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Co-Polyoxetanes with Alkylammonium and Fluorous or PEG-Like Side Chains: Soft Blocks for Surface Modifying Polyurethanes

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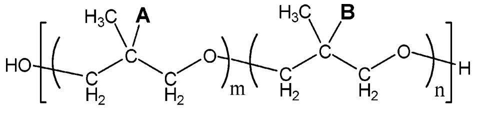
ABSTRACT: The goal of this work was to prepare polyurethanes having P[**AB**] co-polyoxetane soft blocks, where **A** is a surface active (fluorous) or PEG-like side chain and **B** represents a desired function (alkylammonium). To this end, poly(2,2-substituted-1,3-propylene oxide) *ran*-co-telechelics with bromobutoxymethyl ($-CH_2O(CH_2)_4$-Br) and either trifluoroethoxymethyl (3FOx, $-CH_2OCH_2CF_3$)) or PEG-like (2-(2-methoxyethoxy)ethoxy)methyl (ME2Ox, ($-CH_2(OCH_2CH_2)_2OCH_3$)) side chains were prepared via cationic ring-opening polymerization. Characterization utilized ^{1}H NMR spectroscopy, temperature modulated differential scanning calorimetry (MDSC) and thermogravimetric analysis (TGA). Molecular weights (M_n) by ^{1}H NMR end group analysis were ∼6 kDa while bromobutoxymethyl co-telechelic T_gs were −68 and −48 °C for ME2Ox and 3FOx, respectively. Bromobutoxymethyl groups were completely substituted with *N*,*N*-dimethylalkyl amines to obtain oxetane **B** repeats with six carbon (C6) and twelve carbon (C12) alkylammonium side chains. P[**AB**] T_gs remained low after amine substitution. Co-telechelics were incorporated into polyurethanes (PUs) having 4,4′-(methylene bis (*p*-cyclohexyl isocyanate) (H_{12}MDI) and butanediol (BD) as the hard block (30 wt %). Characterization by ^{1}H NMR, GPC, MDSC, and TGA is described. From DSC data, using the Fox equation, the weight fraction of pure soft block in the soft block domain (w_1) was very high (0.96−0.99) for polyurethanes with fluorous soft blocks, while soft blocks with PEG-like side chains were phase mixed ($w_1 = 0.73-0.75$). To our knowledge, this is the first time that a polycationic telechelic has been incorporated in a polyurethane. TGA in nitrogen confirmed stoichiometry and showed that both alkylammonium co-telechelics and polyurethanes had good thermal stability.

Introduction

Polymer surface modifiers that comprise a minority weight percent concentrate desired functionality without altering bulk properties of the majority polymer. In what might be called "beyond oleophobicity", concentrating surface functionality was investigated by Vogl, who attached fluorous tails[1] to UV absorbing groups.[2] Santerre recently described concentrating functionality in a base polyurethane by means of a bifunctional polyurethane modifier with one fluorous chain end the other a peptide. When a modified (2.5−5 wt %) base polyurethane was exposed to aqueous media, peptide surface concentration was proposed to account for enhanced cell compatibility.[3] Yin-ping also used end group alkyl ammonium functionality on polyurethanes for biocidal activity.[12] End group modification obviously limits the composition to two functional groups per chain.

To obtain functional polymer surface modifiers, we have focused on polyurethanes having co-polyoxetane soft blocks **1** with **A** and **B** side chains on a poly(1,3-propylene oxide) main chain, represented as P[**AB**]. Previously, we used a substitution-on-polymer method to introduce hydantoin substituted side chains, **B**.[4] Unexpected contraphilic wetting (dry surface hydrophilic; wet surface hydrophobic) was observed for the fluorous−hydantoin P[**AB**] polyurethanes.[4,5] Fluorous−hydantoin P[**AB**] and P[**ABC**] polyurethanes were effective antimicrobial surface modifiers.[6,7]



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In broadening the P[**AB**] palette, we sought to introduce charge, that is, a cation moiety as **B** (Scheme 1). Cationic functionality is conventionally introduced into the hard block using a chain extender to generate emulsions.[8−10] Using a chain extender approach, Cooper introduced pyridinium groups into linear polyurethanes and evaluated biocidal behavior.[11] Hard block ordering and mechanical properties were adversely affected by incorporation of higher weight percents of pyridinium chain extender. In contrast to the hard block and end group approaches, our goal is introducing charge on the P[**AB**] soft block so as to enhance surface concentration[13−16] without disturbing hard block structure.

Prior to this effort, we used a substitution-on-polymer method to introduce hydantoin groups.[4] Only 60−70% substitution of bromomethyl groups was obtained. A different strategy was employed for introducing charge via quaternary alkylammonium **B** side chains. First, substitution on telechelic was carried out. Second, in order to improve chances for 100% substitution, the substitution site was separated from the main chain using the bromomethyl oxetane comonomer (BBOx, Scheme 1), previously prepared in high yield.[17]

Polyoxetanes are generated via cationic ring-opening polymerization.[18,19] For example, oxetane telechelics with fluorous side chains were synthesized by Malik.[20−22] Herein, the synthesis and characterization of P[**AB**] co-polyoxetane telechelics **2** (Scheme 1) having a reactive **B**-group (bromobutoxymethyl, BBOx) and either fluorous (trifluoroethoxymethyl, 3FOx) or PEG-like (2-(2-methoxyethoxy)ethoxy)methyl, ME2Ox) **A** side chains are described.

