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Polyurethanes from novel 1,3-propyleneoxide co-telechelics having pendant hydantoin and methoxymethyl groups

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Abstract

We report the synthesis of a new oxetane monomer 5,5-dimethyl-3-(2-((3-methyloxetan-3-yl)methoxy)ethyl)-imidazolidine-2,4-dione (Hy4Ox, **1**), an oxetane with a hydantoin-containing moiety in the 3-position. This hydantoin–oxetane monomer is stable to cationic ring-opening polymerization. Copolymerization of Hy4Ox with another new monomer, 3-methyl-3-methoxymethyloxetane (MOx, **2**) provided a series of hydroxy terminated poly(2,2-substituted-1,3-propanediol) co-telechelics (P(Hy4Ox:MOx)) with low T_gs for polyurethane synthesis. ^{1}H NMR spectroscopy was used for establishing stoichiometry and M_n by end group analysis. DSC for P(Hy4Ox:MOx) telechelics shows a single T_g that increases in breadth as the fraction of hydantoin increases suggesting inter- or intrachain hydrogen bonding. The telechelics were incorporated into polyurethanes with HMDI and 1,4-butanediol as the hard block. Characterization of polyurethane composition and bulk properties by ^{1}H NMR, MDSC, and GPC is described. The new monomers and telechelics have promise in optimizing effectiveness of biocidal polyurethane polymeric surface modifiers.

Keywords: Polymeric surface modifier; Telechelics; Contact biocidal polymers

1. Introduction

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

Polymeric surface modifiers are often employed to change wetting characteristics. Surfaces are made hydrophobic with poly(dimethylsiloxane) PSMs [10–15] or both hydrophobic and oleophobic with fluorinated PSMs [16–22]. Polymeric surface modifiers have value in enhancing surface properties such as biocompatibility [1], and biodurability [23], and controlling biofouling [24], and adhesion [25].

Our objective is to provide a broader palette of polymeric surface modifiers. In working toward this goal, we have incorporated functional groups into 2,2-substituted-1,3-propylene oxide telechelics derived from oxetane polymerization. Such functional telechelics are then precursors to polyurethane surface modifiers. This approach leverages the tendency of soft blocks to concentrate at the air–polymer interface [26–28]. We are focusing on examining soft block surface phase separation [29], novel soft block compositional effects on wetting behavior [30], and the incorporation of specific soft block functionality. Of particular interest is high fidelity expression of pure PSM surface characteristics at the surface of modified conventional polymers. Ideally, coatings with 1% or less PSM may be considered nanosystems where the PSM occupies a phase separated surface nanodomain more or less ‘on top’ of the conventional polymer. The compositional and processing variations that give control of the desired high fidelity PSM surface properties in at 1 wt% or less are of key interest.

One desirable PSM surface property is contact biocidal activity [31–35]. Biocidal surfaces have drawn attention for a wide range of applications in health care [36–38] for helping protect against adventitious exposure to pathogens. Surface modification with hydantoin effects contact biocidal activity after activation with hypochlorite [39–41]. Covalent attachment of alkylammonium functionality to surfaces has been shown to provide effective contact biocidal action [42–45]. Previously, we reported the first polymeric surface modifier that introduces contact biocidal activity into coatings [46]. With PSM concentrations as low as 1.6 wt% the biocidal activity of the hypochlorite activated surfaces was highly

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effective for inactivating *Staphylococcus aureous*, *Escherichia coli*, and *Pseudomonus aeruginosa* in 15–30 min contact. Furthermore, the novel soft block generated by reaction-on-polymer conferred unprecedented contraphilic wetting behavior, whereby the dry surface was hydrophilic but the wet surface hydrophobic [30]. However, the overall PSM synthesis was lengthy and the hydantoin substitution reaction was slow and incomplete. We, therefore, sought a hydantoin monomer that would survive cationic ring-opening conditions so that soft block composition could be better controlled.

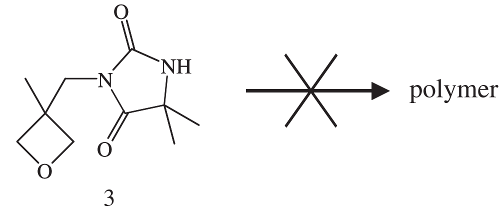
Ring-opening polymerization of oxetanes is well known [47,48]. Poly(2,2-substituted-1,3-propylene oxide)s are usually prepared using BF_3–etherate and 1,4-butanediol as a co-catalyst [49]. Molecular weights were controlled (780–2500 g/mol) varying the monomer to butanediol ratio. Ring-opening of 2-hydroxymethyloxetanes catalyzed using BF_3 complexes has been studied by Bednarek [50,51]. Oxetane telechelics with semifluorinated side chains were synthesized using cationic ring-opening polymerization in several ways [16,17,52]. In the reported examples, M_n (2500–9000 g/mol) was controlled by varying the monomer/catalyst ratio and maintaining a low reaction temperature (5 °C or less).

