Synthesis and Characterization of Novel Amphiphilic Telechelic Polyoxetanes

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ABSTRACT: Alcohol-terminated telechelic polyoxetanes with semifluorinated (FOx) and alkyl ether pendant groups (ME2Ox) were synthesized and characterized. These are amphiphilic telechelics by virtue of incorporation of both hydrophilic and hydrophobic repeat units. The ME2Ox/FOx telechelic copolymers were characterized by NMR spectroscopy for composition and molecular weight through end-group analysis. Differential scanning calorimetry revealed decreasing T_g with increasing incorporation of ME2Ox and provided evidence for copolymer structure. Monomer reactivity ratios were determined in two solvents with different polarity. In methylene chloride, an active end derived from 5FOx monomer reacts preferentially with ME2Ox whereas the ME2Ox-derived end shows no selectively. The reactivity ratios are 0.97 for ME2Ox and 0.12 for 5FOx. In methylcyclohexane, the monomer reactivity ratios are more characteristic of ideal copolymerization. The parameters are 1.65 for ME2Ox and 0.49 for 5FOx.

Introduction

Polyurethanes (PUs) constitute an important class of polymers for materials and biomaterials applications.[1] The solid-state structure is comprised of a hard or reinforcing phase through hydrogen bonding and a soft or low-T_g domain. The degree of phase mixing is wide-ranging depending on the nature of hard and soft blocks. Understanding the nature of the polyurethane−air interface and changes that occur during the formation of an aqueous interface is of importance for a broad range of materials and biomaterials development. Our work is aimed at new telechelic polymers that will control the nature of these interfaces.

Recent results from tapping mode atomic force microscopy (TM-AFM) on polyurethanes utilizing poly(tetramethylene oxide) (PTMO) have refocused attention on the soft block as the predominant surface domain.[2] The AFM results reinforce and add a new dimension to prior spectroscopic studies and contact angle measurements, such as the work of Andrade,[3] that emphasized the important interfacial role of the soft block. Interestingly, PTMO was the first polyether used as a low-T_g polyurethane soft block for elastomers[4] and is utilized in a variety of commercially available thermoplastics, coatings, and foams. As the work of Runt demonstrates, thermoplastics containing PTMO soft blocks continue to be actively studied as biomaterials.[1,5−7]

A number of approaches have been pursued to modify the surface properties of polyurethanes. Changing the soft block changes surface properties but creates an entirely new material so that the whole gamut of bulk properties must be evaluated. The introduction of fluorinated functionality is well-known for providing polymer surfaces that are oleophobic as well as hydrophobic.[8−11] In a series of patents, Malik et al. reported the synthesis of semifluorinated oxetanes useful as soft blocks ($T_g \sim -40$ °C) in polyurethanes.[12,13] We reported polyurethanes incorporating the poly(3-heptafluorobutoxymethyl-3-methyloxetane) as the soft block ($T_g \sim -50$ °C) with a hard block generated conventionally using benzenedimethanol (BDM)−methylene diphenyl isocyanate (MDI).[14] McGrath confirmed and extended the synthesis of polyurethanes containing semifluorinated oxetane polymers.[15]

To effect economical surface modification while retaining bulk properties, a surface-modifying additive (SMA) approach is attractive.[16,17] As the term “additive” suggests, a specialized surface-active soft block PU (usually about 1%) is coprocessed with a standard bulk polyurethane. Fluorinated polyoxetanes (FOx) have been used as SMAs in blends, resulting in fluorinated surfaces with characteristic hydrophobicity and oleophobicity. Thomas and McGrath found that only 2 wt % 3-trifluoroethoxymethyl-3-methyloxetane telechelic polymer in a conventional polyurethane composition resulted in 95% fluorinated oxetane surface composition (by ESCA at a 15° takeoff angle).[18]

Considering the important role of soft blocks in controlling surface properties, modification of soft blocks to effect surface functionalization is attractive. The surface exclusion of end groups[19,20] was coupled with surface soft block concentration to generate PU−SMA compositions that are effective against protein adsorption.[16] Functionalization of end groups has given SMAs that favor growth of endothelial cells on a commercial PTMO-based PU.[21]

The importance of the soft block in defining the nature of the PU surface has led us to explore a new architecture that may be useful in SMAs. We have focused on telechelic polyoxetanes incorporating differing functional groups pendant to the main chain. In one model, we are interested in using “air-philic” fluorinated groups to bring functional groups to the polymer surface. The resulting “dual functional telechelics” (DFTs) have side chains with contrasting driving forces at the polymer−air and polymer−water interfaces (Figure 1). Using DFT-containing polyurethanes as PU−SMAs is expected to lead to PUs with novel combinations of surface and bulk properties.

In initiating work on DFT containing polyurethanes, we have reported wetting behavior of polyurethane surfaces containing a bromomethyl-substituted polyoxetane.[22] The present report focuses on the synthesis of DFTs with hydrophobic semifluorinated and hydro-