The P[**AB**] telechelics (B = BBOx) were then quaternized with tertiary amines and incorporated into polyurethanes via a soft-block first method.[23,24] To our knowledge, the compositions reported herein are the first polyurethanes with cationic side chains on the soft block. The highly efficient antimicrobial behavior of the P[**AB**]−polyurethane surface modifiers was previously communicated.[25] A subsequent paper will describe

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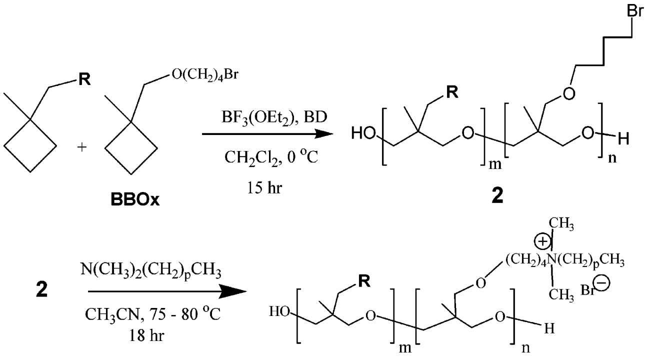
Scheme 1. Cationic Ring Opening Polymerization of BBOx and R−Oxetane: R = $-OCH_2CF_3$ (3FOx) or $-(OCH_2CH_2)_2OCH_3$ (ME_2Ox) and Quaternization of BBOx *Co*-Telechelic Using C-6 (*p* = 5) or C-12 (*p* = 11) Dimethylamines.



the physical surface characterization of conventional polyurethanes modified by alkylammonium P[**AB**]−polyurethanes and multiple effects of contrasting fluorous (hydrophobic/oleophobic) or PEG-like (hydrophilic) **A** co-repeat units.

Experimental Section

Materials. 3-(2,2,2-Trifluoroethoxymethyl)-3-methyloxetane (3FOx) and 3-bromomethyl-3-methyloxetane (BrOx) were gifts from OMNOVA Solutions (Akron, OH). *N,N*-Dimethyldodecylamine (C-12) was a gift from Lonza (Allendale, NJ). BrOx and 3FOx monomers were distilled prior to use (3FOx at100 °C/5mmHg and BrOx at 85 °C/5mmHg). Methylene chloride (CH_2Cl_2), *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF) and 2-propanol (IPA) were obtained from Aldrich and dried by storing over 4 Å molecular sieves. Boron trifluoride dietherate ($BF_3O(C_2H_5)_2$), 4,4′-(methylenebis(*p*-cyclohexyl isocyanate), dibutyltin dilaurate catalyst (T-12), *N,N*-dimethylhexylamine (C-6), tetrabutylammonium bromide (TBAB), 3-(hydroxymethyl)-3-methyloxetane, 1,4-dibromobutane, and sodium hydride (NaH) were also obtained from Aldrich and used as received. 1,4-Butanediol (BD) and 2-(2-methoxyethoxy)ethanol were purchased from Acros Chemicals and used as received.

Synthesis. Monomers. 3-((4-Bromobutoxy)methyl)-3-methyloxetane (BBOx) monomer was prepared according to a literature method.[17] 3-((2-(2-Methoxyethoxy)ethoxy)methyl)-3-methyloxetane (ME2Ox) was synthesized as follows: A mixture of 2-(2-methoxyethoxy)ethanol (20 g, 0.17 mol) and NaH (4 g, 0.17 mol) in 50 mL anhydrous tetrahydrofuran (THF) was stirred vigorously at room temperature until H_2 generation stopped. The system was cooled to 0 °C (ice−water bath), and 3-bromomethyl-3-methyloxetane (BrOx) (27 g, 0.17 mol) was added dropwise within 2 h. The reaction mixture was brought to room temperature and stirred over night. After filtration, 100 mL of H_2O was added. The product was extracted with CH_2Cl_2 and distilled in the presence of CaH_2 (60 °C/0.1 mmHg). ^1H NMR ($CDCl_3$): δ 1.32 ($-C\mathbf{H}_3$, 3H, s), δ 3.39 ($-OC\mathbf{H}_3$ 3H, s), δ 3.55 ($-OC\mathbf{H}_2C\mathbf{H}_2O-$, 4H, m), δ 3.67 ($-OC\mathbf{H}_2C\mathbf{H}_2O-$, 4H, and $-C\mathbf{H}_2$, 2H, m), δ 4.35 (ring C$\mathbf{H}_2$, 2H, d), δ 4.52 (ring C$\mathbf{H}_2$, 2H, d).

Telechelics. BBOx was copolymerized with either 3FOx or ME2Ox monomers via cationic ring-opening polymerization[24] to give P[(3FOx)(BBOx)-m:n-(M_n)] and P[(ME2Ox)(BBOx)-m:n-(M_n)], where "P" indicates the ring-opened monomer-in-telechelic and specific ratios of segments (m:n) follow the repeat unit designations. Molecular weights (M_n) are indicated in the designations. Details are provided in the following example.

P[(3FOx)(BBOx)-0.89:0.11-(5900)]. 1,4-Butanediol (0.45 g, 5 mmol) and $BF_3\cdot OEt_2$ (1.42, 10mmol) were added to 20 mL anhydrous CH_2Cl_2 and kept at ambient temperature for 45 min under a slow nitrogen purge, then cooled to −5 °C. Through an additional funnel, 3FOx (16.56 g, 90 mmol) and BBOx (2.37 g, 10 mmol) dissolved in 20 mL of CH_2Cl_2 were added dropwise to the solution over a 3 h period. After 15 h, the mixture was warmed to ambient temperature and quenched with 40 mL of H_2O. The organic layer was washed with 30 mL of 3 wt % HCl(aq) and then with 30 mL of 3 wt % NaCl(aq). The solution was added dropwise into a 400 mL water:methanol (3:1) mixture to precipitate the telechelic. Solvent was evaporated under vacuum at 60 °C. The ^1H NMR spectrum showed that m = 0.89, which was close to the feed ratio. ^1H NMR ($CDCl_3$): δ 0.91 ppm ($-C\mathbf{H}_3$, 3H, s), 1.68 ppm ($-C\mathbf{H}_2-$, 2H, m for BBOx), 1.92 ppm ($-C\mathbf{H}_2-$, 2H, m for BBOx), 3.19 ppm (backbone $-C\mathbf{H}_2-$, 4H, m), 3.4 ppm ($-C\mathbf{H}_2Br-$, 2H, t), 3.45 ppm ($-OC\mathbf{H}_2-$, 2H, s), 3.75 ppm ($-C\mathbf{H}_2CF_3-$, 2H, m). Details of ^1H NMR spectra that address the ratio of **A**:**B** groups are addressed in the Results and Discussion.

