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Preparation and Characterization of Polyurethanes Based on a Series of Fluorinated Diols

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This research is part of an effort directed toward obtaining polymers with minimally adhesive surfaces. Fluorinated polyurethanes based on a series of ethylene–fluoroalkyl–ethylene diols and hexamethylene diisocyanate were prepared and characterized to include a preliminary evaluation of surface properties. Polymerization was carried out both in bulk and in tetrahydrofuran solution. Glass transition temperatures of the resulting polymers were ca. 20 °C. Average molecular weights, determined by GPC, were in the range $M_w = (12\text{–}54) \times 10^3$. Mechanical properties were determined using an Instron tester. Young's modulus ranged from 1 to 56 MPa depending on composition and processing history. High strain-at-break values were observed ranging from ca. 900 to 1800%. A significant decrease in surface free energy from 31.5 to 25.5 erg/cm^2 was seen with an increase in the fluorocarbon content from 58 to 64 wt %.

Introduction

Problems with toxicant release coatings, which inhibit the settlement of organisms in the marine environment through the release of agents such as tributyltin hydroxide,[1,2] have led to the exploration of an alternative approach to fouling control based on the design of minimally adhesive polymer surfaces.[3] This work is an extension of the "fouling release" concept pursued by Griffith et al.[4] Our effort is ultimately aimed at discerning the compositional and morphological features which create a surface minimally attractive for the settlement of marine organisms.

In the pursuit of this goal, we have taken advantage of the availability of a new family of fluorinated diols of the formula $HOC_2H_4[CF_2CF(CF_3)]_x(CF_2)_4[CF_2CF(CF_3)]_yC_2H_4OH$ synthesized by Baum.[5,6] Previously, fluorinated diisocyanates,[7] diols, and diamines[8,9] have been incorporated into polyurethanes to enhance environmental stability and antithrombogenicity of the materials. In this investigation we have sought to incorporate the new fluorinated diols into polymers which might have interesting surface properties. Polymerization reactions between members of this family of diols and hexamethylene diisocyanate (HDI) were carried out (Scheme I). HDI was chosen for study because polyurethanes based on aliphatic diisocyanates have been known to exhibit good resistance to weathering, chemicals and abrasion.[10]

Scheme I

$$HOCH_2CH_2(CF_2CF(CF_3))_x(CF_2)_4(CF_2CF(CF_3))_y\text{-}CH_2CH_2OH$$

1a, C_7 diol, $x + y = 1$
1b, C_9 diol, $x + y = 1.67$
1c, C_{11} diol, $x + y = 2.47$

$$+ \underset{\mathbf{2}}{OCN\text{–}(CH_2)_6\text{–}NCO} \rightarrow$$

$$\text{–}[OCH_2CH_2(CF_2CF(CF_3))_x(CF_2)_4(CF_2CF\text{-}(CF_3))_yCH_2CH_2O\text{–}OCNH\text{–}(CH_2)_6\text{–}NHCO]_n\text{–}$$

3, $x + y = 1$, polymerized in bulk
4, $x + y = 1.67$, polymerized in THF
5, $x + y = 1.67$, polymerized in bulk
6, $x + y = 2.47$, polymerized in THF
7, $x + y = 2.47$, polymerized in bulk

The interesting time dependence of morphology and mechanical properties for polymers derived from C_7 diol (**1a**) and HDI (**2**) has been described previously.[3] In this paper, an investigation of polyurethanes prepared according to Scheme I with higher "mixed diols" is presented. These mixed diols were derived from the successive addition of hexafluoropropene to the perfluorobutane diiodide starting material, followed by addition of ethylene to the terminal carbon-iodine bonds and conversion of C–I functionality to alcohol.[5,6] The purpose of this work

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(1) Evans, C. J. *Tin Its Uses* **1978,** *115,* 11.
(2) Phillip, A. T. *Prog. Org. Coatings* **1973,** *2,* 159.
(3) Ho, T.; Wynne, K. J. *Macromolecules* **1992,** *25,* 3521.
(4) Brady, R. F.; Griffith, J. R.; Love, K. S.; Field, D. E. *J. Coatings Technol.* **1987,** *59,* 113.
(5) Baum, K.; Malik, A., private communication.
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was to compare the properties of C_9- and C_{11}-derived polymers to those based on C_7 diols.

Experimental Section

Materials. Fluorinated diols **1a–c** molecular weights 440, 540, and 660, respectively, were prepared at Fluorochem, Inc., Azusa, CA.[5,6] We refer to the diols as C_7-, C_9-, and C_{11}- because these designations represent the average number of carbons bearing fluorines. Hexamethylene diisocyanate (HDI, MONDUR HX from Mobay) was distilled under vacuum. THF was distilled from Na/benzophenone under nitrogen.

Polymerization. Polymerization of the fluorinated diols **1a–c** with HDI (**2**) was carried out in bulk as well as in tetrahydrofuran (THF) solution (Scheme I). In each case, the polymerization was carried out in a dried three-necked flask under dried nitrogen, and dibutyltin dilaurate was used as catalyst. Because of the exploratory nature of these reactions, a detailed account is presented in the Results and Discussion section.

Characterization. *Viscometry.* Absolute viscosities of the diols were measured with a Brookfield viscometer (Model RVTD, spindle no. 4). The viscometer was calibrated with silicone oil viscosity standards supplied by Brookfield Engineering Laboratories, Inc. The diol was contained in a test tube, i.d. = 7.25 mm, and temperature control was achieved through a water bath.