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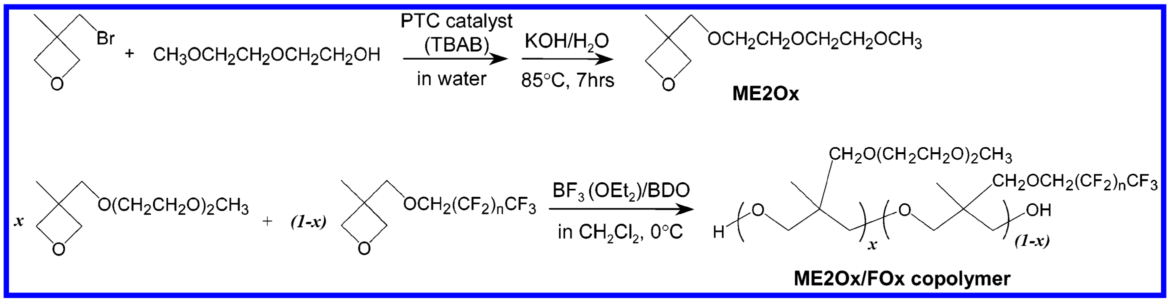
Scheme 1



philic alkyl ether (methoxyethoxyethoxy) pendant groups. Synthesis via cationic ring-opening polymerization was utilized as previously described for semifluorinated polyoxetanes by Malik.[13] Ring-opening polymerization of oxetane monomers using BF_3 catalyst is well-known. Saegusa et al. have investigated reactivities of differently substituted oxetanes in polar and nonpolar solvents.[23] Bucquoye and Goethals determined copolymerization reactivity ratios for oxetane and 3,3-dimethyloxetane and analyzed microstructure of the copolymer by triad abundances.[24] Manser and Ross have demonstrated the living-like character of oxetane oligomerization using BF_3/1,4-butanediol initiation at a molar ratio of 2/1.[25] Prud'homme et al. recently reported the copolymerization of 3,3-bis(chloromethyl)oxetane and ϵ-caprolactone and modification to poly(3,3-bis(azidomethyl)oxetane-*co*-ϵ-caprolactone).[26] Kubisa summarized the propagation mechanisms of cyclic ethers with hydroxyl groups.[27,28]

In preparing polyoxetanes with hydrophobic semifluorinated and hydrophilic alkyl ether (methoxyethoxyethoxy) pendant groups, we provide telechelic polymers that can be used to explore surface properties of polymers incorporating these DFTs. The novel DFTs described herein were characterized by NMR spectroscopy to analyze composition and molecular weight, and their thermal properties were determined by DSC analysis.

We use ME2Ox to designate the oxetane made from 2-(2-methoxyethoxy)ethanol and 3-bromomethyl-3-methyloxetane. ME2Ox is also used for the derived polymer segment. This acronym is a shortened version from that previously utilized.[29] We do so in anticipation of work with longer oligomeric side chains such as ME3Ox.

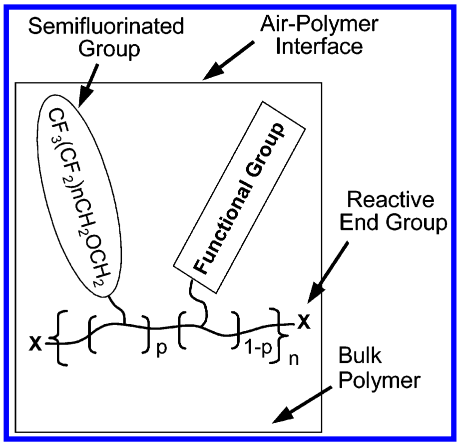


Figure 1. Depiction of synergistic dual functionality by which a fluorinated group $[CF_3(CF_2)_n]$ brings desired surface functionality to the elastomer (polyurethane) surface.

Experimental Section

Materials. 3-(2,2,3,3,3-Pentafluoropropoxymethyl)-3-methyloxetane (5FOx), 3-(2,2,3,3,4,4,4-heptafluorobutoxymethyl)-3-methyloxetane (7FOx), and 3-bromomethyl-3-methyloxetane (BrOx) were synthesized from published procedures[13] or generously provided by Gencorp Aerojet (Sacramento, CA) or Omnova Solutions (Akron OH). All monomers were distilled under vacuum before use: 5FOx and 7FOx at 100 °C/5 mmHg and BrOx at 85 °C/5 mmHg. 2-(2-Methoxyethoxy)ethanol from Aldrich and 1,4-butanediol from Acros Organics were distilled under vacuum before use. Boron trifluoride dietherate $[BF_3O(C_2H_5)_2, BF_3{-}OEt_2]$ and tetrabutylammonium bromide (TBAB) were used as received. Methylene chloride and other organic solvents were used as received or kept with molecular sieves 4A.

Monomer Synthesis. 3-(Methoxyethoxyethoxymethyl)-3-methyloxetane (ME2Ox) was synthesized using phase transfer catalysis (PTC) (Scheme 1). A mixture of 2-(2-methoxyethoxy)ethanol (60.1 g, 0.5 mol), BrOx (82.5 g, 0.5 mol), TBAB (8.0 g, 0.025 mol), and water (20 mL) was stirred and heated to 75 °C. Then, a solution of KOH (35.5 g, 87%, 0.55 mol) in water (50 mL) was added. The reaction mixture was stirred vigorously at 80−85 °C for 7 h. The mixture was cooled to room temperature, filtered, and diluted with water. The product was extracted with methylene chloride and distilled at 100 °C/8 mmHg. ME2Ox monomer. ^{1}H NMR ($CDCl_3$): δ 1.32 (−C**H**$_3$, 3H, s), δ 3.39 (−OC**H**$_3$ 3H, s), δ 3.55 (−OC**H**$_2$C**H**$_2$O−, 4H, m), δ 3.67 (−OC**H**$_2$C**H**$_2$O−, 4H, and −C**H**$_2$−, 2H, m), δ 4.35 (ring −C**H**$_2$−, 2H, d), δ 4.52 (ring C**H**$_2$, 2H, d). ^{13}C NMR ($CDCl_3$): δ 21.5 (−**C**H$_3$), δ 40.0 (−**C**−), δ 59.1 (−O**C**H$_3$), δ 70.7, 71.1, and 72.1 (−O**C**H$_2$**C**H$_2$O−), δ 76.6 (−**C**H$_2$−), δ 80.2 (ring −**C**H$_2$−).