P[(ME2Ox)(BBOx)-m:n-(M_n)] was prepared following the same procedure. ^1H NMR ($CDCl_3$): δ 0.89 ppm ($-C\mathbf{H}_3$, 3H, s), 1.69 ppm ($-C\mathbf{H}_2-$, 2H, m for BBOx), 1.92 ppm ($-C\mathbf{H}_2-$, 2H, m for BBOx), δ 3.14−3.66 ppm (broad region is for the remaining $-C\mathbf{H}_2-$ protons and $-O-C\mathbf{H}_3$ on ME2Ox).

P[(3FOx)(BBOx)-m:n-(M_n)] and P[(ME2Ox)(BBOx)-m:n-(M_n)] were quaternized by amine substitution on C−Br. An example is provided below.

P[(3FOx)(C12)-0.89:0.11-(6500)]. First, 3.38 g of P[(3FOx)-(BBOx)-0.89:0.11-(5900)] and *N,N*-dimethyl dodecylamine (C-12) (1.5 mL, 8.8 mmol) were dissolved in 20 mL of acetonitrile. The mixture was heated to reflux and stirred for 18 h under nitrogen. The solvent and excess *N,N*-dimethyl dodecylamine were evaporated under vacuum to give highly viscous P[(3FOx)(C12)-0.89:0:11-(6500)]. Here, "C12" represents the 2-alkylammonium butoxymethyl-2-methyl 1,3-propylene oxide segment. ^1H NMR ($CDCl_3$): δ 0.91 ppm ($-C\mathbf{H}_3$, 3H, s), 1.35 ppm ($-C\mathbf{H}_2-$, 18H, broad), 1.68 ∼ 1.92 ppm ($-C\mathbf{H}_2-$, 6H, broad), 3.19 ppm (backbone $-C\mathbf{H}_2-$, 4H, m), 3.40−3.42 ppm ($-C\mathbf{H}_2N^+-$, 2H, $C\mathbf{H}_3-N^+-C\mathbf{H}_3$, 6H), 3.45 ppm ($-OC\mathbf{H}_2-$, 2H, s), 3.75 ppm ($-C\mathbf{H}_2CF_3-$, 2H, m). As indicated by ^1H NMR, the bromomethyl group was converted quantitatively to the alkylammonium bromide.

Polyurethanes. Alkylammonium functionalized telechelics were incorporated into polyurethanes (PUs) by using a two-step polymerization via solution reaction procedure.[23] A $H_{12}MDI$/BD hard block was utilized. An example is provided below.

P[(3FOx)(C12)-0.89:0:11-(6500]-PU. P[(3FOx)(C12)-0.89:0:11-(6500)] telechelic (8.13 g, 1.25mmol) in 5.44 g of THF was added to three-necked round-bottom flask containing $H_{12}MDI$ (2.62 g, 10 mmol) and heated to 70 °C under nitrogen purge. Dibutyltin dilaurate (6 drops, 10 wt % in DMF) was added as the catalyst. The prepolymer reaction was followed using FT-IR by observing the appearance of carbonyl peak (1716 cm^{-1}). After 3−4 h, the carbonyl peak remained unchanged, suggesting the completion of the prepolymer reaction. After the prepolymerization step, 1,4-butanediol (0.79 g, 8.77 mmol) in 3.5 g of DMF was added dropwise. The mixture was kept at 70 °C until complete disappearance of NCO peak at 2267 cm^{-1} (ca. 4 h). The mixture was cooled to room temperature and added dropwise to 400 mL water to affect precipitation of the polyurethane. Residual solvent was evaporated under vacuum at 60 °C for 48 h.

Polyurethane formation was followed using FT-IR by observing the appearance of carbonyl peak (1716 cm^{-1}) with concomitant disappearance of isocyanate peak (2267 cm^{-1}). All polyurethanes were soluble in THF/ IPA (5:1). The composition was confirmed by ^1H NMR.

Characterization. Purity of monomers was determined by gas chromatography−mass spectroscopy (GC-MS) with Hewlett-Packard-5973 mass selection detector. Telechelic ($CDCl_3$) and polyurethane (DMSO-d_6) ^1H NMR spectra were recorded using a Varian spectrometer (Inova 400 MHz). FT-IR spectra were obtained using a Nicolet 400 FT-IR spectrometer. Telechelics were deposited and spread as a thin layer while polyurethanes were cast from solution to obtain thin films on KBr disks.

Molecular Weight Determination. End Group Analysis. The degree of polymerization (DP) and M_n of telechelics were determined by end group analysis, which utilizes the reaction of trifluoroacetic anhydride (TFA) with telechelic hydroxyl end groups.[26] An estimated 2−4 fold molar TFA excess was added to

Table 1. Molecular Weights for Telechelics and Polyurethanes Including Degree of Polymerization (D_p) for Telechelics and Polydispersity Indices (PDI) for Polyurethanes

	telechelics[a]						
	−BBOx		$-NR_3^+$		polyurethanes[b]		
composition	$M_n \times 10^{-3}$	D_p	$M_n \times 10^{-3}$	D_p	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	PDI
P[(3FOx)(C6)-0.89:0.11]	5.9	31	6.3	31	46	70	1.5
P[(3FOx)(C12)-0.89:0.11]			6.5	30	8.3	23	2.8
P[(ME2Ox)(C6)-0.86:0.14]	5.6	27	6.1	27	2.9	4.7	1.7
P[(ME2Ox)(C12)-0.86:0.14]			6.2	26	8.1	21	2.5

[a] Determined by using end group analysis. [b] Determined by GPC using 0.05 M LiBr in NMP as solvent.

the telechelic solution in $CDCl_3$. The solution was stirred at 40 °C for 1 h, and the ^1H NMR spectrum was obtained. The ratio of signals of methylene protons next to the fluoroacetyl group (~4.4 ppm) compared to the methyl of the repeat unit (~0.9 ppm) was used for calculation of DP for the telechelic.

