



Synthesis and surface mobility of segmented polyurethanes with fluorinated side chains attached to hard blocks

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Abstract

Novel polyurethanes with fluorinated side chains attached to hard blocks were synthesized and characterized by NMR, mass spectroscopy, DSC and gel permeation chromatography (GPC). A unique chain extender, 3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-octyloxy)-propane-1,2-diol (PFOPDOL) was prepared from 3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-octyloxymethyl)-oxirane (PDFOMO) by reacting it with diluted perchloric acid. Poly(ether urethane)s and poly(carbonate urethane)s containing various amounts of the chain extender with fluorinated side chains were then synthesized using methylenebis(phenylene isocyanate) (MDI), polytetramethyleneoxide (PTMO), poly(1,6-hexyl-1,5-pentylcarbonate) diol (PHPCD), 1,4-butandiol (BDO) and PFOPDOL. Mechanical properties of the polyurethanes were characterized by Instron. Surface properties were characterized by X-ray photoelectron spectroscopy (XPS) and contact angle measurements. Results from GPC and Instron studies indicated that fluorinated polyurethanes with high molecular weights and good mechanical properties were obtained. Results from XPS and contact angle studies indicated that the surface of fluorinated polyurethanes were very nonpolar due to migration of fluorinated side chains to the surface.

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1. Introduction

Fluorinated polymers exhibit unique low surface energies [1–4], biocompatibility and biostability [5–8], low water absorptivity, lubricity, thermal and oxidative stability and nonsticking behavior [9]. Consequently, these polymers have attracted considerable interest. Polyurethanes, containing a repeating urethane linkage and having alternating hard and soft segments, exhibit a typical two-phase microstructure and have found wide applications in medical devices due to their good mechanical properties and biocompatibility. Previous studies have shown that hybridizing polyurethane with fluorinated polymers improved the interaction of polyurethane with blood and provided better control of its phase-separated structure at surface [3,10–18]. A majority of these works involved in polymerization and characterization of polyurethanes that contained fluorinated soft segments. Phase-separated surface morphology of

polyurethanes containing fluorinated polyol was studied by Kim et al. [18]. Ratner et al. [19–21] studied the bulk structure of polyurethanes containing fluorinated hard segments with various perfluorinated chain extenders. They noticed that surface topography of such polymers depended strongly on the extent of their phase separation. They concluded that the existence of discrete domains on the surface of these fluorinated polyurethanes was improbable.

One may expect interesting surface mobility for polyurethanes with the fluorinated side chains attached to the hard blocks. Since the hard segments of polyurethanes are usually in their glassy state, the soft segments have higher mobility and can easily migrate to the surface region [21,22]. However, once fluorine side chains are attached to the hard blocks, structure and cohesion of the hard segments can be changed. It becomes possible that both hard segments and soft segments migrate to the surface. Hard segments may migrate to the surface due to the low surface energy of fluorine attached to them, while soft segments migrate to the surface due to their chain mobility

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at room temperature, which is above glass transition temperature (T_g). There is a competition between the rates of migration, which depends on the content of fluorinated side chains attached to hard segments and the T_g of the soft segments.

In this paper, we report the synthesis of polyurethanes with fluorinated side chains attached to the hard blocks. A unique chain extender 3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentafluoro-octyloxy)-propane-1,2-diol (PFOPDOL) was prepared from 3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentafluoro-octyloxymethyl)-oxirane (PDFOMO) by reacting it with diluted perchloric acid (Fig. 1). A series of poly(ether urethane)s and poly(carbonate urethane)s containing various amounts of chain extender with fluorinated side chains were then synthesized using a two-step polymerization method. Surface properties of fluorinated polyurethanes were examined by X-ray photoelectron spectroscopy (XPS) and contact angle measurements using goniometry. We have demonstrated a new methodology of preparing polyurethanes having fluorinated side chains attached to their hard blocks. The fluorinated polyurethanes had relatively high molecular weights and showed good mechanical property. This is important because in many applications good mechanical properties of polyurethanes are required. Effects of fluorine side groups on the surface properties of the fluorinated polyurethanes were also studied.

2. Experimental

2.1. Materials

2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluorooctan-1-ol (PDFOL) was purchased from Aldrich (98% purity). Diiodomethane was purchased from ACROS (99% purity). Epichlorohydrin, 1,6-hexanediol (HD), 1,5-pentanediol (PD), sodium ethoxide and diethyl carbonate (DEC) were used as received. Methylenebis(phylene isocyanates) (MDI) and 1,4-butanediol (BDO) were distilled under vacuum. *N,N*-dimethylacetamide (DMAc) was dried over CaH_2 for 2 days at room temperature, then distilled under vacuum, and stored over 4 Å molecular sieve. Polytetramethylene oxide (PTMO, $M_w = 1000$) from Dupont was dehydrated under reduced pressure at 100 °C for 4 h.