The present paper describes the homo- and co-polymerization of 3-methoxymethyl-3-methyloxetane (MOx, **2**) and 5,5-dimethyl-3-(2-((3-methyloxetan-3-yl)methoxy)ethyl)-imidazolidine-2,4-dione (Hy4Ox, **1**). 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]. 5,5-Dimethyl-3-((3-methyloxetan-3-yl)methyl)imidazolidine-2,4-dione (**3**) does not polymerize (Scheme 1). However, lengthening the spacer unit between hydantoin and oxetane ring from 1 to 4 units led to the successful synthesis of telechelics with low T_gs. Using the new P(Hy4Ox:MOx) telechelics, where 'P' designates telechelics derived from the respective oxetanes, polyurethanes were prepared employing 4,4′-methylenebis(cyclohexylisocyanate) (HMDI)–1,4-butanediol (BD) hard blocks.

2. Experimental

2.1. Materials

3-Bromomethyl-3-methyloxetane was generously provided by Gencorp Aerojet. Ethylene glycol (99%), chloroform, *p*-toluenesulfonyl chloride (96%) (TsCl), 5,5-dimethylhydantoin, pyridine, ethanol (denatured), tetrahydrofuran (HPLC grade) (THF), boron trifluoride etherate (48% BF_3), 4,4′-methylenebis(cyclohexyl isocyanate) (HMDI), trifluoroacetic anhydride (TFA), and dibutyltin dilaurate were purchased from Aldrich. Potassium hydroxide and 1,4-butanediol (BD) were purchased from Acros Chemicals. All materials were used as received.



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Scheme 1.

2.2. Monomer syntheses

2.2.1. Preparation of 2-((3-methyloxetan-3-yl)methoxy)ethanol (HE1Ox, 5)

Ethylene glycol (26.25 g, 0.42 mol) and KOH (19.45 g, 0.35 mol) were added to a round-bottom flask equipped with a magnetic stirrer and a reflux condenser. When all KOH had dissolved the 3-bromomethyl-3-methyloxetane (**4**) (46.30 g, 0.28 mol) was added. The system was heated to 70 °C for 3 h. The reaction material was then distilled under vacuum (10 Torr) and collected as a single fraction. The distilled material was then extracted with diethyl ether and water. The water fraction was then extracted with $CHCl_3$ multiple times to obtain 11.98 g (29.2% yield) of the final product, though analysis of the water phase indicated a significant amount of HE1Ox was unextracted. ^1H NMR ($CDCl_3$): δ 1.31 ppm (–CH_3, 3H, s), δ 2.63 ppm (–OH, 1H, t), δ 3.54 ppm (–CH_2–, 2H, s), δ 3.60 ppm (–OCH_2–, 2H, t), δ 3.76 ppm ($HOCH_2$–, 2H, q), δ 4.38 ppm (oxetane CH_2, 2H, d), δ 4.55 ppm (oxetane CH_2, 2H, d).

2.2.2. Preparation of 2-((3-methyloxetan-3-yl)methoxy)ethyl 4-methylbenzenesulfonate (TE1Ox, 6)

HE1Ox (15.20 g, 0.10 mol) and pyridine (17.93 g, 0.23 mol) were added to a round-bottom flask equipped with a magnetic stirred and a drying tube and placed in an ice bath. Once chilled, *p*-toluenesulfonyl chloride (23.53 g, 0.12 mol) was added to the flask and the ice bath was maintained for 30 min. The ice bath was then removed and the system was vigorously mixed for another 3.5 h. The flask was then returned to the ice bath and 1.0 M HCl (35 mL) was added to the flask. The product was then extracted with $CHCl_3$ and vacuum dried. A colorless liquid (26.44 g, 84.6% yield) was obtained. ^1H NMR ($CDCl_3$): δ 1.24 ppm (–CH_3, 3H, s), δ 2.45 ppm (–CH_3, 3H, s), δ 3.46 ppm (–CH_2–, 2H, s), δ 3.68 ppm (–OCH_2–, 2H, t), δ 4.18 ppm (–CH_2OTs, 2H, t), δ 4.30 ppm (oxetane CH_2, 2H, d), δ 4.42 ppm (oxetane CH_2, 2H, d), δ 7.35 ppm (aromatic CH, 2H, d), δ 7.80 ppm (aromatic CH, 2H, d).