Gel Permeation Chromatography. Attempts were made to determine molecular weight of polyurethanes in chloroform using both light scattering and RI detectors. No light scattering signal was observed; the signal from the RI detector was barely discernible. The observed molecular weights were between 1 and 5 kDa. Details are not reported as these results are inconsistent with the fact that these polyurethanes form films in a manner typical of molecular weights in the range of 20−50 kDa. Neither 3FOx nor ME2Ox polyurethanes were adequately soluble in THF. The low mole fraction of alkylammonium side chains and alkyl groups on nitrogen precluded solubility in water. Alkylammonium soft block polyurethane molecular weights (M_n and M_w) were finally estimated by GPC with a Waters RI detector-Viscotek dual detector system. Solutions (2.5-3 mg/mL) were prepared with 0.05 M LiBr in *N*-methylpyrrolidone (NMP) as solvent. Results are reported in Table 1.

Thermal Behavior. Temperature modulated differential scanning calorimetry (MDSC) was done with a TA-Q 1000 Series instrument (TA Instruments) with modulation amplitude of ± 0.5 °C, modulation period of 60 s, and heating rate of 3 °C/min from −70 to +20 °C (for telechelics) or to 150 °C (for polyurethanes). Indium metal was used for calibration. Telechelics were highly viscous and were deposited on DSC pans by using a small glass rod; small pieces of polyurethanes were simply placed in the pan. Thermal decomposition of telechelics and polyurethanes was examined by thermogravimetric analysis (TGA) with a TA-Q 5000 Series. Using a nitrogen purge, samples on platinum pans were heated to 600 °C with a heating rate of 20 °C/min. DSC and TGA plots were analyzed by using TA Universal Analysis software.

Results and Discussion

P[**AB**]−telechelics **1** serve as precursors to P[**AB**]−polyurethanes. Some of these polymers have surprising surface properties by themselves such as contraphilic wetting,[4] and others serve as highly efficient surface modifiers.[6] In designing the P[**AB**]−polyurethane surface modifiers described herein, the site for substitution was removed further from the main chain compared to the bromomethyl moiety previously employed.[6] This strategy was implemented via BBOx (Scheme 1), which was previously reported by Kawakami.[17] Having the $-CH_2-O-(CH_2)_4-$ side chain was thought to provide an "extension" for separating charge from the main chain in a way similar to "BIN" pyridinium chain extender substitution.[11] However, it was hoped that having the side chain charge on the soft block would be less disruptive to polyurethane morphology, moisture uptake, and mechanical properties. Consistent with our targeted application, it seemed plausible that relatively long alkylammonium side chains might provide pseudo-chain ends for enhancing surface concentration.[27]

Preliminary results have been reported on the alkylammonium P[**AB**]−soft block polyurethane surface modifiers as highly efficient contact antimicrobials.[25] Fluorous 3FOx ($CF_3CH_2OCH_2-$) or PEG-like ME2Ox ($CH_3(CH_2CH_2O)_2-$) **A** groups were chosen to provide contrasting surface concentration characteristics and wetting behavior. Six carbon (C6) and twelve carbon (C12) quaternary alkyl ammonium chains **B** were chosen to evaluate effects on surface concentration and antimicrobial activity.[25] The mole fraction of charged (**B**) to neutral (**A**) took into account that found in naturally occurring polypeptides (0.2−0.3) such as magainins and defensins.[28,29] In this initial research, the mole fraction of charged **B** groups was kept somewhat lower than the antimicrobial polypeptides to minimize impact on physical properties. The synthesis of monomers, P[**AB**]−telechelics, and P[**AB**]−polyurethanes are discussed below along with spectroscopic and thermal analysis.

Monomers. Cationic ring-opening polymerization is very sensitive to monomer impurities. Therefore, multiple fractional distillations were performed. Monomers having less than 98% purity were re-distilled. 3-((4-Bromobutoxy)methyl)-3-methyloxetane (BBOx) was synthesized by reaction of 3-(hydroxymethyl)-3-methyloxetane with 1,4-dibromobutane in the presence of NaOH via phase transfer catalysis.[17] The monomer was purified by vacuum distillation (70 °C/0.2mmHg). Monomer purity was 99.8% by GC−MS. ME2Ox monomer was synthesized from 3-bromomethyl-3-methyloxetane (BrOx) by reaction with 2-(2-methoxyethoxy) ethanol. After distillation, 99.3% purity (GC−MS) was obtained.

Telechelics. BBOx-Co-Telechelics. Oxetane co-telechelics were synthesized from the corresponding monomers (Scheme 1). Cationic ring-opening polymerization was carried out between −5 and 0 °C. Reaction below or above this temperature range yielded low molecular weights. BF_3−etherate and 1,4-butanediol (2:1) were used as catalyst and cocatalyst, respectively.

Co-polyoxetane repeat unit mole ratios were determined using ^1H NMR spectroscopy by integration of methylene groups (Figure 1, parts b and c) to methyl groups (Figure 1, part a). The observed ratio for P[(3FOx)(BBOx)-0.89:0.11-(5900)] was close to the feed ratio of respective monomers (0.90:0.10). With the same feed ratio, the range of compositions (Table 1) was m = 0.86−0.89 and n = 0.11−0.14, which indicated good reproducibility.