2.2. Synthesis of 3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentafluoro-octyloxymethyl)-oxirane (PDFOMO)

2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluorooctan-1-ol (PDFOL) (4.898 g, 0.012 mol) and epichlorohydrin (7.54 ml, 0.096 mol) were dissolved in 1,4-dioxane (80 ml). Finely powdered sodium hydroxide (0.528 g, 0.132 mol) was added to the stirring solution. The mixture was then heated for 8 h at approximately 70 °C. The mixture was filtered. The filtrate was washed twice with 1,4-dioxane. The combined solution was concentrated under reduced pressure to give PDFOMO. The crude PDFOMO was purified by silica gel column chromatography using hexane/EtOAc (50:1) to yield 2.7 g of PDFOMO (59%), and PDFOL (0.79 g) was recycled. IR (KBr) 3065, 3008, 2936, 2879, 1241, 1209, 1149, 1105, 1020, 960; APCImS (positive mode) m/z theoretical 456 g/mol, observed 495 g/mol (456 + K^+); ^1H NMR (CDCl_3 , TMS) δ ppm (Fig. 1): 2.64 (1H, q, $J = 7.6$ Hz, Hb), 2.84 (1H, t, $J = 9.2$ Hz, Ha), 3.02 (1H, m, Hc), 3.54 (1H, q, $J = 6.0$ Hz, -CH-O-), 3.96–4.13 (3H, m, -CH-O-, - OCH_2CF_2 -).

2.3. Synthesis of 3-(2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentafluoro-octyloxy)-propane-1,2-diol (PFOPDOL)

Thirty milliliter perchloric acid (8%) was added to a solution of PDFOMO (2.7 g, 0.0592 mol) in 60 ml THF. The mixture was stirred for 12 h at room temperature. The perchloric acid was neutralized with sodium bicarbonate. The THF and water were removed on a rotary evaporator, and the residue was dissolved with 50 ml diethyl ether. The salt was removed by two applications of diethyl ether. The diethyl ether was evaporated under reduced pressure. The crude PFOPDOL was purified by silica gel column chromatography using hexane/EtOAc (4:3) to yield 2.25 g of PFOPDOL (80%). IR (KBr) 3387 (-OH), 2926 (- CH_2 -), 2854 (-CH-), 1205–1146 (- CF_2 -, - CF_3), 1052 (C-O-C); APCImS (positive) m/z theoretical 474 g/mol, observed 513 g/mol (474 + K^+); ^1H NMR (DMSO, TMS) δ ppm (Fig. 1): 3.31 (2H, d, $J = 5.2$ Hz, - CH_2 -OH), 3.50 (1H, m, -CH-OH), 4.20 (2H, t, $J = 14.0$ Hz, - OCH_2 - CF_2 -), 4.57 (1H, br, HO- CH_2 -), 4.79 (1H, br, HO-CH-).

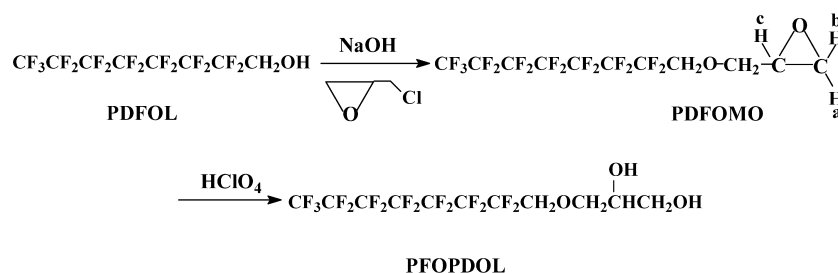


Fig. 1. Synthesis route of PFOPDOL.

2.4. Synthesis of poly(1,6-hexyl-1,5-pentyl carbonate)diol (PHPCD)

1,6-Hexanediol (HD) 40.96 g (0.347 mol), 1,5-pentane-diol (PD) 24.09 g (0.231 mol), diethyl carbonate (DEC) 60.0 g (0.508 mol) and sodium ethoxide 0.21 g (0.031 mol) were added to a three-necked round-bottomed flask fitted with a nitrogen inlet tube. The mixture was heated to 120–130 °C and ethanol was distilled. The temperature was then raised to 140–200 °C, at which time ethanol was completely distilled under vacuum (50 mm Hg) for 6 h. The resulting product was dissolved in methylene chloride, washed with dilute alkali aqueous solution and de-ionized water, and then precipitated with *n*-heptane. The poly(carbonate)diol was dried in vacuum. Yield: 63.5 g (86%). IR (KBr): 3546 (OH), 2939, 2863 (CH₂), 1744 (–CO–), 1256 (OC–O–CH₂); ¹H NMR (CDCl₃, TMS) δ ppm (Fig. 2): 1.42–1.44 (m, 3-H), 1.47–1.52 (m, 6-H), 1.54 (s, OH), 1.58–1.64 (m, 5-H), 1.68–1.76 (m, 2-H), 3.64–3.69 (m, 4-H), 4.12–4.18 (m, 1-H). Hydroxyl number [23]: 106.1 ± 1.3. *M_n*: 1058.