7FOx monomer was prepared from BrOx and 2,2,3,3,4,4,4-heptafluorobutanol by the same procedure used for ME2Ox monomer. 7-FOx monomer. ^{1}H NMR ($CDCl_3$): δ 1.31 (−C**H**$_3$, 3H, s), δ 3.67 (−C**H**$_2$−, 2H, s), δ 3.99 (−C**H**$_2$CF$_2$−, 2H, t), δ 4.34 (ring −C**H**$_2$−, 2H, d), δ 4.50 (ring −C**H**$_2$−, 2H, d).

Telechelic Polyoxetane Synthesis. Homo- and copolymerization of ME2Ox and FOx monomers were carried out by a modification of a published procedure for FOx and 3-bromomethyl-3-methyloxetane.[13] Cationic ring-opening polymerization was employed using BF_3 and 1,4-butanediol as catalyst and cocatalyst, respectively. Methylene chloride (10 mL) was poured into a round-bottom flask under nitrogen. 1,4-Butanediol (165 mg, 1.84 mmol) and $BF_3{-}OEt_2$ (520 mg, 3.67 mmol) in methylene chloride (10 mL) were added and stirred at room temperature for 45 min under nitrogen. Then the solution was cooled to 0−5 °C in ice bath, and a mixture of ME2Ox and FOx monomers (e.g., total 36.7 mmol) in methylene chloride (10 mL) was added dropwise at the rate of 0.5 mL/min. The reaction was kept at 0−5 °C for 4 h with stirring. The reaction mixture was then brought to room temperature and quenched with 30 mL of water. The organic phase was separated and washed with 0.2% HCl and NaCl aqueous solution, and then solvent was evaporated. The product (a viscous, opaque liquid) was redissolved in acetone and reprecipitated in water. The resulting viscous liquid was separated and dried in a vacuum oven at 70 °C, 5 Torr overnight to give a transparent oily product with >80% yield.

ME2Ox homopolymer. ^{1}H NMR ($CDCl_3$): δ 0.91 (−C**H**$_3$, 3H, s), δ 3.19 (backbone −C**H**$_2$−, 4H, m), δ 3.30 (−C**H**$_2$−, 2H, s), δ

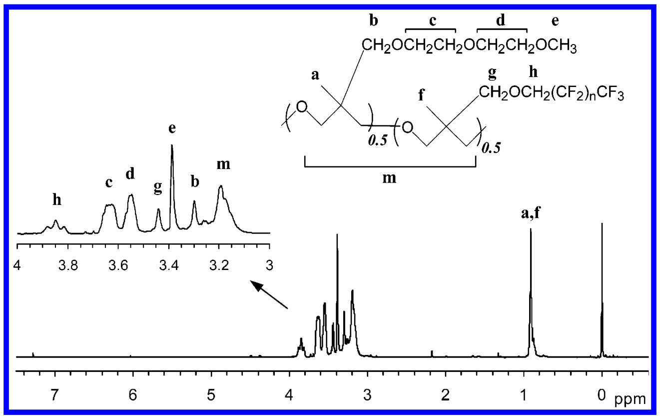


Figure 2. Typical ^{1}H NMR spectrum of ME2Ox/5FOx (1/1) copolymer.

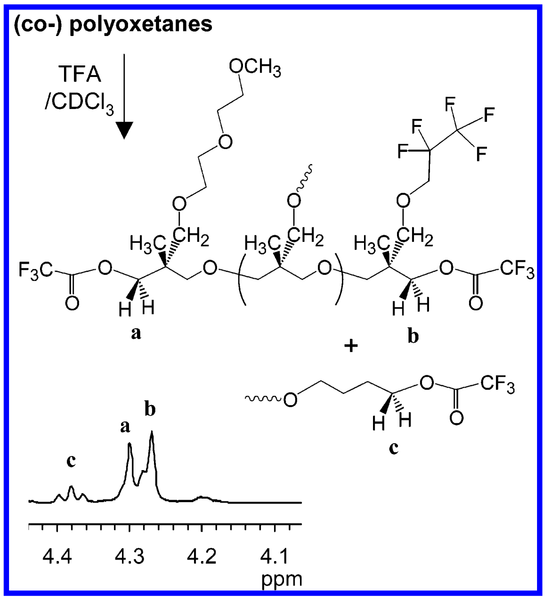


Figure 3. Structure and ^{1}H NMR spectrum of trifluoroacetyl end groups of copolymers.

3.38 (−OC**H**$_3$ 3H, s), δ 3.55 (−OC**H**$_2$C**H**$_2$O−, 4H, m), δ 3.64 (−OC**H**$_2$C**H**$_2$O−, 4H, m). ^{13}C NMR (CDCl$_3$): δ 17.3−17.9 (−**C**H$_3$), δ 40.8−41.3 (backbone −**C**−), δ 58.9 (−O**C**H$_3$), δ 70.4 and 71.9 (−O**C**H$_2$**C**H$_2$O−), δ 70.9−71.3 (−**C**H$_2$−), δ 74.0 (backbone −**C**H$_2$−).

