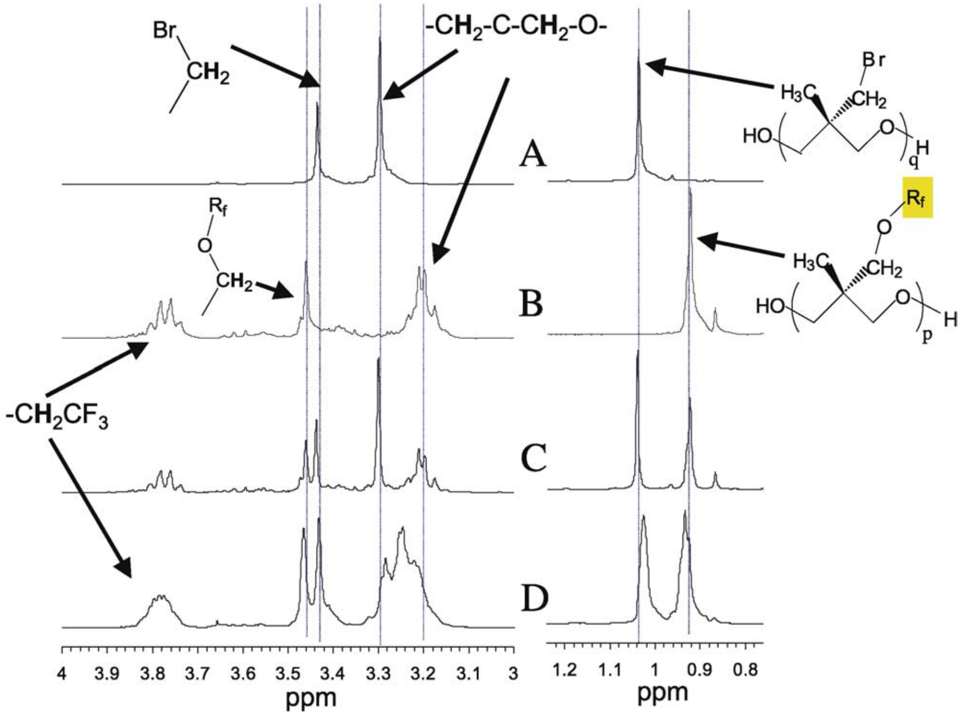


Fig. 1. ^{1}H NMR spectra of homo telechelics, (A) P(BrOx), (B) P(3FOx), (C) physical mixture of P(BrOx) and P(3FOx), and (D) co-telechelic, P(3FOx:BrOx-1:1).

homo-telechelics. The peaks for the –CH_2–C–CH_2–O– protons appear at 3.3 ppm for P(BrOx), Fig. 1A, and 3.2 ppm for P(3FOx), Fig. 1B. The ^{1}H NMR spectrum obtained at 400 MHz reveals an interesting feature for P(3FOx) not reported previously [20]. The main chain methylene protons, which are diastereotopic, appear as a broadened AA$'$ quartet. In P(BrOx) telechelic, there is a much smaller chemical shift difference between these protons, and they appear as a singlet.

For the P(3FOx:BrOx-1:1) telechelic, the main chain methylene protons have a broad envelope of peaks intermediate between those for the P(3FOx) and P(BrOx) telechelics. This has the appearance of a broad, three-peaked envelope centered at 3.25 ppm, an intermediate chemical shift not observed for either of the homo-telechelics. This new resonance provides evidence for a co-telechelic with a random AB sequence distribution. Additional support comes from ^{1}H-NMR peaks for the trifluoroethoxy methylene peaks. A distinct quartet at 3.8 ppm is present in Fig. 1B and C, from spin–spin splitting of –CH_2– protons next to CF_3 ($J_{^{19}F-^{1}H}$, 8.0–8.2 Hz). The co-telechelic (Fig. 1D) has a peak at 3.8 ppm, but a distinct quartet is not seen. Broadening of the peak reflects the presence of various triad sequences of 3FOx and BrOx. In summary, ^{1}H NMR spectra give clear evidence that ring-opening copolymerization of the fluoro- and bromo-oxetane monomers gives a poly(co-oxetane) telechelic.