2.5. Synthesis of poly(ether urethane)s

A series of poly(ether urethane)s based on MDI, PTMO, and the chain extender were synthesized using two-step bulk polymerization. The feed ratios are shown in Table 1. In the first step, MDI was added to the stirred PTMO at 40 °C under a dry nitrogen atmosphere. In the second step, after stirring for 40 min at 60–70 °C, chain extender and 1% stannous octoate were added to the melting reaction mixture. The temperature was gradually raised to 100–110 °C. The reaction mixture was cast on a TEFLON plate and put in oven at 100 °C for 10 h and stored at room temperature for 1 week. These polymers were dissolved with THF and precipitated in methanol to remove the low molecular weight fraction, and dried under vacuum at 60 °C for 24 h.

2.6. Synthesis of poly(carbonate urethane)s

A series of poly(carbonate urethane)s based on MDI, PHPCD, and chain extender were synthesized using two-step solution polymerization in DMAc. The feed ratios are shown in Table 1. MDI was added to the stirred DMAc solution of PHPCD under a dry nitrogen atmosphere at 50 °C, and stirred for 1 h at 55–60 °C. Chain extender and 1% stannous octoate were added to the reaction solution while the temperature was kept at 65–70 °C for 20 min, and then the stirring was continued at 80–90 °C for 5 h. Stirring continued at 100–110 °C for 1 h. After the solution was cooled to room temperature and stored for 1 week, the polymer was precipitated in methanol to remove the low molecular weight fraction, and dried under vacuum at 60 °C for 24 h.

2.7. Characterization

2.7.1. Instrumentation

¹H NMR data were obtained with a Varian^{unity} Inova-400 spectrometer (400 MHz). Mass spectra of PDFOMO and PFOPDOL were obtained on an HP1100-LC/MSD with atmosphere pressure chemical ionization (positive mode). The mass spectrum of PHPCD was obtained with a Finnigan LQC^{DECA} (ESI mode).

2.7.2. Mechanical testing

Mechanical testing was carried out with an Instron 4302 Model Universal Testing machine at 23 °C and relative humidity of 50%. The crosshead speed was 500 mm/min. Each sample was cast to form film from 10% (w/v) THF or mixture solvent of THF and DMAc (5:1). They were cut into dumbbells of 5 cm in length and 1 cm in width; the narrow section was 2 cm × 0.5 cm in area and 0.3 mm in thickness. The results reported are the mean values of five replicates.

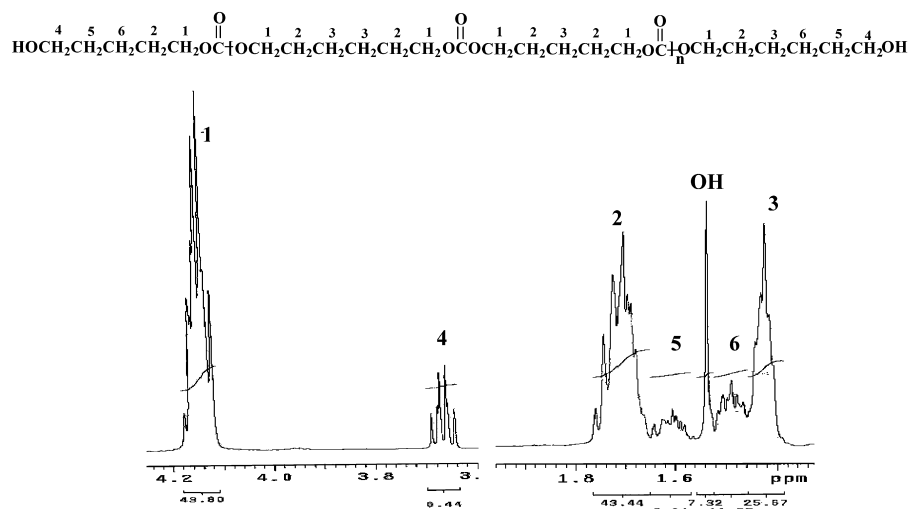


Fig. 2. ¹H NMR spectra of PHPCD.