In FT-IR spectra of telechelics, asymmetric C−O−C stretching, O−H stretching, and C−H stretching were observed at 1120, 3400−3300, and 2950−2850 cm^{-1}, respectively. For 3FOx co-telechelics strong bands at 1170 and 1280 cm^{-1} were also observed. For BBOx telechelics, expected CH_2 wagging (CH_2-Br) ~1260 cm^{-1} was not identified due to overlapping bands.

Telechelic molecular weights (M_n) were determined by end group analysis using trifluoroacetic anhydride (Table 1).[26] Figure 1 shows representative ^1H NMR spectra for co-telechelic end group analysis using P[(3FOx)(BBOx)-0.89:0.11-(5900)] as an example. Telechelic molecular weights are 5.6−5.9 kDa, which

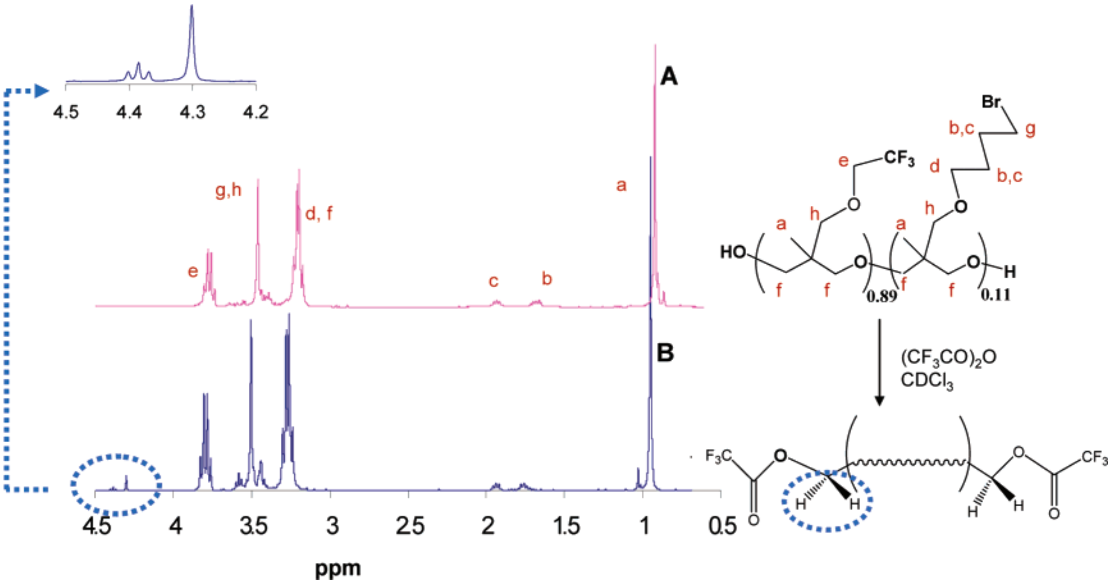


Figure 1. ^1H NMR of P[(3FOx)(BBOx)-0.89:0.11] before (A) and after (B) reaction with TFA. M_n is determined by integrating methylene protons next to the fluoroacetyl group (∼4.4 ppm, circled) and methyl of the repeat unit (∼0.9 ppm, a).

is typical for soft blocks. The DP range for the co-telechelics (27−31) is similar to the commonly employed PTMO-2000 (28). However, unlike PTMO, the atactic P[**AB**]−co-telechelics do not crystallize.

Quaternized Telechelics. BBOx co-telechelics were quaternized by nucleophilic substitution using either C-6 or C-12 alkyldimethylamines. The substitution reaction was carried out at 70 °C in acetonitrile (Scheme 1). Quaternized telechelics were isolated as slightly yellow, viscous oils after evaporation of unreacted amine and solvent. Absence of solvent and unreacted amine was confirmed by ^1H NMR spectroscopy. Quaternization was validated by the appearance of peak ∼1.3 ppm due to alkylammonium methylene groups for $-(CH_3)_2N^+(CH_2CH_2\text{-}(C\mathbf{H}_2)_pCH_3$, where $p = 3$ for C6 and $p = 9$ for C12 (Figure 1S). By integration of this methylene peak and BBOx methylenes, the extent of substitution was found to be 100% after 18 h at 70 °C. The molecular weight of alkylammonium telechelics was determined by TFA/end group analysis. The same degree of polymerization was found (27−31 ± 1) as for the unsubstituted telechelics suggesting the stability of chain length after amine substitution (Table 1, Figure 1S).

Glass Transition Temperatures. Telechelic T_gs were analyzed using the second heating cycle of modulated DSC (MDSC) thermograms as described in experimental section. MDSC resolves the normal heat flow into reversing and nonreversing components[30] and thereby enables separation of transitions occurring in close proximity such as glass transition and enthalpy relaxation.[31] Glass transitions identified in Figure 2 are on reversing heat flow curves.

As shown in Table 2, T_gs for BBOx co-telechelics were relatively low, namely, −68 °C for P[(ME2Ox)(BBOx)-0.86:0.14-(5600)] and −48 °C for the 3FOx analog. Interestingly, these low T_gs increase only modestly after quaternization. Substitution with C12 amine resulted in a smaller increase in T_g (1 °C for 3FOx; 9 °C for ME2Ox) compared to C6 (10/18 °C, respectively). The lower T_gs for C12 may be associated with decreased charge clustering due to the larger side chain length hindering electrostatic interactions. Enhancement of chain movement (lower T_g) with longer side chains has been observed for a vinyl system with alkylammonium side chains.[32]