4.1.3. Monomer reactivity ratios

Copolymerization kinetics of vinyl monomers are well known and give important insight into reactivity and chain composition [37]. The binary copolymerization equation [38] has been applied with success to ring opening copolymerization of oxetane monomers (cationic polymerization), although mechanistic details remain to be clarified. For example, the copolymerization of oxetane with 3,3-dimethyloxetane using a BF_4-OEt_2 catalyst provides r_1 (1.19) and r_2 (0.95), respectively [39]. In this case the r_1r_2 product is 1.1 indicating completely random or ideal polymerization [38]. For the copolymerization of tetrahydrofuran with 3,3-dimethyloxetane, r_1 (0.13) and r_2 (8.1), respectively, and the r_1r_2 product is 1.0 again consistent with near-ideal selectivity [40]. Copolymerization of 3,3-bis(chloromethyl)oxetane with ε-caprolactone reveals an alternating tendency with r_1 (0.26) and r_2 (0.48), respectively, an r_1r_2 product of 0.13 [41]. We have reported a nearly random monomer distribution for copolymerization of 3-methoxyethoxyethoxy-3-methyloxetane, ME2Ox, (r_1, 1.65) and 5FOx (r_2, 0.49) an $r_1r_2=0.81$ in methylcyclohexane [28].

The Finemann–Ross (F–R) method was used to estimate the reactivity ratios for 3FOx (monomer 1) and BrOx as well as copolymer composition. The values r_1 (k_{11}/k_{12}) and r_2 (k_{22}/k_{21}) are the ratios of homopropogation/crosspropogation rate constants for the respective monomers. The F–R plot shown in Fig. 2A was fitted to a straight line with $R^2=0.99$. Two separate data sets were collected to demonstrate reproducibility. The r_1 and r_2 values obtained from this plot are 2.11 for 3FOx and 0.23 for BrOx. These r_1 and r_2 values indicate that the active ends derived from either 3FOx or BrOx favor reaction with the 3FOx monomer, so that the 3FOx growing species has monomer selectivity. The values show $r_1>1>r_2$ and r_1r_2 ($=k_{11}k_{22}/k_{12}k_{21}$)$=0.49$, smaller than unity.

This analysis indicates that in the beginning of the reaction, while the monomer ratio is close to 1:1, the copolymer units formed have a BrOx–BrOx dyad mole fraction below the statistically predicted amount. That is, most BrOx exists in dyads combined with 3FOx. Also the 3FOx–3FOx dyad mole fraction is greater than the statistical composition. If this trend is extrapolated, the final telechelic dyad composition obtained at complete reaction is not very different from a statistical copolymer.

Fig. 2B shows the composition diagram. That is, a plot of mole fraction for BrOx in copolymer (F_2) as a function of its mole fraction in the monomer feed (f_2). The dashed line corresponds to the ideal random copolymerization ($r_1=r_2=1$). The solid line is the F–R curve for $r_1=2.11$ and $r_2=0.23$ ($r_1r_2=0.49$). This reactivity analysis focuses on chain growth via chain end reaction and ignores other possible polymerization and depolymerization reactions. However, the conclusion from kinetic analysis that a statistical copolymer exists at complete reaction is consistent with its ^{1}H NMR spectrum. A broad, three-peaked envelope centered at 3.25 ppm for main chain –CH_2CCH_2– seen in Fig. 1 is that expected from a statistical copolymer.

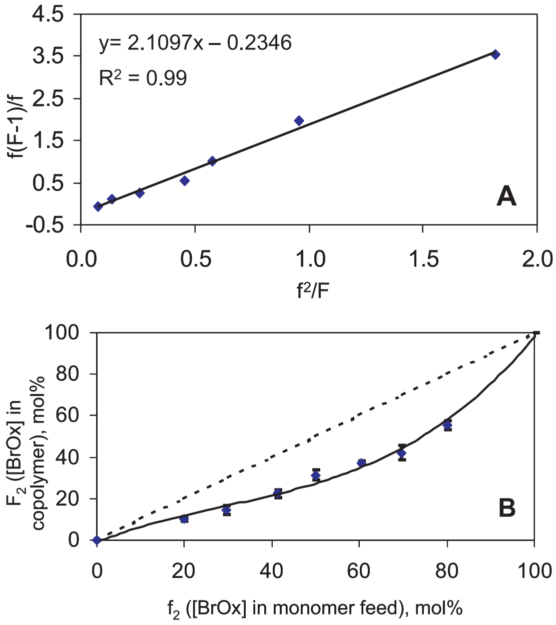


Fig. 2. F–R plot (A), and composition diagram (B) for 3FOx/BrOx copolymerization in CH_2Cl_2.