Table 1
Theoretical composition of segmented poly(ether urethane)s and poly(carbonate urethane)s with various amounts of fluorinated chain extender

Sample	Molar ratio of MDI/chain extender/PTMO (or PHPCD)	Chain extender BDO, PFOPDOL (mol)	Hard segment (wt%)	Fluorine atom (wt%)
PEU	2:1:1	1.0, 0.0	37.1	0.0
FPEU20	2:1:1	0.8, 0.2	40.0	3.4
FPEU50	2:1:1	0.5, 0.5	43.9	8.0
FPEU100	2:1:1	0.0, 1.0	49.3	14.4
PCU	2:1:1	1.0, 0.0	35.8	0.00
FPCU20	2:1:1	0.8, 0.2	38.7	3.3
FPCU50	2:1:1	0.5, 0.5	42.5	7.7
FPCU100	2:1:1	0.0, 1.0	47.9	14.0

2.7.3. Molecular weight determination

GPC was carried out on an HP1100 using two PLgel columns ($10\mu\text{m } 10^4\text{ \AA}$, $10\mu\text{m } 500\text{ \AA}$). Molecular weights are relative to monodisperse polystyrene standards. The mobile phase was THF or DMF. Sample concentration was 1.000 g/l. The detector was RID and the flow rate was 1.000 ml/min.

2.7.4. X-ray photoelectron spectroscopy

XPS was carried out on an XSAM-800 electron spectrometer. The spectrometer was equipped with a Mg K α achromatic X-ray source (20 kV, 10 mA) and two take-off angles of 30 and 90° were used with X-ray source. Each sample for XPS was prepared by casting the polymer onto a clean silicon wafer from 10% (w/v) THF or a mixture of the solvents THF and DMAc (5:1). The samples were kept in an oven at 40 °C for 24 h, 50 °C for 12 h, and 60 °C for 3 days under vacuum.

2.7.5. Contact angle measurements and evaluation of surface tension

Contact angles were measured with an Eyma contact angle goniometer. Each sample for contact angle measurement was prepared by casting the polymer onto a clean silicon wafer from 10% (w/v) THF or a mixture of the solvents THF and DMAc (5:1). The silicon wafers were kept in an oven at 40 °C for 24 h, 50 °C for 12 h, and 60 °C for 24 h under vacuum. Contact angles were measured on 3 μl of wetting solvent at 20 °C, and the results reported are the mean values of 10 replicates.

2.7.6. DSC measurements

TA instrument 2910 thermal analyzer was used in this study to measure T_g . The polymer samples (15–20 mg) were cut off from dry films. These samples were cooled to –100 °C using liquid nitrogen. Data were collected at a heating rate of 10 °C/min from –100 to 80 °C.

3. Results and discussion

3.1. Synthesis of poly(1,6-hexyl-1,5-pentyl carbonate)diol (PHPCD)

The PHPCD was prepared with 1,6-hexanediol/1,5-pentanediol (3:2) and diethyl carbonate [24]. From the ^1H NMR spectrum of the PHPCD (Fig. 2), we assign the multiple peak at $\delta = 4.12\text{--}4.18$ ppm to the methylene protons bonded with carbonyl groups because the peak of the methylene protons bonded with hydroxy group is at $\delta = 3.64\text{--}3.69$ ppm. In addition, integration of the multiple peaks at $\delta = 4.12\text{--}4.18$ ppm is approximately seven times as that of the peak at $\delta = 3.64\text{--}3.69$ ppm, and the multiple relationship between these two peaks is identical to the polymerization degree of PHPCD according to its molecular weight ($M_n = 1058$). It is concluded that the reaction between 1,6-hexanediol/1,5-pentanediol and diethyl carbonate indeed takes place and PHPCD is obtained. This is further proved by mass spectrum results (Fig. 3). The dominating molecular ionic peaks ($M + \text{Na}^+$) are from PHPCD, indicating that the PHPCD is a copolymerization product of 1,6-hexanediol with (HD), 1,5-pentanediol (PD) and diethyl carbonate (DEC). Molecular ionic peaks of the oligomer of eight degree of polymerization are listed in Table 2. As an example, the peak at 1079.7 belongs to the oligomer (1 mol) copolymerized from HD (3 mol), PD (5 mol) and DEC (7 mol). It can be concluded that PHPCD is a copolymerization product of 1,6-hexanediol/1,5-pentanediol and diethyl carbonate.