ME2Ox/5FOx (ME2Ox/7FOx) copolymer. ^{1}H NMR (CDCl$_3$): δ 0.91 (−C**H**$_3$ for ME2Ox and FOx, 3H, s), δ 3.19 (backbone −C**H**$_2$−, 4H, m), δ 3.30 (−C**H**$_2$− for ME2Ox, 2H, s), δ 3.38 (−OC**H**$_3$ 3H, s), δ 3.44 (−C**H**$_2$− for FOx, 2H, s), δ 3.55 (−OC**H**$_2$C**H**$_2$O−, 4H, m), δ 3.64 (−OC**H**$_2$C**H**$_2$O−, 4H, m), δ 3.85 (−C**H**$_2$CF$_2$−, 2H, t). ^{13}C NMR (CDCl$_3$): δ 16.9−17.8 (−**C**H$_3$ for ME2Ox and FOx), δ 40.8−41.5 (backbone −**C**−), δ 58.6 (−O**C**H$_3$), δ 68.0 (−**C**H$_2$CF$_2$−, t), δ 70.4 and 71.9 (−O**C**H$_2$**C**H$_2$O−), δ 70.9−71.3 (−**C**H$_2$− for ME2Ox), δ 73.4 (backbone −**C**H$_2$− for FOx), δ 74.0 (backbone −**C**H$_2$− for ME2Ox), δ 75.3 (−**C**H$_2$− for FOx), δ 110.0−123.3 (−(**C**F$_2$)$_n$**C**F$_3$).

Molecular Weight Determination. The degree of polymerization (D_p) and equivalent molecular weight are determined by end-group analysis. End-group analysis was performed by the reaction of trifluoroacetic anhydride (TFA) with the hydroxyl end group of polyoxetanes. A molar excess of TFA was added to the polymer solution in CDCl$_3$. The solution was stirred at room temperature for 1 h before measuring the ^{1}H NMR spectrum. Figure 3 shows the signals of methylene protons next to the fluoroacetyl group for ME2Ox (a), FOx (b), and butanediol (c) end groups. D_p and molecular weight are calculated from the sum of those peaks against the methyl peak of all oxetane repeat units.

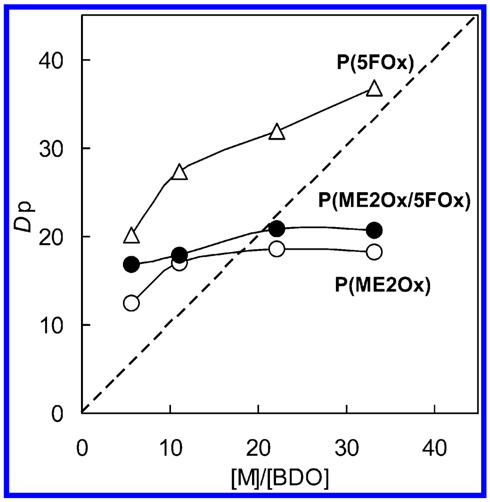


Figure 4. Plot of degree of polymerization as a function of monomer/cocatalyst ratios.

Instruments. The chemical structures of synthetic materials were established by ^{1}H and ^{13}C NMR (Varian, Inova 400 MHz) in CDCl$_3$. The molecular weight and composition were determined from the integration of specific peaks in ^{1}H NMR spectra. Gel permeation chromatography (GPC) was performed on a Viscotek TriSEC triple detector system in THF with sample concentrations of 3−6 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. A TA-Q Series (TA Instruments) differential scanning calorimeter (DSC) was used for obtaining glass transition temperatures of polyoxetanes. The measurements were made using indium for calibration at a heating rate of 20 °C/min from −80 °C.

Results and Discussion

Characterization and Molecular Weight Analysis. A new series of oxetane polymers have been prepared containing hydrophobic fluoroalkyl groups and a hydrophilic alkyl ether group (Scheme 1). A typical ^{1}H NMR spectrum for ME2Ox/5FOx (1/1) copolymer is shown in Figure 2. The composition ratios of ME2Ox and FOx monomers in copolymer were determined from integration of the ^{1}H NMR peaks for the methylene group **b** next to the alkyl ether chain (3.30 ppm) and the methylene group **g** next to the semifluoroalkyl ether chain (3.44 ppm).

Table 1 lists the molar ratios of monomer feed as well as the compositions of polymers. Monomer/1,4-butanediol ratios were varied in order to make polyoxetanes with differing molecular weights. The BF_3−OEt_2/1,4-butanediol ratio was kept constant at 2.2/1, and in all compositions in Table 1, the reactions were done under a nitrogen atmosphere with a temperature at 0−5 °C. Monomer ratios in copolymers are very close to feed ratios.

GPC results are also listed in Table 1. The number-average molecular weights (M_n) correlate well with end-group analysis results for ME2Ox homopolymers and ME2Ox/FOx copolymers but show higher values for 5FOx homopolymer. The molecular distribution has a trend that the polydispersity (M_w/M_n) decreases as monomer/cocatalyst ratio increases for all polymer series. When the monomer/cocatalyst ratio is above 22, the polydispersities are 1.9−2.2.