4.1.4. Molecular weight

Table 1 lists telechelic molecular weights determined by end group analysis. The number average molecular weights (M_n) were obtained by integrating the high field methylene peaks next to the trifluoroacetyl group at 4.2–4.3 ppm and CH_3, P(FOx), 0.92 ppm, and CH_3, P(BrOx), 1.05 ppm [16]. For those telechelics having a refractive index different from THF, molecular weights were determined by GPC using universal (PS) calibration. The observed values for M_w and M_n (footnote to Table 1) give the following polydispersities: 1.58 for P(BrOx), 2.04 for P(3FOx:BrOx-1:2), and 1.35 for P(5FOx:BrOx-1:2). These values are similar to those previously reported for P(3FOx) and P(5FOx) polyoxetane telechelics polymerized using BF_3-THF/neopentyl glycol catalyst/co-catalyst system [34].

4.1.5. FT-IR

Strong C–F bands between 1190 cm^{-1} and 1300 cm^{-1} are observed for P(3FOx) and P(5FOx) homo-telechelics. P(3FOx) has a strong band at 1280 cm^{-1} due to CF_3 asymmetric stretch. P(5FOx) has two absorbances due to CF_3 asymmetric and symmetric stretches at 1197 cm^{-1} and 728 cm^{-1}, respectively. In addition, P(5FOx) has a CF_2 absorbance at 1212 cm^{-1} that is absent in P(3FOx). The band due to CH_2–Br (CH_2 wagging) is found at 1278 cm^{-1}, that is, in the same region as the CF_3 asymmetric stretch in P(3FOx). Other absorption bands were asymmetric C–O–C stretching at 1160 cm^{-1}, OH at 3530–3450 cm^{-1}, and C–H stretching at 2980–2860 cm^{-1}. As noted above, a strong carbonyl absorbance at 1716 cm^{-1} was observed for some co-telechelics. The origin is unknown, but running the polymerization reaction at −20 to −25 °C with slow addition of co-monomers eliminated the carbonyl peak.

4.1.6. Thermal analysis

Standard and temperature modulated DSC (MDSC) were used to measure the telechelic T_gs (Table 2). MDSC experiments were performed at a heating rate of 3 °C/min with a modulation temperature and period of ±0.5 °C/min and 60 s, respectively, in a manner similar to that previously employed [28]. MDSC measurements resolve the normal heat flow into reversing and non-reversing components [42]. T_g is reported using the reversing heat flow curves. This is a more accurate measure compared to values measured from the total heat flow curves since complications due to enthalpic relaxation are not present [43]. The reversing heat flows for the telechelics are shown in Figs. 3 and 4. P(BrOx) has the highest (−24 °C) and P(3FOx) has the lowest (−51 °C) T_g. As the amount of P(BrOx) increases the telechelic T_g shifts to higher temperatures. T_gs were calculated using the Fox equation, $T_{g(cal)}^{-1} = w_1 T_{g1}^{-1} + w_2 T_{g2}^{-1}$, where w_1 and w_2 are the weight fractions of each component (Table 2). The calculated T_gs are close to those observed. Two distinct T_gs were observed for the physical mixture of P(BrOx) and P(FOx) telechelics. These T_gs were within 2–3° of the pure telechelics indicating these materials are essentially immiscible.

Table 2
Measured and calculated glass transition temperatures of homo and co-telechelics

Homo- or Co-telechelic poly(oxetane)	T_g (°C) (DSC)	T_g (°C) (Calculated[a])
P(BrOx)	−24	–
P(3FOx)	−51	–
P(5FOx)	−48	–
P(3FOx:BrOx-1:2)	−33	−32
P(3FOx:BrOx-1:1)	−37	−36
P(3FOx:BrOx-2:1)	−38	−39
P(5FOx:BrOx-1:2)	−34	−33
P(5FOx:BrOx-1:1)	−36	−36
P(5FOx:BrOx-2:1)	−39	−39

[a] From the Fox equation.