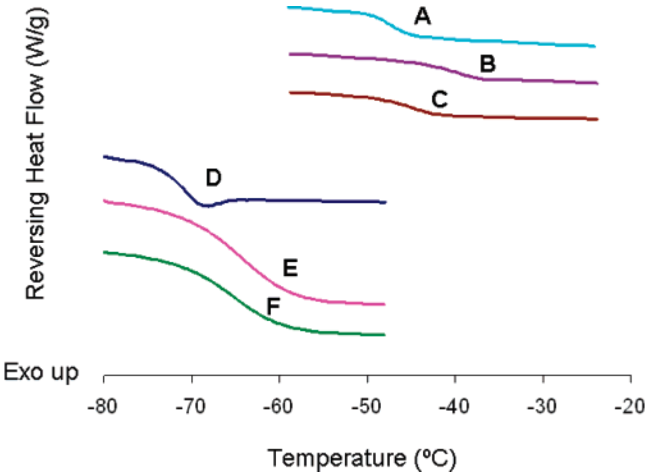


Figure 2. Glass transitions (MDSC, second cycle) for precursor and alkylammonium co-telechelics. Key: (A) P[(3FOx)(BBOx)-0.89:0.11]; (B) P[(3FOx)(C6)-0.89:0.11]; (C) P[(3FOx)(C12)-0.89:0.11]; (D) P[(ME2Ox)(BBOx)-0.86:0.14]; (E) P[(ME2Ox)(C6)-0.86:0.14] (F) P[(ME2Ox)(C12)-0.86:0.14]. $T_g$values are given in Table 2.

Table 2. Glass Transition Temperatures for BBOx and Alkylammonium Co-Telechelics and Polyurethane Soft Blocks

	T_g °C			
	telechelics			
composition	−BBOx	$-NR_3^+$	PU soft block[a]	wt fraction of pure soft block in soft segment[b]
P[(3FOx)(C6)-0.89:0.11]	−48	−38	−37	0.99
P[(3FOx)(C12)-0.89:0.11]	−48	−47	−44	0.96
P[(ME2Ox)(C6)-0.86:0.14]	−68	−50	−27	0.75
P[(ME2Ox)(C12)-0.86:0.14]	−68	−59	−33	0.73

[a] Hard block is HMDI/BD(∼30 wt %). [b] The value for the weight fraction of pure soft block in mixed soft block (w_1) from the Fox equation (see text).

Thermal Decomposition. The limits of thermal stability in nitrogen were investigated by TGA. Decomposition temperatures for telechelics are given in Table 3. The first thermal decomposition for BBOx co-telechelics was observed at 250−255 °C giving mass loss of 9.9 and 10.2% for 3FOx and ME2Ox, respectively.

A decomposition route that fits the first observed mass loss process (250−255 °C) is given in Scheme 2, eq 1. The product

Table 3. Decomposition Temperatures and Calculated and Observed Mass Loss for Decomposition of BBOx and Quaternary Ammonium Telechelics

	decomposition temp (°C)		calculated mass loss (wt %)			
telechelic composition	first	second	bromobutyl aldehyde	amine	total	obsd mass loss at first decomposition (wt %)
P[(3FOx)(BBOx)0.89:0.11]	254	380	8.8	0.0	8.8	9.9
P[(3FOx)(C6)0.89:0.11]	220	420	8.2	7.0	15	15
P[(3FOx)(C12)0.89:0.11]	231	427	7.8	11	19	19
P[(ME2Ox)(BBOx)0.86:0.14]	250	390	10	0.0	10	12
P[(ME2Ox)(C6)0.86:0.14]	220	436	9.4	8.0	17	16
P[(ME2Ox)(C12)0.86:0.14]	227	433	8.9	13	22	18

Table 4. Decomposition Temperatures and Soft Block Content for Polyurethanes; Calculated and Observed Mass Loss for Decomposition of Quaternary Ammonium Polyurethanes

polyurethane composition	decomposition temp (°C)	soft block (wt %)[a]	calculated amine + bromobutylaldehyde mass loss in PU (wt %)	observed mass loss in PU (wt %)[b]
P[(3FOx)(C6)-0.89:0.11]−PU	215	72.2	10.9	10.4
P[(3FOx)(C12)-0.89:0.11]−PU	220	71.1	13.4	12.9
P[(ME2Ox)(C6)-0.86:0.14]−PU	213	72.5	12.6	14.1
P[(ME2Ox)(C12)-0.86:0.14]−PU	218	73.5	15.8	13.5

[a] Determined by ^{1}H NMR (DMSO-d_6) spectra for polyurethanes. [b] Mass loss is measured between 150 and 270 °C.

Scheme 2. Proposed Initial Thermal Decomposition Route for BBOx (eq 1) and Alkyl Ammonium (eq 2) Co-Telechelics.

$$XY(\text{-}O(CH_2)_4Br) \rightarrow XY + \underset{\text{4-bromobutylaldehyde}}{O{=}CHCH_2CH_2CH_2Br} \qquad \text{(Eq 1)}$$

$$XY(\text{-}N^+R_3Br^-) \rightarrow XY + O{=}CHCH_2CH_2CH_2Br + \underset{\text{alkyldimethylamine}}{(CH_3)_2N(CH_2)_pCH_3}, \qquad \text{(Eq 2)}$$

where p=5 for C6 and p=11 for C12.
X = poly(1,3-propylene oxide) main chain with methyl side chains.
Y = **A** side chain ($-CH_2OCH_2CF_3$ or $-CH_2O(CH_2CH_2)_2OCH_3$).

may be 4-bromobutylaldehyde as suggested for ether decomposition.[33] In order to validate this point, weight percentage of bromobutoxy groups were calculated and compared with measured values (Table 3). Calculated and measured values are in agreement suggesting that bromobutoxy groups decompose first. The decomposition for the remaining material occurs at 380 and 390 °C for 3FOx and ME2Ox co-telechelics, respectively. Interestingly, these second decomposition temperatures are the same as those for the respective homotelechelics suggesting similar compositions.

For quaternized co-telechelics, the first thermal decomposition was about 30 °C lower than the BBOx parent (Table 3). The percent mass loss for the first decomposition event was higher compared to the BBOx parent. The additional mass loss is assigned to the decomposition of alkyl ammonium side chain to yield amine as reported for quaternary ammonium salts (Scheme 2, eq 2).[32,34] The mass loss at 220−230 °C was close to calculated mass loss for amine plus bromobutylaldehyde for each telechelic composition (eq 2, Table 3).