Table 2
The molecular ionic peaks and composition of the oligomer (1 mol) with eight degree of polymerization

m/z peak	HD (mol)	PD (mol)	DEC (mol)
1079.7	3	5	7
1093.7	4	4	7
1107.7	5	3	7
1121.6	6	2	7

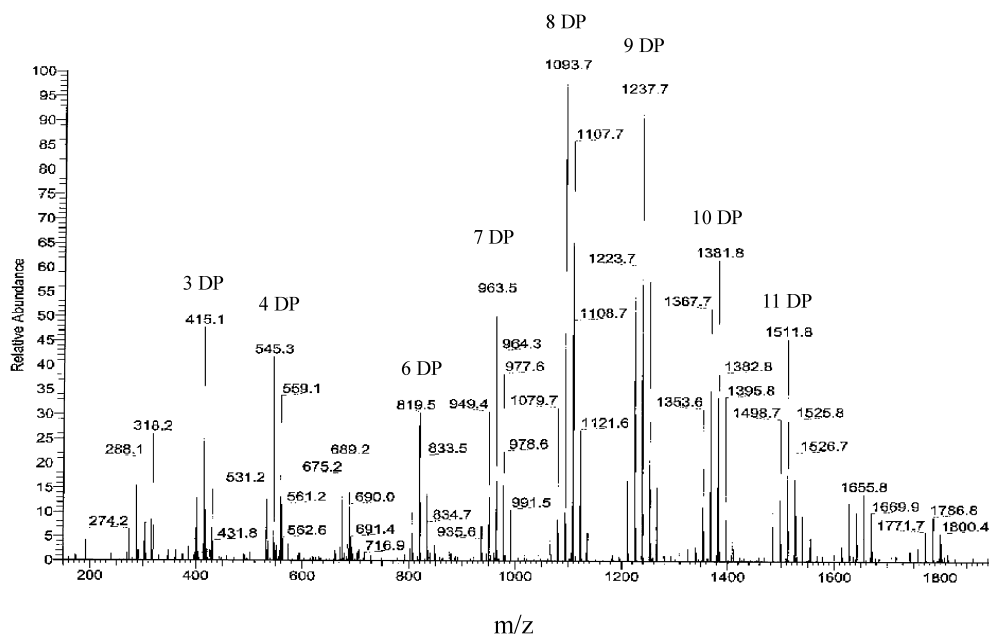


Fig. 3. MS spectra of PHPCD (DP, degree of polymerization).

3.2. Synthesis of polyurethanes with fluorinated side chains attached to hard blocks

A series of fluoropoly(ether urethane)s and fluoropoly(carbonate urethane)s with various amounts of chain extender containing 1*H*,1*H*-perfluorooctyl groups in the side chain (C_7F_{15}) were prepared. The schematic structures of these fluoropolyurethanes are shown in Fig. 4. By changing the ratio of MDI/chain extender/PHPCD (or PTMO), the content of fluorine attached on the hard block can be controlled, as listed in Table 1. The chain extender without fluorine was also used to prepare conventional polyurethanes (PCU or PEU) for comparison. The fluorine contents are in the range of 3.3–14.4 wt% (atomic percentage of fluorine: 2.4–11.1%) and the content of hard segments slightly increase from 38.5 to 49.3 wt% with increasing fluorine content. To study the surface properties of our fluorinated polyurethanes, all polymers in solution were precipitated in methanol to remove the low molecular

weight fractions [19]. The gel permeation chromatography (GPC) traces of unpurified and purified of FPEU20 are shown in Fig. 5. It confirms that the low molecular weight fraction is removed by the purification method described above. Molecular weights and molecular weights distribution were determined by GPC vs. polystyrene standards, and the result is listed in Table 3. The molecular weights of FPCU50 and FPCU100 were determined in DMF because these samples were not completely dissolved in THF. All the samples have relatively high molecular weight (M_n is from about 40,000 to about 60,000) and narrow molecular weight distribution. The highest M_n (about 128,000) was obtained from FPEU50. Tensile properties of the fluoropoly(ether urethane)s and fluoropoly(carbonate urethane)s are summarized in Table 4. Since there are differences in molecular weight among the samples, tensile strengths cannot be compared straightly. The general trend is that tensile strength and elongation decrease with increasing fluorine content. Nevertheless, FPCU20 and PCU, both