As shown in Table 1, the D_p of polymer is not directly related to the monomer/cocatalyst ratios. Figure 4 is a plot of D_p of polymers as a function of monomer/

Table 1. Copolymerization of ME2Ox and FOx Monomers via BF_3-OEt_2 Catalyst System at 0 °C in Methyene Chloride

	monomer feed ratio			[monomer]/	polymers				
sample	ME2Ox	5FOx	7FOx	[cocatalyst][a]	ME2Ox/FOx	D_p[b]	equiv MW[b]	M_n[c] ($/10^3$)	M_w/M_n[c]
M-1	1			5.5		12.4	2540	3.4	2.7
M-2	1			11		16.9	3450	3.6	3.2
M-3	1			22		18.6	3810	3.0	2.1
M-4	1			33		18.2	3710	3.3	2.2
M5F-1	0.5	0.5		5.5	0.53/0.47	16.8	3680	4.0	2.6
M5F-2	0.5	0.5		11	0.54/0.46	17.9	3910	4.8	2.8
M5F-3	0.5	0.5		22	0.53/0.47	20.8	4570	4.7	1.9
M5F-4	0.5	0.5		33	0.52/0.48	20.6	4520	4.8	1.9
F-1		1		5.5		20.1	4720	8.7	2.4
F-2		1		11		27.3	6390	11.6	2.1
F-3		1		22		31.9	7470	11.8	1.9
F-4		1		33		36.8	8620	12.9	2.0
M7F-1	0.5		0.5	22	0.55/0.45	18.6	4550	5.3	2.2
M7F-2	0.67		0.33	22	0.66/0.34	14.9	3440	4.5	1.9

[a] Monomer to cocatalyst (1,4-butanediol) molar ratio, $[BF_3-OEt_2]/[1,4\text{-butanediol}] = 2.2$ (constant). [b] Determined by ^1H NMR end-group analysis. [c] Determined by GPC.

cocatalyst ratio. The D_p of ME2Ox homopolymer, 5FOx homopolymer, and their copolymer are not dependent on the monomer/1,4-butanediol ratios. At low monomer/1,4-butanediol ratio, all polymers have higher molecular weight than calculated values. However, when the monomer/1,4-butanediol ratio is increased, the increase of D_p is small. The insensitivity of D_p to monomer/1,4-butanediol ratio is especially noteworthy for ME2Ox homo- and copolymers, where D_p plateaus at a monomer/cocatalyst ratio of 20/1.

From the literature, polyoxetane molecular weight is controllable in favorable cases.[26,27,30-32] It is known that ring-opening propagation of heterocyclic monomers using BF_3 catalyst proceeds via two different mechanisms.[30] The active chain-end mechanism is typical for cationic polymerizations. Alternatively, polymerization may occur by an activated monomer mechanism. That is, in the presence of alcohol or diol, monomers compete with alcohol groups, [OH], as transfer agents. Which mechanism predominates depends on the kinetics of each process. An important factor influencing the mechanism is the instantaneous [M]/[OH], which depends on the rate of monomer addition and/or temperature. Well-controlled living-like polymerization of cyclic ethers using the BF_3-OEt_2/1,4-butanediol system has been reported to occur only through the activated monomer mechanism.[26,27]

For ME2Ox and FOx polymers, ^1H NMR analysis (vide infra) indicates the polymerization proceeds via mixed mechanisms. Chain transfer or chain termination may be favored for ME2Ox monomer due to competition from oxygen in ether side groups. Whatever the cause, under the reaction conditions used, D_p reaches a maximum value for ME2Ox-containing polyoxetanes. Fortunately, the molecular weights obtained approximate those required for utilization as PU soft blocks. Changing reaction conditions, such as lowering temperature, may be necessary for gaining a stronger dependency of molecular weight on the monomer-to-catalyst ratio.

Monomer Reactivity Ratios. The majority of copolymerization studies to determine reactivity ratios involve vinyl monomers.[33] However, there are a few reports applying this classic method to the evaluation of reactivity ratios for ring-opening polymerizations where one comonomer is an oxetane. For example, the copolymerization of oxetane and 3,3-dimethyloxetane using BF_4-OEt_3 in methylene chloride is almost ideally nonselective with the r_1 and r_2 equal to 1.19 and 0.95, respectively.[24] Also, the copolymerization of 3,3-bis(chloromethyl)oxetane and THF using BF_3-OEt_2 is also nearly nonselective, with the r_1 and r_2 equal 0.82 and 1.00, respectively.[34] Thus, in these cases cyclic ether reactivities are close to unity and copolymerization gives random sequences. Near-ideal selective copolymerization is observed for tetrahydrofuran and 3,3-dimethyloxetane with the r_1 and r_2 equal 0.13 and 8.1, respectively.[35] Similar behavior is observed for 3-methyltetrahydrofuran and 3,3-dimethyloxetane.[36] Finally, a case of alternating tendency has been shown for an oxetane copolymerization with caprolactone. The r_1 and r_2 for 3,3-bis(chloromethyl)oxetane and ϵ-caprolactone are 0.26 and 0.48, respectively.[26]

To estimate copolymer composition, the reactivity ratios r_1 and r_2 for ME2Ox and 5FOx, respectively, were determined using Finemann−Ross (F−R)[37] and Kelen−Tudos (K−T)[38] methods. The values of $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ are the ratio of homopropagation/cross-propagation rate constant for each monomer species. All polymerizations were performed in methylene chloride at the same conditions described in the Experimental Section and terminated below 10% monomer conversion to minimize errors due to changes in the feed ratio. The copolymer compositions were calculated from each ^1H NMR spectrum for methylene groups next to the ME2Ox and 5FOx side chains, that is, peaks **b** and **g** (Figure 2).