4.2. Polyurethanes

4.2.1. Synthesis

In designating compositions, such as IPDI-BD(40)/P(3FOx:BrOx-1:1)(4700), the hard block composition is followed with hard block wt% in parentheses. The soft block segments are next, followed by their mole ratio and M_n in parenthesis. The segmented PUs were synthesized by the two-step procedure shown in Scheme 2. First, an excess of IPDI was added to telechelic. When all the alcohol groups were consumed, BD chain extender was added until no isocyanate absorption was detectible by FT-IR. As the viscosity increased, DMF or THF/DMF was added so that the solution contained about 30–40% solids at the end of the reaction.

Polyurethanes having different concentrations of soft block were obtained by changing the ratio of telechelic to chain extender (1,4-butanediol) ratio. The optimum hard segment concentration was 40–45 wt%. Polyurethanes having lower hard block content (25–35%) are mechanically weak while those with higher hard block content (45–60%) are rigid. Table 3 provides compositions, molecular

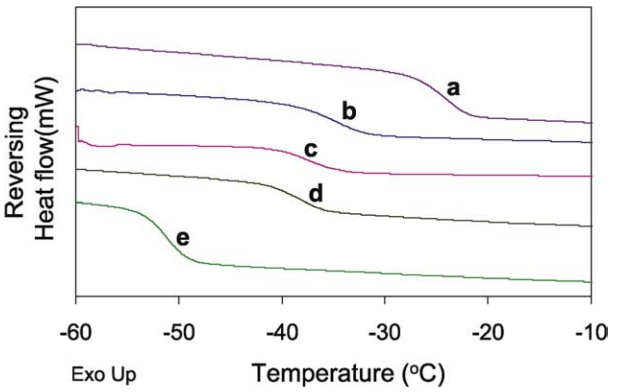


Fig. 3. Modulated DSC curves for P(3FOx:BrOx) co-telechelics. (a) P(BrOx), (b) P(3FOx:BrOx-1:2), (c) P(3FOx:BrOx-1:1), (d) P(3FOx:BrOx-2:1), (e) P(3FOx).

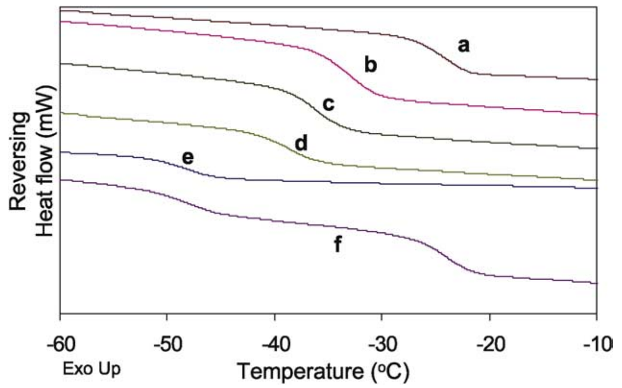


Fig. 4. Modulated DSC curves for P(5FOx:BrOx) co-telechelics. (a) P(BrOx), (b) P(5FOx:BrOx-1:2), (c) P(5FOx:BrOx-1:1), (d) P(5FOx:BrOx-2:1), (e) P(5FOx), (f) Physical mixture of P(5FOx) and P(BrOx).

weights, and DSC information. We were not able to synthesize P(5FOx) homo-telechelic polyurethane. The reaction mixture phase separated during the chain extension apparently due to the different solubility parameters of P(5FOx) soft and polyurethane hard blocks.