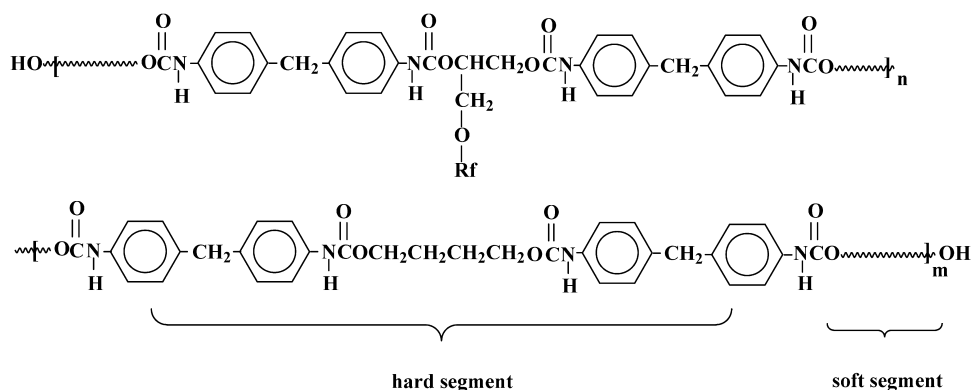


Fig. 4. Schematic structure of fluoropolyurethanes. $R_f = CH_2(CF_2)_6CF_3$; $n = 1, 2, 3, \dots$, $m = 0, 1, 2, 3, \dots$. Soft segment is PTMO or PHPCD.

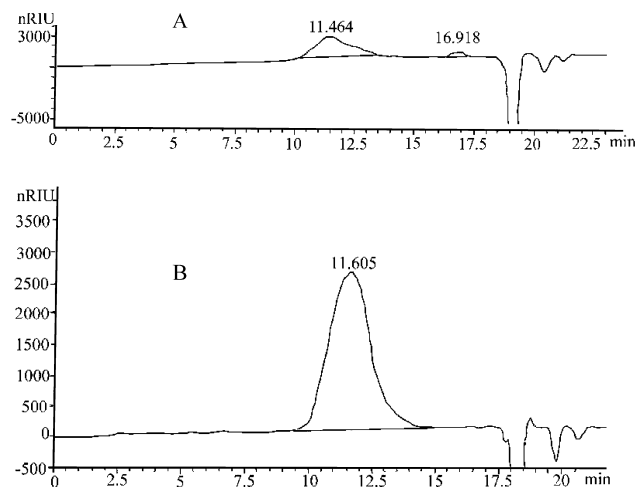


Fig. 5. Gel permeation chromatograms for unpurified (A) and purified (B) of FPEU20. The low molecular weight fraction was removed by reprecipitation in methanol.

having similar molecular weight, showed similar mechanical properties. Our results indicate that it is possible to synthesize fluorinated polyurethanes with high molecular weight and good mechanical properties comparable to conventional polyurethanes.

3.3. Surface properties

Several methods are currently used to estimate surface tension (γ) of a solid from contact angle data. The method developed by Owens and Wendt [25] has been criticized because the polar interactions depend on the probe liquids chosen [26–28]. Fowkes' equation [29] neglected the polar interaction term such that its predicted interfacial tension values have significant error for polar polymer pairs [30,31].

Kaelble [32] extended Fowkes' equation to include a polar energy term $2(\gamma_1^p \gamma_2^p)^{1/2}$:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^d \gamma_2^d)^{1/2} - 2(\gamma_1^p \gamma_2^p)^{1/2} \quad (1)$$

in which γ_{12} is interfacial tension, γ_1 and γ_2 are surface tensions, d is dispersion component and p is polar component. Wu [33] found an equation (Eq. (2)) for

calculating the interfacial tension between polymers and an ordinary liquid. This harmonic mean equation is preferable to the geometric-mean equation (Eq. (1)).

$$\gamma_{12} = \gamma_1 + \gamma_2 - \frac{4\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} - \frac{4\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p} \quad (2)$$

Eq. (2) can also be used to estimate γ^d and γ^p of a solid polymer from its contact angles of water and diiodomethane [33]. Consequently, the equation is used to estimate the surface tension of fluorinated polyurethanes using nonlinear regression by a computer program in our study. For our calculation, Eq. (2) is rearranged into two equations (Eq. (3) for water and Eq. (4) for diiodomethane) according to Wu:

$$(1 + \cos \theta_{\text{H}_2\text{O}})\gamma_{\text{H}_2\text{O}} = 4 \left(\frac{\gamma_{\text{H}_2\text{O}}^d \gamma^d}{\gamma_{\text{H}_2\text{O}}^d + \gamma^d} + \frac{\gamma_{\text{H}_2\text{O}}^p \gamma^p}{\gamma_{\text{H}_2\text{O}}^p + \gamma^p} \right) \quad (3)$$

$$(1 + \cos \theta_{\text{CH}_2\text{I}_2})\gamma_{\text{CH}_2\text{I}_2} = 4 \left(\frac{\gamma_{\text{CH}_2\text{I}_2}^d \gamma^d}{\gamma_{\text{CH}_2\text{I}_2}^d + \gamma^d} + \frac{\gamma_{\text{CH}_2\text{I}_2}^p \gamma^p}{\gamma_{\text{CH}_2\text{I}_2}^p + \gamma^p} \right) \quad (4)$$