The second decomposition processes were at 420 and 430 °C for 3FOx and ME2Ox co-telechelics, respectively. Thus, this mass loss for the quaternized telechelics was 40−50 °C higher than those for the corresponding BBOx telechelics (Figure 3). Although the reason is unclear, repetitive TGA runs confirm the increased thermal stability of the remaining product after the initial thermal mass loss.

Polyurethanes. Alkylammonium P[**AB**]−*co*-telechelics were incorporated into polyurethanes as soft blocks by a conventional soft block first method. To our knowledge, this is the first time that a polycationic telechelic has been incorporated in a polyurethane. The resulting polyurethanes were soluble in THF/IPA (5:1 v:v) mixtures. Films and coatings were clear but slightly yellow. General structures for the polyurethanes are given in Figure 2S. A complete polyurethane designation is HMDI/BD(30)-P[(3FOx)(C12)-0.89:0:11-(6500)],[24] where hard block composition is followed by weight percent, soft block composition, the ratio of **A**:**B**, and soft block molecular weight. Polyurethanes reported herein have 30 wt % HMDI/BD so that the designation P[(3FOx)(C12)-0.89:0:11]-PU is used for brevity, as soft block molecular weights are invariant (Table 1).

^{1}H NMR was used to confirm the hard segment content (wt%) of polyurethanes (Figure 3S). For this purpose, the ratio of N−H peak (4.5 ppm) to soft block methyl group peak (1.0 ppm) was used to determine the relative ratio of HMDI to soft block. By using these stochiometric ratios, soft block content (wt %) was calculated (Table 4).

Polyurethanes had typical properties including the formation of highly viscous solutions at 20 wt %. Qualitatively, films were elastomeric suggesting molecular weights higher than 20 kDa. As noted in the Experimental Section, quantitative determination of polyurethane molecular weights was challenging due to a combination of factors. The best results were obtained using a universal calibration method employing polystyrene standards in 0.05 M LiBr/NMP. Light scattering signals were weak. Except for P[(3FOx)(C6)-0.89:0.11]-PU, observed molecular weights were relatively low. Both M_n and M_w values were very low, especially for P[(ME2Ox)(C6)-0.89:0.11]-PU, which gave a molecular weight lower than the telechelic (Table 1). Research is continuing on the development of a more satisfactory molecular weight determination method. Fortunately, for application as polymer surface modifiers, molecular weights are not critical as the majority polymer provides bulk properties.

In FT-IR spectra of 3FOx polyurethanes, NH stretching due to urethane amide (3300 cm^{-1}), carbonyl peak (non-H-bonded, 1720 cm^{-1}; H-bonded, 1680 cm^{-1}) were observed. C−F stretching bands at 1170 and 1280 cm^{-1} were also identified (Figure 4). These absorptions were used previously to confirm surface concentration for 2 wt % fluorous−P[**AB**]−polyurethane/98 wt % base polyurethane compositions.[25] FTIR spectra for P[(ME2Ox)(C6)-0.86:0.14] telechelic and P[(ME2Ox)(C6)-0.86:0.14]−polyurethane are given in the Supporting Information (Figure 4S).

Glass Transition Temperatures. Differential scanning calorimetry has long been used to assess the degree of phase mixing

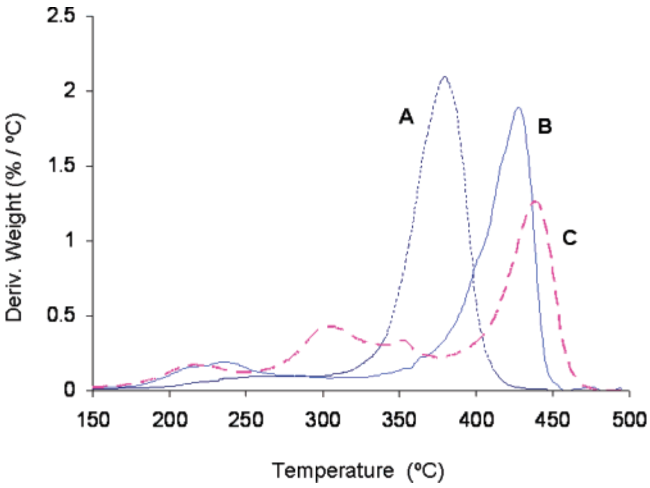


Figure 3. Thermal decomposition of (A) P[(3FOx)(BBOx)-0.89:0.11], (B) P[(3FOx)(C12)-0.89:0.11], and (C) P[(3FOx)(C12)-0.89:0.11]−polyurethane.

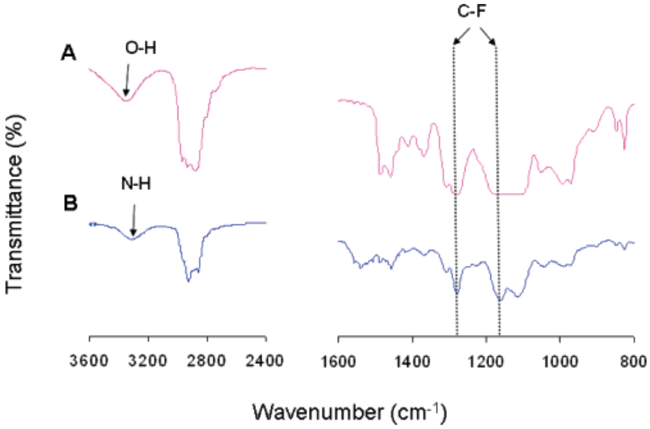


Figure 4. FT-IR spectra for (A) P[(3FOx)(C6)-0.89:0:11] telechelic, (B) P[(3FOx)(C6)-0.89:0:11]−polyurethane. C−F stretch = 1170 and 1280 cm^{-1}; OH stretches for telechelic and NH stretch for polyurethane are labeled.

for soft and hard blocks.[24,35,36] If the polyurethane is well phase separated, the soft block T_g is close to that of the telechelic precursor. Good bulk-phase separation results in enhanced soft block surface concentration.[15] Because of interest in surface functionalization by concentrating P[**AB**]-soft blocks, the degree of bulk-phase separation was examined by MDSC.