2.2.3. Preparation of 5,5-dimethyl-3-(2-((3-methyloxetan-3-yl)-methoxy)ethyl)-imidazolidine-2,4-dione (Hy4Ox, 1).

Ethanol (7.9 mL), KOH (2.27 g, 0.040 mol), and 5,5-dimethylhydantoin (5.60 g, 0.044 mol) were added to a flask equipped with a magnetic stir bar and reflux condenser. When dissolved, TE1Ox (9.99 g, 0.033 mol) in ethanol (8.8 mL) was added and the mixture was heated to reflux with a heating mantle. After heating overnight (~15 h), the reaction mixture was allowed to cool to room temperature. The ethanol was mostly removed by rotary evaporation and then extracted with $CHCl_3$. Vacuum drying yielded 8.52 g (100% yield) of a pale yellow, viscous oil. ^1H NMR ($CDCl_3$): δ 1.28 ppm (–CH_3, 3H, s), δ 1.41 ppm (–CH_3, 6H, s), δ 3.50 ppm (–OCH_2–, 2H, s), δ 3.70 ppm (–NCH_2CH_2O–, 4H, m), δ 4.30 ppm (oxetane CH_2, 2H, d), δ 4.48 ppm (oxetane CH_2, 2H, d), δ 6.71 ppm (amide NH, 1H, s).

2.2.4. Preparation of 3-methoxymethyl-3-methyloxetane (MOx, **2**).

KOH (52.30 g, 0.93 mol) was added to methanol (113 mL) in a 250 mL flask. When the KOH had dissolved, the flask was placed in an ice bath and 3-bromomethyl-3-methyloxetane (118.51 g, 0.72 mol) was slowly added dropwise. When the addition was complete, the ice bath was maintained until the exotherm subsided. Then the ice bath was replaced with a heating mantle and the mixture was heated to reflux (65 °C) for 30 min. The KBr precipitate was filtered, methanol was removed under vacuum, and the product was distilled at 37 °C and 10 Torr. A colorless liquid (65.08 g, 78.1% yield) was obtained. ^{1}H NMR ($CDCl_3$): δ 1.29 ppm (–CH_3, 3H, s), δ 3.38 ppm (–OCH_3, 3H, s), δ 3.42 ppm (–CH_2O–, 2H, s), δ 4.33 ppm (oxetane CH_2, 2H, d), δ 4.48 ppm (oxetane CH_2, 2H, d).

2.3. Ring-opening polymerization.

A solution of Hy4Ox (2.73 g, 10.7 mmol) and MOx (4.32 g, 37.2 mmol) was prepared in methylene chloride (9.41 g) and dried over 4 Å molecular sieves. A 100 mL three-necked, round-bottom flask equipped with a 50 mL addition funnel and sealed with rubber septa was charged with BD (0.4163 g, 4.62 mmol) and methylene chloride (0.74 g). The monomer solution was transferred to the addition funnel and the system was purged with N_2 for 30 min at room temperature then placed in an ethylene glycol/water (50/50 v/v) bath at −5 °C. Once the flask was chilled, BF_3 etherate (2.07 g, 14.6 mmol, 48 wt% BF_3) was added and the system was allowed to stand for 30 min. The contents for the addition funnel were then added slowly over a period of 1 h. The bath temperature was maintained for an additional 4 h then allowed to warm to room temperature. Water (5 mL) was added to quench the reaction. The reaction mixture was extracted with water and chloroform. The solvent was removed yielding the telechelic as a viscous oil (80.2% yield). Telechelics of other Hy4Ox:MOx ratios were prepared in the same manner with similar yields.

2.4. Polyurethane synthesis

To a 100 mL round-bottom flask was added P(Hy4Ox:MOx-16:84) (0.96 g, 0.47 mmol), BD (0.14 g, 1.5 mmol), dibutyltin dilaurate (three drops, 10 wt% in THF), dimethylformamide (0.74 mL). An addition funnel was attached and HMDI (0.61 g, 2.3 mmol) and DMF (2.45 mL) were added. The system was heated to 70 °C and purged with N_2 for 20 min. The contents of the addition funnel were added rapidly. The extent of reaction was determined by removing small aliquots and observing the decrease of the 2268 cm^{-1} isocyanate peak in the FT-IR spectrum. 1,4-Butanediol in DMF was added to the reaction mixture until the isocyanate was consumed (32.8 mg, 0.36 mmol BD and 2 mL DMF). The product was precipitated in H_2O, dried, dissolved in THF, and reprecipitated in H_2O. Polyurethanes using other P(Hy4Ox:MOx) telechelics were prepared in a similar manner.