4.2.2. Molecular weights

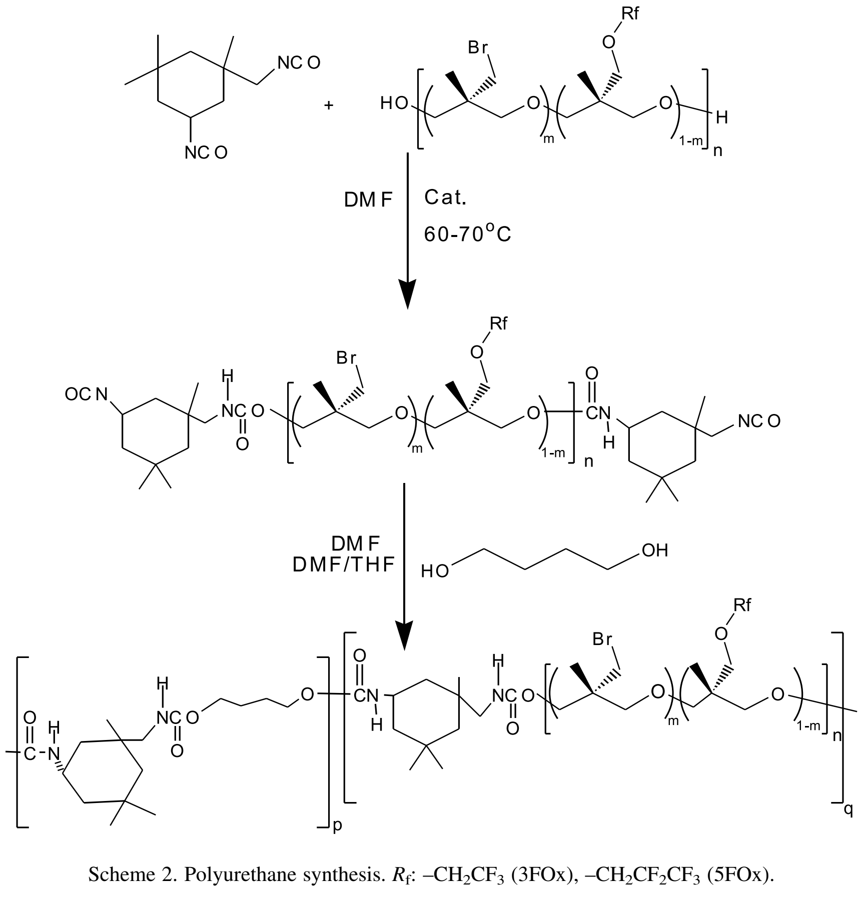
Compositional designations, molecular weights, and polydispersities of the new polyurethanes are shown in Table 3. GPC analyses gave M_ws in the range of 30–60,000. With one exception, M_w for P(FOx:BrOx) polyurethanes are lower than the conventional PTMO analog. While molecular weights are modest, all the polyurethanes formed smooth, optically transparent coatings and freestanding films.

4.2.3. Differential scanning calorimetry

Polyurethanes may have a lower soft block T_g and a higher hard block T_g [44–47]. To gain information on phase separation, thermal analysis was performed with temperature modulated DSC (MDSC) as well as conventional DSC. A hard block T_g was not detected by standard DSC, but T_gs for hard and soft segments were detected by MDSC.

As a point of reference, the MDSC for IPDI-BD(50)/PTMO(2000) was evaluated. Consistent with previous work on IPDI-BD(50)/PTMO PUs [48], a melting endotherm was not detected by MDSC scans to 250 °C. A soft block T_g (−46 °C) and hard block T_g (38 °C) were observed.

Values for pure PTMO T_g are reported from −60 to −86 °C [49–51]. We observed a −78 °C T_g for PTMO by MDSC. 17.2 K IPDI-BD was synthesized and found to have a T_g of 85 °C. Considering the pure soft block T_g (−78 °C) and hard block T_g (85 °C), it is evident that considerable phase mixing occurs in the IPDI-BD(50)/PTMO(2000) PU. We use 85 °C for the IPDI–BD hard block T_g but the



Scheme 2. Polyurethane synthesis. R_f: $-CH_2CF_3$ (3FOx), $-CH_2CF_2CF_3$ (5FOx).