The F−R plot shown in Figure 5a was fitted to a straight line with $R^2 = 0.990$. Two separate data sets were collected demonstrating reproducibility. The values of r_1 and r_2 obtained from this plot are 0.97 for ME2Ox and 0.12 for 5FOx, respectively. Similar values are calculated by the K−T method ($r_1 = 0.98$, $r_2 = 0.28$). These r_1 and r_2 values indicate that the active end derived from ME2Ox reacts with both monomers equally, whereas the 5FOx-derived end favors reaction with the ME2Ox monomer. Generally, the reactivity of the cyclic ether itself depends on basicity and ring strain. One might expect similar reactivities for ME2Ox and 5FOx monomers because of the similar nucleophilicity reflected in similar chemical shifts of ring-methylene ^1H NMR peaks for both monomers. However, the result obtained indicates that the 5FOx growing species has clear monomer selectivity. The values show $r_1 \approx 1 > r_2$ and r_1r_2 ($= k_{11}k_{22}/k_{12}k_{21}$) $= 0.12$, much smaller than unity.

This analysis indicates that, while the instantaneous monomer ratio is 1:1, the copolymer units being formed have a composition in which the 5FOx−5FOx dyad mole

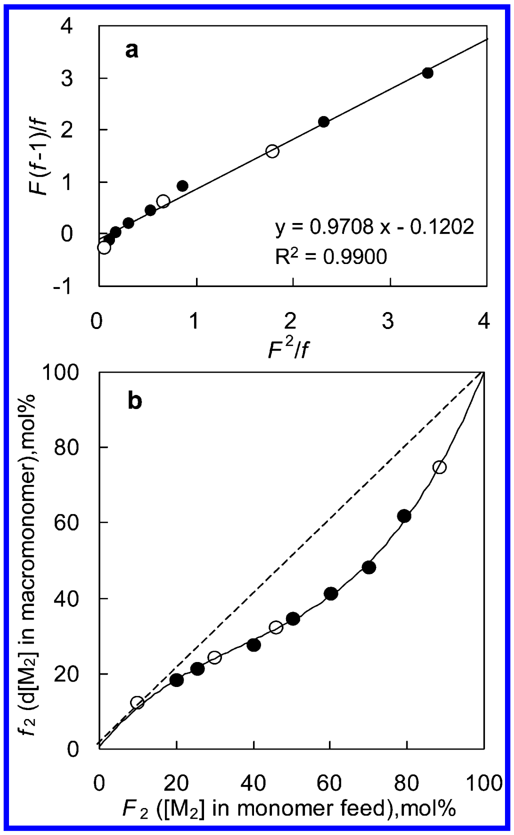


Figure 5. F−R plot (a) and composition diagram (b) for ME2Ox/5FOx copolymerization in methylene chloride.

fraction is well below the statistically predicted amount. That is, most 5FOx exists in dyads combined with ME2Ox. Also, there is a greater than statistical amount of ME2Ox−ME2Ox dyads. However, the telechelic polyoxetanes isolated at the completion of the batch syntheses are expected to have dyad compositions that are not very different from a statistical copolymer.

Figure 5b shows the composition diagram, which is a plot of mole fraction for 5FOx in copolymer (f_2) as a function of its mole fraction in the monomer feed (F_2) for 11 experiments. The dashed line corresponds to ideal random copolymerization ($r_1 = r_2 = 1$). The solid line, the theoretical curve for $r_1 = 0.97$, $r_2 = 0.12$, does not intersect the ideal line.

To investigate the monomer sequence issue further, monomer reactivity ratios in a nonpolar solvent were examined. Methylcyclohexane has a solvent polarity parameter of 0.563 compared to 0.875 for methylene chloride from the solvent polarity/polarizability (SPP) calculation by Catalán.[39] The F−R plot and the composition diagram are shown in Figure 6a,b. Ratios r_1 and r_2 are 1.65 for ME2Ox and 0.49 for 5FOx, with $R^2 = 0.998$. In methylcyclohexane $r_1 > 1 > r_2$, and r_1r_2 ($= k_{11}k_{22}/k_{12}k_{21}$) is closer to unity (0.81), indicating near-ideal copolymerization.

Generally, solvent polarity shows an effect on reactivity in ionic polymerization when the structures or basicities of two monomers are different. Basicities of ME2Ox and 5FOx are presumably similar but might have slight differences caused by electron-donating alkyl ether group vs the electron-accepting fluoro group. This substituent effect can be larger in a polar solvent than that in a nonpolar solvent, accounting for the results in methylene chloride. However, monomer selectivity of the growing species decreases in nonpolar methylcyclohexane, resulting in an ideal random copolymer composition.

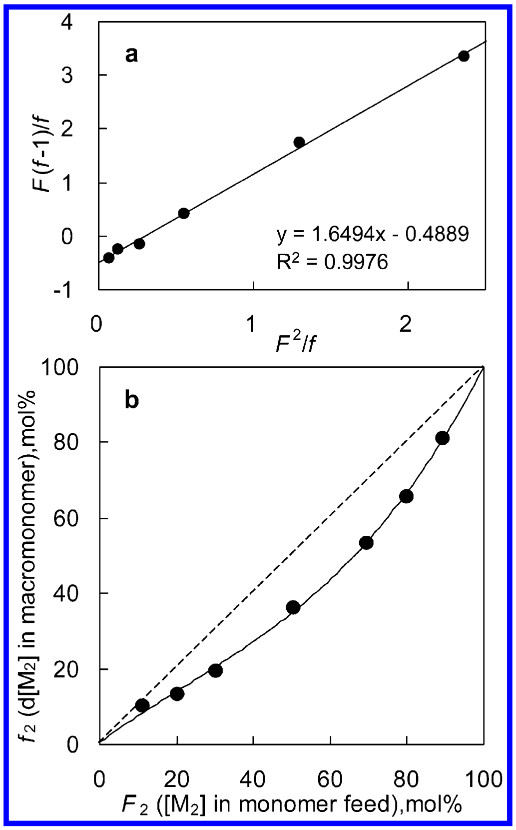


Figure 6. F−R plot (a) and composition diagram (b) for ME2Ox/5FOx copolymerization in methylcyclohexane.