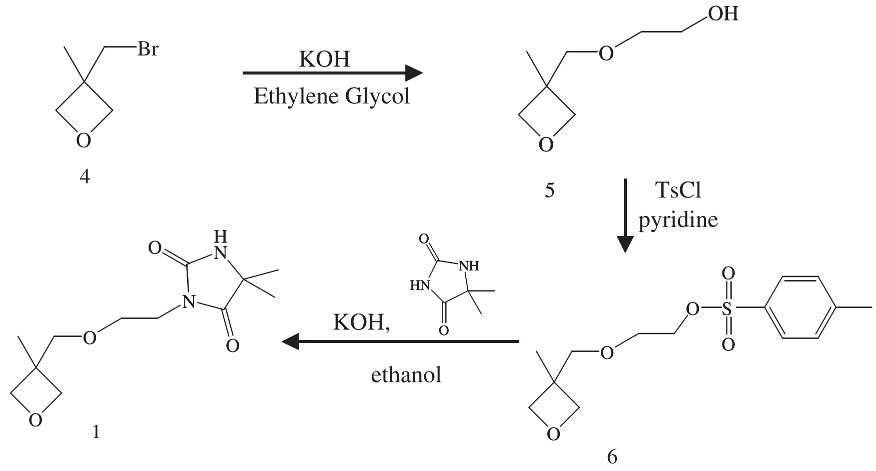
2.5. Physical property measurements

Glass transition temperatures were measured using a TA Instruments DSC Q1000 dynamic scanning calorimeter at 10 °C/min from −90 to 150 °C over two heating and cooling cycles. A small endotherm for water evolution (ca. 100 °C) was usually observed in the first cycle. Curves in figures are for second heating cycle where no endotherm for water volatilization was observed. The figure NMR spectra were obtained on a Varian Spectrometer (Inova 400 MHz). Infrared spectra were obtained on a Nicolet Magna IR 760.

3. Results and discussion

3.1. Hy4Ox synthesis

The Hy4Ox monomer was prepared according to Scheme 2 starting with 3-bromomethyl-3-methyloxetane (BrOx, **5**).



Scheme 2.

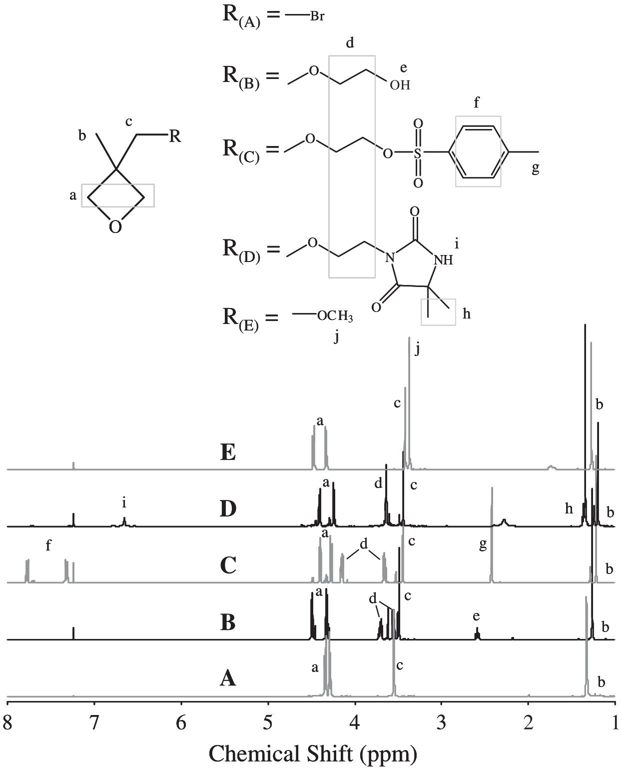
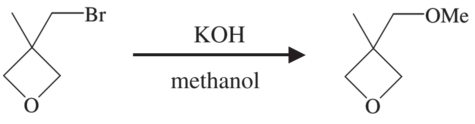


Fig. 1. ^{1}H NMR of A, BrOx, B, HE1Ox, C, TE1Ox, D, Hy4Ox, and E, MOx.

Reaction of the latter with an excess of ethylene glycol gave the mono-substituted glycol HE1Ox (**4**). Intermediate **4** was then tosylated (TE1Ox, **6**) and the tosyl group was displaced by 5,5-dimethylhydantoin to form the Hy4Ox (**1**) monomer.

Identification of intermediates and the product was accomplished with ^{1}H NMR analysis. The 3,3-substituted oxetane ring ^{1}H NMR has a characteristic doublet of doublets that provides a reference in analyzing ^{1}H NMR spectra (Fig. 1). After reaction with ethylene glycol, the oxetane peaks are still present and three new peaks are observed (Fig. 1B): a quartet (1B-d, 3.76 ppm), a triplet (1B-d, 3.60 ppm), and a triplet (1B-e, 2.63 ppm) which integrate to the expected 2:2:1 ratio for HE1Ox (**4**). The side chain protons have a 5:4 with respect to the oxetane ring peaks. The peak at 3.42 ppm due CH_2Br (1A-c) is absent and a new peak at 3.54 ppm (1B-c) that integrates as two hydrogens with respect to the oxetane ring hydrogens indicates substitution of the bromide with an ether linkage.