Table 3
Molecular weights, and glass transitions temperatures of polyurethanes

Designation		M_n ($\times 10^{-3}$)	M_w ($\times 10^{-3}$)	PD	T_g[a] (ss)	T_g[b] (hs)	Phase sep[c]
IPDI-BD(50)/PTMO(2000)	Base PU	23.3	52.5	2.26	−46	38	0.62
IPDI-BD(40)/P(BrOx)(2800)	PU-1	19.4	42.9	2.21	−10	56	0.81
IPDI-BD(40)/P(3FOx)(3400)	PU-2	17.5	37.4	2.14	−37	46	0.84
IPDI-BD(40)/P(3FOx:BrOx-2:1)(4700)	PU-3	18.9	46.0	2.43	−29	73	0.89
IPDI-BD(40)/P(3FOx:BrOx-1:1)(4700)	PU-4	17.9	36.8	2.05	−29	62	0.90
IPDI-BD(40)/P(3FOx:BrOx-1:2)(3400)	PU-5	16.5	33.9	2.06	−24	56	0.89
IPDI-BD(40)/P(5FOx:BrOx-2:1)(2500)	PU-6	18.9	40.1	2.12	−27	57	0.88
IPDI-BD(40)/P(5FOx:BrOx-1:1)(4100)	PU-7	29.6	61.2	2.07	−25	64	0.89
IPDI-BD(40)/P(5FOx:BrOx-1:2)(3400)	PU-8	16.6	33.8	2.04	−29	64	0.89
IPDI-BD	Hard block	17.2	31.8	1.85	NA	85	na[d]

[a] Soft segment (ss) glass transition temperature.

[b] Hard segment (hs) glass transition temperature.

[c] The maximum error for T_g measurement is ±2.7°, which leads to an estimated deviation of ±0.03 in estimating pure soft phase content using the Fox equation.

[d] Not applicable.

molecular weight of hard segments in the polyurethanes must be considerably lower. If the T_g is lower than 85 °C due to lower molecular weight of the IPDI-BD hard block segments, the estimated percent pure soft block in the soft block domain represent lower limits. The weight fraction of the soft block in the soft-segment phase calculated by using the Fox equation is 62%. For comparison, Cooper reported the soft segment weight fraction in the soft segment phase for IPDI-BD/PTMO as 0.99 for PTMO-1250 and 0.38 for PTMO-3000 using the Couchman equation [48].

Fig. 5 shows the MDSC reversing heat flows for representative P(3FOx:BrOx) PUs. The soft block T_gs are shifted to higher temperatures (5–14°) compared to the telechelics. For example, the T_g for P(3FOx:BrOx-1:1) is −37 °C while the corresponding value for PU-3 is −29 °C. The hard segment T_gs are lower (12 to 37 degrees) than the T_g of pure hard block (IPDI-BD). For example, the hard block T_g for IPDI-BD(40)/P(3FOx:BrOx-1:1)(4700) is 62 °C while the corresponding value for the pure hard block (IPDI-BD) is 85 °C. These changes are attributed to phase mixing of the urethane soft and hard segments [47, 52]. Knowing the T_gs of pure hard and soft segments and their respective T_gs and weight fractions, phase mixing was estimated by applying the Fox equation [48,53]. The calculated values are shown in Table 3 expressed as weight fraction of soft block in the soft-segment phase. The 'pure' soft block phase accounts for about 90% of the soft segment for all co-telechelic PUs. According to this analysis, the co-telechelic PUs are more phase separated than the P(BrOx) homo-telechelic PU and marginally better phase separated than the P(3FOx) homo-telechelic PU.

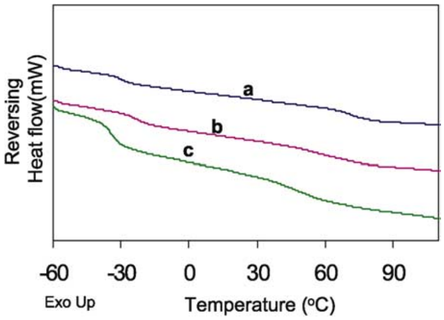


Fig. 5. Modulated DSC curves for P(3FOx:BrOx) co-telechelic polyurethanes. (a) PU-3, (b) PU-4, (c) PU-5.