There are relatively few studies of oxetane copolymerization. In the polymerization of oxetane with 3,3-dimethyloxetane, the reactivity ratios are both close to unity.[24] That may also be the case in the copolymerization of 3,3-bis(hydroxymethyl)oxetane with 3-ethyl-3-(hydroxymethyl)oxetane[40] and in the reaction of 3,3-bis(azidomethyl)oxetane with either 3-azidomethyl-3-(2,5-dioxaheptyl)oxetane or 3-azidomethyl-3-(2,5,8-trioxadecyl)oxetane.[41] In the solution-phase copolymerization of 3,3-bis(chloromethyl)oxetane with 3-ethyl-3-(chloromethyl)oxetane[42] and the reaction of 3,3-bis(azidomethyl)oxetane with 3-chloromethyl-3-(2,5,8-trioxadecyl)-oxetane,[43] selectivity is inferred from the composition of products at high conversion. The selectivity observed for the ME2Ox−5FOx system in methylene chloride may be somewhat unusual. However, the effect on the structure and composition of the telechelic polyoxetanes isolated from synthetic procedures is confounded because these reactions are run to high conversion.

Tacticity. Polymer tacticity is often affected by catalyst, counteranion, monomer substituent, solvent polarity, and reaction temperature. Stereoregularity in cationic polymerization in homogeneous systems has been investigated for poly(vinyl ether)s. Isotactic-rich polymer was obtained using $BF_3{-}OEt_2$ in nonpolar solvent at low temperature.[44,45] Tacticity of polyethers obtained from cyclic ethers by cationic polymerization has not been reported.

Figure 7 shows a typical ^{13}C NMR spectrum of ME2Ox/5FOx (1/1) copolymer. Of all polyoxetane carbons, three carbons ($-\mathbf{C}H_3$ (**a**, **a′**) and $-\mathbf{C}H_2-$ (**d**, **d′**) side groups and $-\mathbf{C}-$ for main chain (**b**, **b′**)) give multiple peaks. Peaks for $-\mathbf{C}H_3$ (**a**, **a′**) are shown in the

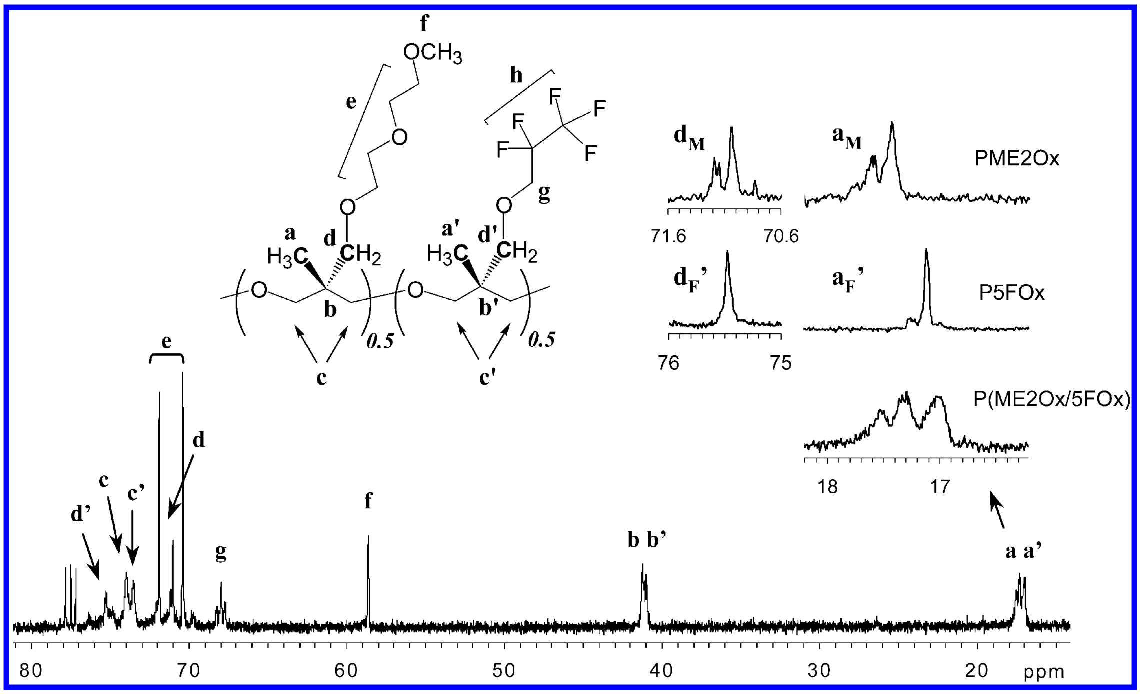


Figure 7. Typical ^{13}C NMR spectrum of ME2Ox/5FOx (1/1) copolymer. The expanded spectra are the part of ME2Ox homopolymer, 5FOx homopolymer, and copolymer.