After reaction of **4** with *p*-toluenesulfonyl chloride the oxetane ring doublet of doublets was still present (Fig. 1C). The peak due to the alcohol is now absent and the ethylene peaks (1C-d, integrate 1:1 to oxetane ring peaks) have shifted downfield to 3.68 and 4.18 ppm due to the replacement of the alcohol proton with a strong electron-withdrawing group. A pair of doublets (1C-f, integrate 1:1 to the oxetane ring peaks) at 7.35 and 7.80 ppm and a singlet (1C-g, integrate 3:4 to the oxetane ring peaks) at 2.45 ppm is consistent with a *p*-toluene sulfonate group of the desired TE1Ox (**6**).



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Scheme 3.

After reaction under basic conditions to displace the tosyl group from **6** with a 5,5-dimethylhydantoin the oxetane ring peaks are present (Fig. 1D). The peaks due to the *p*-toluene sulfonyl ring system are absent. A new singlet at 1.41 ppm (1D-h, integrates 3:2 to oxetane ring peaks) and a singlet at 6.71 ppm (1D-i, integrates 1:4 to oxetane ring peaks) are consistent with the dimethyl and amide protons of the desired Hy4Ox (**1**). The peaks of the ethylene spacer now appear as a single unresolved multiplet (1D-d, integrate 1:1 to the oxetane ring peaks) at 3.70 ppm.

3.2. MOx synthesis

The MOx monomer (**2**) was also prepared starting with BrOx (**4**) (Scheme 3). The displacement of the bromine by methoxide was facile and exothermic. The monomer was pure enough for use in ring-opening polymerization after a single distillation.

A characteristic doublet of doublets is observed for the MOx oxetane ring methylenes (Fig. 1E, 1E-a). The singlet (1E-c, integrates 1:2 with the oxetane ring CH_2 peaks) at 3.42 ppm indicates substitution of bromide (CH_2Br) by alkoxide (CH_2OR). The singlet (1E-j, integrates 3:4 to the oxetane ring CH_2 peaks) at 3.38 ppm is consistent with formation of a methoxide (OCH_3) group.

3.3. Oxetane ring-opening polymerization

New oxetane telechelics and cotelechelics were prepared with several Hy4Ox:MOx ratios for use as polyurethane soft blocks. The oxetane polymerization required an extra equivalent of BF_3 for every Hy4Ox equivalent, as the amide

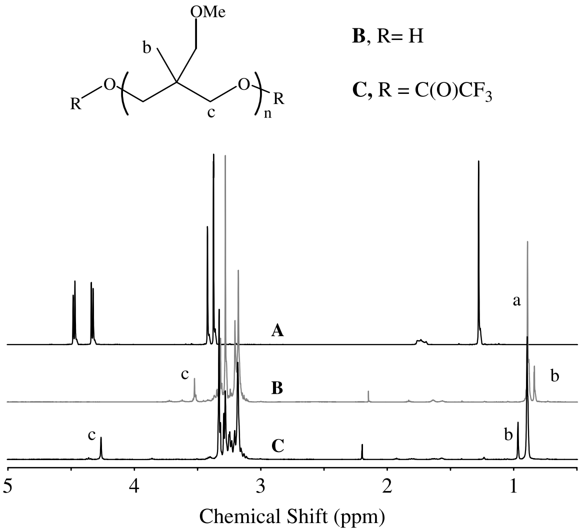

Fig. 2. ^{1}H NMR of A, MOx, B, P(MOx), and C, P(MOx) after reaction with trifluoroacetic acid.

Table 1
Calculated values for Hy4Ox incorporation in the telechelic, number-average molecular weight, and T_g of the telechelics

	Hy4Ox[a] (mol%)	M_n (g/mol)	T_g (°C)		
			Onset	Inflection	End
P(MOx)	0	1.36×10^3	−52.5	−49.8	−47.5
P(Hy4Ox:MOx-8:92)	0.083	1.95×10^3	−39.3	−35.4	−32.2
P(Hy4Ox:MOx-16:84)	0.163	2.03×10^3	−46.2	−42.2	−35.6
P(Hy4Ox:MOx-39:61)	0.386	2.68×10	−9.0	−4.5	4.7
P(Hy4Ox)	1	2.51×10^3	7.0	7.0	29.7

[a] Error for telechelic content of Hy4Ox is ±6%.

hydrogen of the hydantoin ring was acidic enough to deactivate BF_3.

Fig. 2 shows the NMR spectrum of MOx (A) and P(MOx) (B). The characteristic doublet of doublets due to the oxetane ring at 4.33 and 4.48 ppm is absent in the telechelic. The peak due to the 3-methyl group of the oxetane at 1.29 ppm shifts upfield to 0.89 ppm due to release of ring strain and a small peak at 0.84 ppm appears that is assigned to the pendant methyl group of the repeat unit on the chain end. A group of peaks from 3.1 to 3.8 ppm of the P(MOx) spectrum contains the pendant methoxymethyl and main chain methylenes. A small peak at 3.52 ppm is assigned to the methylene groups at the end of the telechelic chain. These features were observed for all telechelics.