in which $\gamma = \gamma^d + \gamma^p$, $\gamma_{\text{H}_2\text{O}} = \gamma_{\text{H}_2\text{O}}^d + \gamma_{\text{H}_2\text{O}}^p$, $\gamma_{\text{CH}_2\text{I}_2} = \gamma_{\text{CH}_2\text{I}_2}^d + \gamma_{\text{CH}_2\text{I}_2}^p$, γ is surface tension, d is dispersion component and p is polar component, $\theta_{\text{H}_2\text{O}}$ and $\theta_{\text{CH}_2\text{I}_2}$ are contact angles of the polymer with water and diiodomethane, respectively. The numerical values used are $\gamma_{\text{H}_2\text{O}}^d = 22.1$ dyn/cm, $\gamma_{\text{H}_2\text{O}}^p = 50.7$ dyn/cm, $\gamma_{\text{CH}_2\text{I}_2}^d = 44.1$ dyn/cm, $\gamma_{\text{CH}_2\text{I}_2}^p = 6.7$ dyn/cm.

Surface structure of polymers containing small amount of fluorinated blocks or end fluorinated chains is dramatically different from the bulk structure. Surface topography of poly(ether urethane)s and poly(ether urethane urea)s with various perfluorinated chain extenders depended strongly on the extent of phase separation [19,21]. Chains ending with a fluorinated group were found to migrate to the surface of polymers easily [34–36]. For our polyurethanes with fluorinated side chains attached to the hard blocks, it is possible that both hard segments and soft segments can migrate to the surface. Hard segments migrate to surface due to the low surface energy of fluorine attached on them, while soft segments migrate to surface due to their chain mobility

Table 3
Molecular weights and glass transition temperature (T_g) of segmented poly(ether urethane)s and poly(carbonate urethane)s

Sample	$M_n (\times 10^{-4})$	$M_w (\times 10^{-4})$	M_w/M_n	Soft segment T_g ($^{\circ}\text{C}$)	Hard segment T_g ($^{\circ}\text{C}$)
PEU	5.8529	12.390	2.1168	-45.2	-
FPEU20	4.5771	8.2454	1.8014	-45.1	-
FPEU50	12.782	32.080	2.5097	-33.4	-
FPEU100	4.6964	6.9224	1.4740	-37.2	-
PCU	5.8264	9.9543	1.5249	-3.6	52.4
	16.311 ^a	24.873 ^a	1.7085 ^a		
FPCU20	4.1176	5.9757	1.4513	1.5	57.3
	12.347 ^a	21.226 ^a	1.7192 ^a		
FPCU50	6.4687 ^a	9.4571 ^a	1.4620 ^a	-7.5	58.1
FPCU100	6.0226 ^a	9.1818 ^a	1.5245 ^a	-8.9	57.2

^a Solvent is DMF in GPC measurement.

Table 4
The strain–stress results of fluoropoly(ether urethane)s and fluoropoly(carbonate urethane)s

Sample	Ultimate tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)
PEU	41.9 ± 2.1	18.1 ± 3.5	675.3 ± 22.5
FPEU20	24.6 ± 3.0	9.1 ± 0.3	870.6 ± 15.0
FPEU50	28.3 ± 1.7	17.9 ± 4.1	757.7 ± 46.7
FPEU100	/	/	/
PCU	57.9 ± 4.1	22.9 ± 2.2	369.7 ± 31.8
FPCU20	57.5 ± 3.3	20.6 ± 3.1	440.6 ± 32.9
FPCU50	15.5 ± 1.6	39.6 ± 3.7	228.3 ± 43.6
FPCU100	12.4 ± 1.7	76.6 ± 16.3	147.1 ± 45.1

at room temperature (above T_g as shown in Table 3). Measurement of contact angles with water and diiodomethane was carried out, and the result is listed in Table 5. One observes a sharp increase in contact angles with small amount of fluorinated side chain attached to the hard block for both fluorinated polyurethanes. The increased water contact angle and low surface tension of the fluoropoly(ether urethane)s and fluoropoly(carbonate urethane)s demonstrate that the surfaces become significantly non-polar, indicating that the fluorinated side chains in the hard segment indeed migrate to the surfaces. According to prior literature, poly(tetrafluoro ethylene) has a critical surface tension (CST) of 18.5 dyn/cm [37], and a monomolecular film of perfluorododecanoic acid on platinum has a CST of 5.6 dyn/cm [38]. The lower critical surface tension reflects higher concentration of CF_3 groups on the surface [38]. Fluoropoly(ether urethane)s and fluoropoly(carbonate urethane)s in the present study have also shown relatively low surface tensions (Table 5). For FPCU100 and FPEU100, a surface tension of 15.5 and 16.2 dyn/cm is obtained, respectively, indicating that significant amount of CF_3 groups have migrated onto the outermost surface.