T_gs determined by MDSC for the co-polyoxetane soft block polyurethanes and the precursor telechelics are shown in Table 2. A hard block T_g could not be detected in any of the co-polyoxetane polyurethanes. The T_g of the pure HMDI−BD hard block (86 °C) was reported elsewhere.[37] The precursor telechelic T_gs were assumed to be the same as a 100% phase separated soft segments in the corresponding polyurethane. Percent phase mixing was then estimated by applying the Fox equation (eq 3).[38]

$$T_{g(cal)}^{\ \ -1} = w_1 T_{g1}^{\ \ -1} + w_2 T_{g2}^{\ \ -1} \qquad (3)$$

The weight fractions of each component are w_1 and w_2.[35,36] Here, w_1 is chosen as unknown and represents the weight fraction pure soft block in the soft segment phase. T_{g1} is for the pure soft block, T_{g2} for pure hard block, and $T_{g(cal)}$ is for the measured soft block T_g. Table 2 provides the calculated values for w_1. Phase separation is better in the polyurethane series with soft blocks having fluorous side chains. For both C6 (0.97) and C12 (0.99) w_1 is even higher than that reported for the homopolymer based IPDI/BD−P[3FOx].[39] Phase mixing is indicated for P[(ME2Ox)(C6)] ($w_1 = 0.75$) and P[(ME2Ox)(C12)] ($w_1 = 0.73$) polyurethanes. For PEG-like polyurethanes the higher T_gs are likely due to H-bonding between oxygen in the ME2Ox side chains and N−H in hard blocks. This enthalpically driven phase mixing is analogous to that observed for main chain ether-hard block hydrogen bonding.[40]

Thermal Decomposition. P[**AB**]−polyurethane decomposition started at 215 °C and was assigned to amine plus 4-bromobutylaldehyde generation (Scheme 2, eq 2). As above for telechelics, amine and bromobutoxy weight percent was calculated assuming all quaternary ammonium side chains in polyurethane undergo decomposition to yield the corresponding amine and aldehyde. Calculated and measured results given in Table 4 are consistent with loss of amine from alkylammonium and bromobutylaldehyde from remaining **B** side chain. Thermal decomposition between 250 and 400 °C resulted in 30−35% mass loss, which is close to hard block content (Figure 2S). The final decomposition step corresponded to decomposition of remaining soft block at a temperature close to but higher than the corresponding telechelics (450 °C).

Conclusion

Four P[**AB**]−poly(1,3-propylene oxide) co-telechelics **1** were prepared having **A** = 3FOx or ME2Ox and **B** = C6 or C12 alkylammonium side chains (Scheme 1). Substitution on a precursor telechelic with **B** = bromobutoxymethyl was used to introduce the alkylammonium side chains. Telechelics and their precursors were characterized by ^{1}H NMR spectroscopy, including end group analysis for M_n (∼6 kDa). Compositions were confirmed by TGA, as amine and bromobutylaldehyde are generated (220−230 °C) below the decomposition temperature of the main chain.

An interesting result from MDSC showed that soft block T_gs were only modestly perturbed by the formation of alkylammonium side chains. The T_g for the P[(3FOx)(BBOx)-0.89:011] telechelic (−48 °C) may be compared to the corresponding C6 (−38 °C) and C12 (−47 °C) telechelics. The 10 and 1 °C differences in T_gs indicate the introduction of quaternary side chains has little effect on long chain motions associated with T_g. For the ME2Ox telechelics, T_gs were −50 (C6) and −59 °C (C12), which were 18 (C6) and 9 °C (C12) higher than BBOx precursors. The increase in T_{gs} is ascribed to charge clustering as a result of introduction of alkyl ammonium side chains, but since the mole fraction of alkyl ammonium side chains is low, T_g of the telechelics remains well below the room temperature.

Telechelics were incorporated into polyurethanes having 4,4′-(methylene bis(*p*-cyclohexyl isocyanate) (H_{12}MDI) and butanediol (BD) as the hard block. Hard block content was determined by ^{1}H NMR and found close to the feed ratio. Fluorous soft blocks T_gs were close to corresponding telechelics indicating excellent phase separation between hard and soft blocks. Pure soft block weight fractions in soft block domain were 0.96−0.99. ME2Ox soft block T_gs in polyurethanes increased by ∼30 °C, indicating phase mixing, likely due to H-bonding between urethane and ether linkages on the ME2Ox side chain. Thermal decomposition for the alkylammonium polyurethanes started in the same range as the corresponding telechelics. This mass loss is attributed to cleavage of alkylammonium side chains to yield amines and aldehyde. TGA is thus a convenient method for analysis.

Earlier it was noted that charge is conventionally introduced into polyurethanes via hard block modification. For example, water-dispersible polyurethanes are extensively used commercially for coatings.[41-43] Linear polyurethane systems with high percentages of cationic moieties introduced via the chain extender can have drawbacks in terms of mechanical properties and water-swelling.[11]

To our knowledge, this is the first report of polyurethanes with soft blocks bearing charged side chains. At the low mole fractions employed, introducing charge via quaternized side chains on the soft block does not significantly perturb hard block phase separation. Retention of low T_gs for 3FOx containing soft blocks once again provides an example of phase separation driven by a fluorous side chain.

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Supporting Information Available: Figures giving ^{1}H NMR spectra, structures of PSM polyurethanes, and FT-IR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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