Telechelic molecular weights were determined by NMR end-group analysis. Reaction of the hydroxy end-groups with trifluoroacetic anhydride produced up-field ^{1}H NMR shifts in both the adjacent methylene (3C-c, 3.52 ppm) and the pendant methyl group (3C-b, 0.84 ppm) on the end-repeat unit to 4.26 and 0.96 ppm, respectively. We calculated molecular weights using the integration ratios for the methyl groups as those peaks are well separated from mainchain peaks (Table 1). The ratio non-end-group methyl area to end-group methyl gives the number of interior repeat units per end-group. Since, there are two end-groups per telechelic, this ratio is doubled and added to the number of end-groups to obtain the average number of repeat units per telechelic. The molecular weight per repeat unit was averaged based on the calculated composition of the final telechelic.

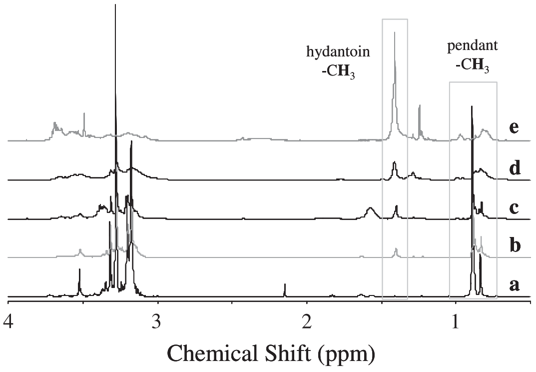

Fig. 3. ^{1}H NMR of a, P(MOx), b, P(Hy4Ox:MOx-8:92), c, P(Hy4Ox:MOx-16:84), d, P(Hy4Ox:MOx-39:61), and e, P(Hy4Ox) telechelics.

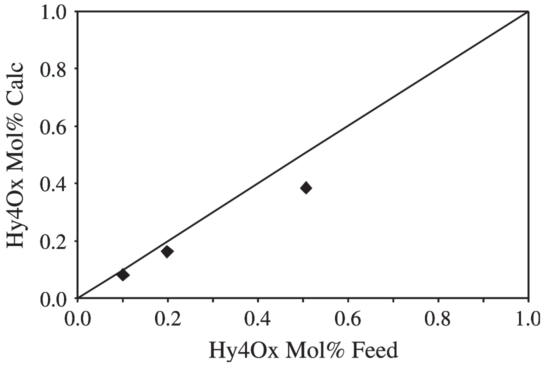

Fig. 4. Molar monomer feed percentage of Hy4Ox to MOx vs. the calculated amount of Hy4Ox incorporated into the telechelic. The straight line indicates ideality. Estimated error is less than symbol size.

The amount of Hy4Ox incorporated into the telechelic was determined from the ratio of methyl peak due to the hydantoin ring to the pendant methyl group from each repeat unit (Fig. 3). This was plotted against the feed ratio in Fig. 4. The final composition of the telechelic becomes more deficient in Hy4Ox with greater feed ratio of Hy4Ox. Presumably, this is due to the amide proton terminating the propagating chain end. The addition of an equivalent of BF_3 per hydantoin group during the ring-opening polymerization either recharges the growing chain end after termination or acts as a sacrificial amount of catalyst. Attempts to protect the amide proton for the ring-opening reaction were unsuccessful.

3.4. Telechelic thermal analysis

All telechelics exhibit a single T_g (Table 1, Fig. 5). The −49.8 °C T_g of the P(MOx) is consistent for an atactic polyether. This T_g may be compared with previously reported polyethers with sidechain oligomeric ethylene oxide or alkoxy groups that also have low T_gs. The trend T_g P(MOx), −49.8 °C > poly(3-(methoxyethoxyethoxymethyl)-3-methyloxetane) (P(ME2Ox), −67 °C) > poly(3-(methoxyethoxyethoxyethoxymethyl)-3-methyloxetane) (P(ME3Ox), −74 °C) is explicable based on the increasing number of ethylene oxide groups in the sidechain [29,53]. The higher (17.7 °C) T_g of the P(Hy4Ox) is expected

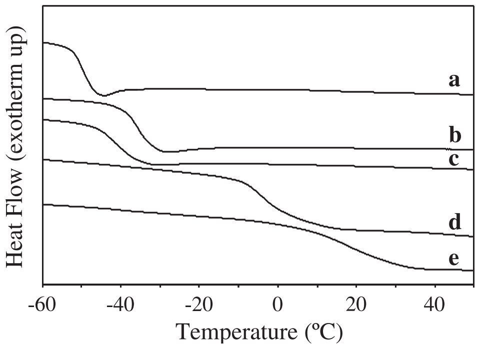

Fig. 5. DSC thermograms of Hy4Ox:MOx telechelics: a, P(MOx), b, P(Hy4Ox:MOx-8:92), c, P(Hy4Ox:MOx-16:84), d, P(Hy4Ox:MOx-39:61), and e, P(Hy4Ox). Thermograms were obtained at 10 °C/min for two cycles between −90 and 150 °C. The second cycle was used for T_g calculations.