To further examine the surface properties, an XPS experiment was carried out. The results are summarized in Table 6. For an XPS measurement, take-off angle correlates to the depth of having been detected. At a take-off angle of

30°, near surface (i.e. about 50 Å) structures are detected. At a take-off angle of 90°, this penetrating depth is about 10 nm from the surface. The amount of nitrogen and elemental fluorine at surface represents the amount of hard block and fluorinated side chain migrating to the surface, respectively. As shown in Table 6, the amount of surface elemental nitrogen increases as the amount of the fluorinated chain extender (i.e. PFOPDOL) increases. This indicates that more hard segments have been pulled to the surfaces with the help of fluorinated side chains. For PCU, its measured surface nitrogen content is 2.1%, compared with 0% for PEU. This is due to phase mixing between hard and soft segments in PCU, resulting from hydrogen bonding between the soft and hard blocks. On the other hand, very interestingly, the highest surface fluorine content is not seen from fluoropolyurethanes with the highest bulk fluorine content (i.e. FPCU100 or FPEU100), but from fluoropolyurethanes with the lowest or intermediate bulk fluorine content. For the fluoropoly(carbonate urethane) system, FPCU50 has the highest surface fluorine content, while FPEU20 has the highest fluorine content for the poly(ether urethane) system.

Also, it is noted that the measured surface nitrogen content is smaller than the theoretical bulk nitrogen content, while the measured surface fluorine content is much higher than the theoretical bulk fluorine content. For fluorine, the ratio of its surface content and theoretical bulk content ($F_{\text{surface}}/F_{\text{bulk}}$) is about 10–20 for FPCU 20 and FPEU20, but decreases with the increasing fluorine content (i.e. 2–3 for FPCU 100 and FPEU100). This result suggests a high mobility of fluorinated side chains at low bulk content but a low mobility at high content.

Table 5
Contact angle and surface tension results of fluoropolyurethanes

Sample	CH_2I_2 (stationary)	H_2O (°) (stationary)	Surface tension (dyn/cm) ^a		
			γ^d	γ^p	γ
PCU	49.5 ± 0.9	75.0 ± 1.5	26.2	13.9	40.1
FPCU20	84.3 ± 1.9	101.6 ± 1.0	13.9	6.8	20.7
FPCU50	88.6 ± 1.6	106.8 ± 0.8	12.9	5.6	18.5
FPCU100	94.5 ± 0.7	113.0 ± 1.4	11.9	3.6	15.5
PEU	56.1 ± 0.7	72.0 ± 1.4	22.8	16.8	39.6
FPEU20	88.0 ± 1.6	100.6 ± 1.4	12.0	8.2	20.2
FPEU50	87.5 ± 1.1	107.0 ± 1.4	13.9	4.8	18.7
FPEU100	93.6 ± 0.8	110.5 ± 1.1	11.6	4.6	16.2

^a γ is the surface tension. γ^d and γ^p are the dispersion and polar components of γ , respectively.

4. Conclusions

In summary, we have successfully prepared novel polyurethanes with fluorinated side chains attached to hard blocks. These fluoropolyurethanes have high molecular weight, narrower molecular weight distribution and good mechanical properties (FPCU20). Surface of the fluoropolyurethanes become very nonpolar with small amount of fluorine side chains attached to the hard blocks due to

Table 6
Atomic percentages of fluorine and nitrogen in the fluoropolyurethanes

Sample	Take-off angle (°)	N (%)	N (%) bulk (theoretical)	F (%)	F (%) bulk (theoretical)	F (%) surface/F (%) bulk ^a
PEU	30	0.0	3.5	0.0	0.0	/
	90	0.7		0.0		/
FPEU20	30	1.9	3.4	39.4	2.6	15.2
	90	2.6		31.8		12.2
FPEU50	30	2.3	3.2	32.3	6.0	5.4
	90	2.6		27.8		4.6
FPEU100	30	2.3	3.0	32.6	11.1	2.9
	90	3.6		27.3		2.5
PCU	30	2.1	3.3	0	0.0	/
	90	3.4		0		/
FPCU20	30	2.7	3.2	26.4	2.4	11
	90	3.4		17.4		7.3
FPCU50	30	2.9	3.0	36.4	5.7	6.4
	90	4.2		27.7		4.9
FPCU100	30	3.3	2.8	29.0	10.5	2.8
	90	4.1		22.4		2.1

^a Data from theoretical value.

migration of fluorine side chains to the surface of fluoropolyurethanes.

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