5. Conclusions

Novel polyoxetane (2,2-substituted-1,3-propylene oxide) telechelics and co-telechelics with semifluorinated and functional (C–Br) side chains were synthesized. The P(FOx–BrOx) co-telechelics were characterized by ^{1}H-NMR spectroscopy to verify composition, microstructure, and to estimate M_n by end group analysis. Analysis of relative reactivity ratios for a 1:1 3FOx to BrOx feed indicates that the final telechelic dyad composition at complete reaction is not very different from a statistical copolymer. Modulated DSC (MDSC) analysis showed telechelic and co-telechelic T_gs ranged from P−51 °C (P(3FOx)) to −24 °C (P(BrOx)). Telechelic molecular weights were convenient for use as soft segments in polyurethanes.

Polyurethanes (PUs) having these polyoxetane telechelics as soft blocks (and a PTMO(2000) PU for comparison) were prepared by employing isophorone diisocyanate (IPDI) with 1,4-butanediol (BD) as the hard block. Thermal characterization by MDSC showed two T_gs due to PU soft and hard segments, respectively. Phase separation of soft and hard segments was modeled using the Fox equation. The order of phase separation is IPDI-BD(50)/PTMO(2000) ≪ PU-1, PU-2 < PU-co-telechelics. Perhaps intra-soft block H-bonding may play a role in minimizing phase mixing for PU co-telechelics.

Studies currently focus on the surface properties of the new P(FOx:BrOx) polyurethanes and replacing -Br by functional groups. Separately, we report an unprecedented copolymer effect on surface wetting behavior for IPDI-BD(40)/P(FOx:BrOx) polyurethanes [54]. A 'reaction on polymer' approach to substitute -Br has been successful in introducing effective biocidal moieties [55].

Acknowledgements

The authors are grateful to the National Science Foundation for support (DMR-0207560). The authors thank Dr Steven Aubuchon, TA Instruments for thermal analysis technical advice and equipment.

References

[1] Ward RS, White KA, Hu CB. In: Planck H, Egbers G, Syre I, editors. Biomedical engineering. Amsterdam: Elsevier Science; 1984.

[2] Hillborg H, Sandelin M, Gedde UW. Polymer 2001;42:7349–62.

[3] Bryjak M, Gancarz I, Pozniak G. Langmuir 1999;15:6400–4.

[4] Poncin-Epaillard F, Legeay G. Ann Chim-Sci Mat 2003;28:55–66.

[5] Grace JM, Gerenser LJ. J Dispersion Sci Technol 2003;24:305–41.

[6] Olander B, Wirsen A, Albertsson AC. Biomacromolecules 2002;3:505–10.

[7] Holmes-Farley SR, Reamey RH, McCarthy TJ, Deutch TJ, Whitesides GH. Langmuir 1985;1:724–40.

[8] Carey DH, Grunzinger SJ, Ferguson GS. Macromolecules 2000;33:8802–12.

[9] Chanunpanich N, Ulman A, Malagon A, Strzhemechny YM, Schwarz SA, Janke A, et al. Langmuir 2000;16:3557–60.

[10] Ratner BD, Yoon SC, Kaul A, Rahman R. In: Planck H, Syre I, Dauner M, Egbers G, editors. Polyurethanes in biomedical engineering II, vol. 3. New York: Elsevier; 1986. p. 213–29.

[11] Tezuka Y, Fukushima A, Matsui S, Imai K. J Colloid Interface Sci 1986;114:16–25.

[12] Smith SD, DeSimone JM, Huang HY, York GA, Dwight DW, Wilkes GL, McGrath JE, et al. 1992;25:2575–81.

[13] Chen X, Lee HF, Gardella JA. Macromolecules 1993;26:4601–5.

[14] Chen X, Gardella JA, Kumler PL. Macromolecules 1992;25:6631.

[15] Ho T, Wynne K. J Polym Adv Technol 1995;6:25–31.

[16] Malik AA, Carlson RP. US Patent 5,637,772, issued to Aerojet General Corporation.

[17] Malik AA, Archibald TG. US Patent 6,037,483, issued to GenCorp.

[18] Ho T, Wynne KJ, Malik AA. Abstr Pap Am Chem Soc 1995;209:319. POLY.

[19] Ho T, Malik AA, Wynne KJ, McCarthy TJ, Zhuang KHZ, Baum K, et al. Acs Symp Ser 1996;624:362–76.