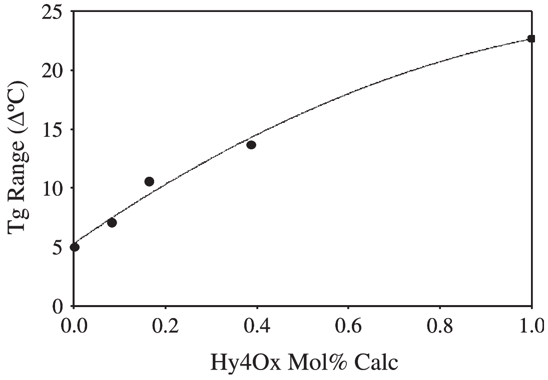

Fig. 6. Calculated difference between the onset of the T_g and the end of the T_g for P(Hy4Ox:MOx) telechelics. The dotted curve is a guide to the eye.

for a telechelic bearing a moiety with both hydrogen donor and acceptor characteristics, i.e. hydantoin. Co-telechelics have intermediate T_gs. These results provide evidence for the formation of random copolymers rather that a mixture of individual homopolymers. The onset, inflection, and end points for the telechelics are shown in Table 1. The T_g range for P(MOx) is quite narrow (5 °C). As the hydantoin content of the telechelic increases, so does the range of the T_g period up to a maximum of 23 °C for P(Hy4Ox) (Fig. 6). This behavior is consistent with an increasing fraction of hydrogen-bonding between polymer chains.

3.5. Polyurethane polymerization

The telechelics were used to synthesize polyurethanes with HMDI and BD as a chain extender (Fig. 7). A slight excess of HMDI was added to the reaction. The excess isocyante was then reacted by addition of additional BD and monitoring the disappearance of the isocyanate peak at 2268 cm^{-1}. Molecular weights were determined by GPC calibrated to polystyrene standards (Table 2). The molecular weights of the polyurethanes were average to high with broad polydispersities.

The final weight percent of the HMDI–BD hard block was determined from NMR integrations (Fig. 8) and are shown in Table 2. The region between 2.0 and 0.9 ppm is due to aliphatic HMDI, the middle methylenes of BD, and the dimethyl group of the hydantoin. The NH peak of the urethane (6.95 ppm) was used to determine the relative area due to HMDI in the hard block region. The amide peak of hydantoin (8.20 ppm) was used to determine the relative amount due to the dimethyl group in the hard block region. The remaining area was assumed to be from BD contributions. These areas were then normalized due to proton contribution (22 for HMDI, four for BD, and six for hydantoin) then multiplied by repeat unit mass to calculate the relative mass due to hard block. The relative mass of the soft block was determined from the area due to pendant methyl group of the soft block (~0.9–0.7 ppm), normalized to proton contribution (3), and multiplied by the average repeat unit mass of the soft block as determined by Hy4Ox content (Table 1).

3.6. Polyurethane thermal analysis

The soft block T_g increases with increasing hydantoin content as one would expect by increasing the quantity of polar, hydrogen bonding donors and acceptors (Fig. 9). The T_g of the pure HMDI–BD hard block is 87 °C (Fig. 9f). A Fox

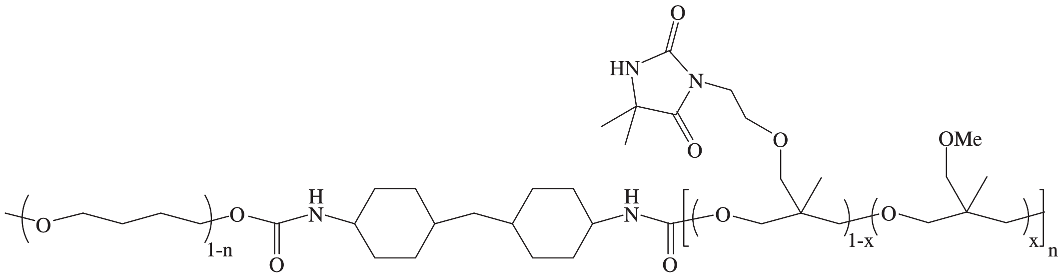

Fig. 7. HMDI–BD-P(Hy4Ox:MOx) polyurethane. The Hy4Ox:MOx ratio in the telechelic is noted with *x* and the telechelic/BD ratio is noted with *n*.