Table 2. Glass Transition Temperatures (T_g) for Polyoxetanes

homo- or copolymers	T_g (°C)	homo- or copolymers	T_g (°C)
ME2Ox	−67.3	ME2Ox/5FOx (1/1)	−56.9
5FOx	−43.5	ME2Ox/7FOx (1/1)	−55.6
7FOx	−52.7	ME2Ox/7FOx (2/1)	−58.3

expanded insert. To understand the origin of these multiple peaks, the spectra of homo-ME2Ox and homo-5FOx were examined. The methyl carbon peaks of homo-ME2Ox ($\mathbf{a_M}$) and homo-5FOx ($\mathbf{a_F}'$) are shown in the inset. ME2Ox homopolymer has multiple peaks whereas 5FOx homopolymer shows a single peak with a small second peak. This pattern is also observed for the methylene carbon ($\mathbf{d_M}$ and $\mathbf{d_F}'$) peaks for ME2Ox and 5FOx homopolymers, respectively.

For ME2Ox homopolymer the origin of the three peaks may be different carbon environments in isotactic, syndiotactic, and atactic configurations. In contrast, one dominant peak is seen for 5FOx. This suggests that the 5FOx polymer may have a dominant tacticity or that the carbon peaks are accidentally degenerate.

For the ME2Ox/5FOx (1/1) copolymer, broad multiple peaks (**a**, **a**′) are observed. The 5FOx methyl group peak is notably broadened compared to the homopolymer, consistent with a copolymer structure vs a mixture of homopolymers.

Tacticity is a very important determinant for properties (e.g., T_g) of polymers. Further investigation of polyoxetanes synthesized under varying reaction conditions will be required for confirmation of tacticity effects in this cationic ring-opening polymerization.

Thermal Analysis. Glass transition temperatures (T_g's) of the polyoxetanes were measured using subambient DSC. Table 2 shows T_g of ME2Ox and FOx homopolymers and their copolymers. ME2Ox homopolymer has the lowest T_g (−67 °C) close to the T_g of PTMO (ca. −70 °C). Typical DSC curves are shown in Figure 8. The T_g of 5FOx homopolymer is −44 °C. Curve b is the scan of a physical mixture of ME2Ox and 5FOx homopolymers. This mixture has two T_g's because the two homopolymers are completely immiscible. In contrast, ME2Ox/5FOx (1/1) copolymer gives one T_g at −57 °C in between the T_g's of the homopolymers. This result supports the composition study of the copolymer that indicates a random or alternating tendency but not blocky sequence. The T_g of copolymer can be estimated by the Fox equation using the T_g's of homopolymers:

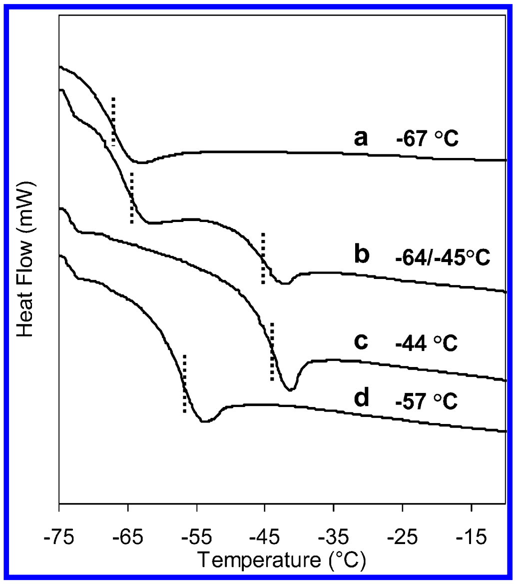


Figure 8. Typical DSC curves of polyoxetanes with heating rate of 20 °C/min: (a) ME2Ox homopolymer, (b) physical mixture of ME2Ox and 5FOx homopolymers, (c) 5FOx homopolymer, and (d) ME2Ox/5FOx (1/1) copolymer.

$$T_{g(cal)}{}^{-1} = w_1 T_{g1}{}^{-1} + w_2 T_{g2}{}^{-1}$$

where w_1 and w_2 are the weight fraction of each component. Using $w_{(ME2Ox)}$ and $w_{(5FOx)}$ and homopolymer T_gs, $T_{g(cal)}$ is −54 °C for ME2Ox/5FOx (1/1). Similarly, $T_{g(cal)}$ of ME2Ox/7FOx (1/1) and ME2Ox/7FOx (2/1) is

−58 and −60 °C, respectively. Calculated T_gs are close to those observed.

Conclusions

Novel alcohol-terminated oxetane DFTs with hydrophobic semifluorinated and hydrophilic alkyl ether (methoxyethoxyethoxy) pendant groups were synthesized. The DFTs (ME2Ox/FOx telechelic copolymers) were characterized by NMR spectroscopy to analyze molecular weight and composition. Molecular weights were conveniently determined by ^{1}H NMR spectroscopy through end-group analysis. For ME2Ox co- and homopolymers, D_p was not very sensitive to the monomer/cocatalyst ratio. This may be due to more than one polymerization mechanism and/or side reactions. Fortunately, the molecular weights obtained approximate those required for utilization as soft blocks in segmented copolymers, a direction of our future work. Monomer reactivity ratios were determined in two solvents with different polarity. In methylene chloride, an active end derived from 5FOx monomer reacts preferentially with ME2Ox whereas the ME2Ox-derived end shows no selectivity. The reactivity ratios are 0.97 for ME2Ox and 0.12 for 5FOx. In methylcyclohexane, the monomer reactivity ratios are more characteristic of ideal copolymerization. The parameters are 1.65 for ME2Ox and 0.49 for 5FOx. The thermal properties of homo- and copolymers were evaluated by DSC analysis. T_g's ranged from −67 °C (ME2Ox homopolymer) to −44 °C (5FOx homopolymer).

Present work is aimed at incorporating these novel telechelic polyoxetanes in polyurethanes and evaluation of surface properties.

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