[20] Kim YS, Lee JS, Ji Q, McGrath JE. Polymer 2002;43:7161–70.

[21] Thomas RR, Glaspey DF, DuBois DC, Kirchner JR, Anton DR, Lloyd KG, et al. Langmuir 2000;16:6898–905.

[22] Anton D. Adv Mater 1998;10:1197–205.

[23] Garrett JT, Siedlecki CA, Runt J. Macromolecules 2001;34:7066–70.

[24] Grasel TG, Cooper SL. Biomaterials 1986;7:315–28.

[25] Tingey KG, Andrade JD. Langmuir 1991;7:2471–8.

[26] Vogl O, Jaycox GD, Hatada K. J Macromol Sci Chem 1990;27:1781–854.

[27] Chen W, McCarthy TJ. Macromolecules 1999;32:2342–7.

[28] Fujiwara T, Makal U, Wynne KJ. Macromolecules 2003;36:9383–9.

[29] Dreyfuss MP, Dreyfuss P. In: Mark HF, Bikales NM, Overberger CG, Menges G, editors. Encyclopedia of polymer science and engineering, vol. 10. New York: Wiley; 1987. p. 653.

[30] Penczek S, Kubisa P. In: Allen G, editor. Comprehensive polymer science, vol. 3. Oxford: Pergamon Press; 1989. p. 751.

[31] Conjeevaram SV, Benson RS, Lyman DJ. J Polym Sci, Polym Chem 1985;23:429–44.

[32] Bednarek M, Biedron T, Kaluzynski K, Kubisa P, Pretula J, Penczek S. Macromol Symp 2000;157:1–11.

[33] Bednarek M, Kubisa P, Penczek S. Macromolecules 2001;34:5112–9.

[34] Kausch CM, Leising JE, Medsker RE, Russell VM, Thomas RR, Malik AA. Langmuir 2002;18:5933–8.

[35] Wynne KJ, Makal U, Uilk J. Abstr Pap Am Chem Soc 2002;224:433. POLY.

[36] Fineman M, Ross SD. J Polym Sci 1950;5:259.

[37] Hagiopol C. Copolymerization—towards a systematic approach (Chapter 2). New York: Kluwer-Academic/Plenum; 1999.

[38] Chanda M. Advanced polymer chemistry. New York: Marcel Dekker; 2000.

[39] Bucquoye M, Goethals EJ. Eur Polym J 1978;14:323.

[40] Garrido L, Guzmán J, Riande E, Abajo Jd. J Polym Sci, Polym Chem 1982;20:3377–85.

[41] Jutier JJ, de Gunzbourg A, Prud'homme RE. J Polym Sci, Polym Chem 1999;37:1027–39.

[42] Boller A, Okazaki I, Wunderlich B. Thermochim Acta 1996;284:1–19.

[43] Verdonck E, Schaap K, Thomas LC. Int J Pharm 1999;192:3–20.

[44] Cooper SL, Seymour RW. Macromolecules 1973;6:48.

[45] Lamba NMK, Woodhouse KA, Cooper SL, editors. Polyurethanes in biomedical applications. Boca Raton, FL: CRC Press; 1998. p. 15.

[46] Koberstein JT, Russell TP. Macromolecules 1986;19:714–20.

[47] Koberstein JT, Galambos AF. Macromolecules 1992;25:5618–24.

[48] Velankar S, Cooper SL. Macromolecules 1998;31:9181–92.

[49] Bednarek M, Kubisa P. J Polym Sci, Polym Chem 1999;37:3455–63.

[50] Niesten MCEJ, ten Brinke JW, Gaymans RJ. Polymer 2000;42:1461–9.

[51] Krijgsman J, Husken D, Gaymans RJ. Polymer 2003;44:7573–88.

[52] Li YJ, Gao T, Liu J, Linliu K, Desper CR, Chu B. Macromolecules 1992;25:7365–72.

[53] Koberstein JT, Galambos AF, Leung LM. Macromolecules 1992;25:6195–204.

[54] Makal U, Wynne KJ. Manuscript in preparation.

[55] Wynne KJ, Makal U, Ohman D, Wood L. Manuscript in preparation.