Table 2
Characterization data for HMDI–BD(wt%)/P(Hy4Ox:MOx)polyurethanes

	M_w[a] (g/mol)	M_w/M_n	Hard block[b] (wt%)	T_g (°C)[c]			Phase mixing[d] (wt%)
				Onset	Inflection	End	
HMDI–BD(52.5)/P(MOx) (PU-A)	1.1×10^5	2.1	52.5	−38.1	−33.3	−29.3	18.1
HMDI–BD(54.0)/P(Hy4Ox:MOx-8:92) (PU-B)	5.0×10^4	1.3	54.0	−9.5	24.6	51.2	59.3
HMDI–BD(56.7)/P(HY4Ox:MOx-16:84) (PU-C)	2.2×10^4	2.5	56.7	−15.3	13.0	33.8	53.8
HMDI–BD(51.1)/P(HY4Ox:MOx-39:61) (PU-D)	7.9×10^3	2.9	51.1	12.9	26.5	41.4	40.7
HMDI–BD(49.7)/P(HY4Ox) (PU-E)	6.9×10^3	2.3	49.7	64.5	72.9	78.1	82.9

[a] Molecular weight and polydispersity (GPC).
[b] Estimated error for hard block content is ±2.4 wt%.
[c] T_g (DSC).
[d] Estimated errors for phase mixing are ±5.0 (HMDI–BD(52.5)/P(MOx) and HMDI–BD(49.7)/P(Hy4Ox)) or ±20.

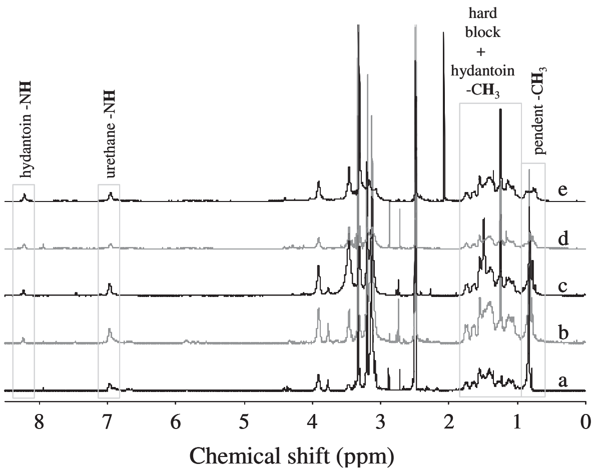

Fig. 8. ^{1}H NMR of a, PU-A, b, PU-B, c, PU-C, d, PU-D, and e, PU-E polyurethanes.

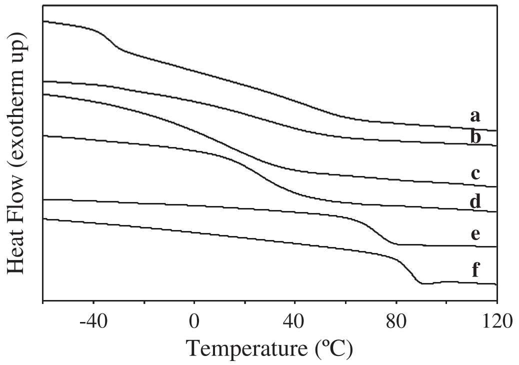

Fig. 9. DSC thermograms of HMDI–BD-P(Hy4Ox:MOx) polyurethanes: a, PU-A, b, PU-B, c, PU-C, d, PU-D, e, PU-E, and f, HMDI–BD hard block (no soft block). Thermograms were obtained at 10 °C/min for two cycles between −90 and 150 °C. The second cycle was used for T_g calculations.

analysis of the measured T_gs using the telechelic T_g as the non-phase mixed soft block indicates that between 18 and 83 wt% of the hard block is phase mixed with the soft block (Table 2). There is a noticeable increase in phase mixing when the telechelic contains Hy4Ox repeat units. Given the large range that the T_g occurs, phase mixing could be occurring in a gradient transition without sharply defined boundaries rather than distinct regions of partial mixing.

4. Conclusions

Novel hydroxy-terminated 1,3-propylene oxide co-telechelics were prepared from new 2-methyl-2-methoxymethyl and 2-methyl-2-(2-hydantyl)ethoxymethyl oxetane monomers. Monomers and telechelics were characterized by ^{1}H NMR. DSC showed that the telechelic T_gs increased with increasing hydantoin content. The new telechelics were incorporated into HMDI–BD based polyurethanes.

The synthesis of the new Hy4Ox monomer is an important step in providing a facile route to telechelics and polyurethane surface modifiers with controlled hydantoin content. We are currently investigating the phase separation and surface wetting behavior of the new polyurethanes and surface modified compositions. Other future work involving these hydantoin-containing polyurethanes is directed at their use as PSMs testing their efficacy against a variety of pathogens.

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