Gel Permeation Chromatography (GPC). Molecular weight was determined by GPC. The equipment consisted of a Hewlett-Packard Series 1050 pump and two Altex μ-spherogel columns (size 10^3 and 10^4 Å, respectively) connected in series. Polymer in the effluent was detected with a Wyatt/Optilab 903 interferometric refractometer, and the average molecular weights were determined using polystyrene standards as references. The mobile phase was THF, and the concentration of the polymer was 1 wt %.

Differential Scanning Calorimetry (DSC). A Perkin-Elmer DSC 7 instrument was used. The scanning rate was 10 °C/min. Samples were inserted at room temperature, taken immediately to −50 °C, scanned to 200 °C, quenched (200 °C/min) to −50 °C, and rescanned.

Infrared (IR) Spectroscopy. Infrared spectra were collected on a Perkin-Elmer 1800 FTIR instrument on KBr plates, using thin films obtained via evaporation of THF solutions.

NMR Spectroscopy. NMR spectra were obtained on a Bruker AMX 400 spectrometer operating at 400.13 and 100.62 MHz for ^{1}H and ^{13}C acquisition, respectively. A 5-s receiver delay was employed for ^{1}H acquisition and a 2.5-s delay for ^{13}C. For both nuclei a 30° pulse width was used. All samples were prepared as solutions in chloroform-*d*, and the spectra were referenced to residual $CHCl_3$ (^{1}H) or chloroform-*d* (^{13}C). The ^{13}C spectra were ^{1}H-decoupled and ^{19}F-coupled. Time constraints prevented full definition of the fluorinated ^{13}C region.

Elemental Analysis. Elemental analyses were performed at E&R Microanalytical, Corona, NY.

Contact Angle Analysis. Advancing contact angle measurements were performed with an NRL A-100 contact angle goniometer (commercially available through Ramé-Hart, Inc). Sample films were prepared from 10 wt % solution in THF, cast into aluminum pans lined with Teflon, and dried in a hood for 1 week. The films were kept under inverted beakers in the hood to reduce contact with contaminants. Only the surface formed at the air–solution interface was examined.

Mechanical Tests. Stress–strain tests were performed in an Instron Universal Testing Instrument (Model 4206). Standard type V specimens as specified in ASTM Standards, Method D-638, were used.

Results and Discussion

Polymerization. *Viscosity of the Fluorinated Diols.* Absolute viscosities of the diols at temperatures from 24 to 66 °C were measured to facilitate the selection of the method and conditions of polymerization. The viscosities of the diols exhibit no dependence on the spin rate (the effective shear rate was from 0.046 to 4.6 s^{-1}) and show an Arrhenius-type dependence on temperature. Correlations between viscosity and the absolute temperature were found using linear regression techniques. They are

$$\text{for } C_7 \text{ diol} \qquad \mu\ (\text{poise}) = 13.9e^{7449(1/T-1/297)}$$

$$\text{for } C_9 \text{ diol} \qquad \mu\ (\text{poise}) = 41.7e^{8588(1/T-1/298)}$$

$$\text{for } C_{11} \text{ diol} \qquad \mu\ (\text{poise}) = 214e^{9523(1/T-1/297.5)}$$

Bulk Polymerization. The mixing of reactants and catalyst in this investigation was achieved using a magnetic stirrer (Corning hot plate stirrer PC-351). Empirically, it was found that 3 P was the upper limit of viscosity for the stirrer to function well. This limit set a threshold temperature for each diol for magnetically stirred bulk polymerizations. Using the above correlations, the threshold temperatures are 43 °C for C_7 diol, 55 °C for C_9 diol, and 70 °C for C_{11} diol.

Mixtures of C_7 diol (**1a**) and HDI exhibit good fluidity and mild reactivity at temperatures between 50 and 70 °C, and the reaction carried out in bulk for 18 h produced polymers soluble in THF. On the other hand, mixtures of C_9 diol (**1b**) and HDI, and C_{11} diol (**1c**) and HDI are more viscous at those temperatures. To achieve the same level of fluidity in the initial reaction mixture, the reaction was carried out at higher temperatures, 70 °C for C_9 diol and 90 °C for C_{11} diol. In these systems, bulk polymerization resulted in a mixture of linear polymers and gel after 18 h. THF was then added into the mixture to extract the soluble linear polymer. The separation of the soluble and insoluble portions was achieved by decantation, and the soluble polymers were recovered as cast films. These latter two polymerizations were also carried out in THF solution.

Solution Polymerization. Fluorinated diols **1b** and **1c** react with hexamethylene diisocyanate in THF in the presence of dibutyltin dilaurate catalyst to give polyurethanes having structures **4** and **6** (Scheme I). In a typical synthesis, 1.7×10^{-6} mol of dibutyltin dilaurate was added to a solution of 1.91×10^{-3} mol of hexamethylene diisocyanate (HDI, **2**) in 0.5 mL of THF. A solution of 1.250 g of **1c** in 1.5 mL of THF was then added. The solution was stirred for 2 h at 25 °C, after which time the solution was very viscous. THF (22 mL) was added, and the mixture was heated at 68 °C. The soluble fraction was decanted from the insoluble fraction. The soluble fraction was poured into 500 mL of methanol, yielding a white precipitate. After filtration and removal of solvent *in vacuo*, the ratio of the weight of the soluble fraction to that of the insoluble was 6.6. The combined yield of these fractions of **6** was 59%. Less than complete turnover, which is a general phenomenon in these solution polymerizations (the range is 49–89%), could conceivably be attributed to biuret and allophanate formation, crosslinking, and subsequent nonprecipitation of unreacted diol or low molecular weight polymer.[11] The catalyst is necessary for reasonable reaction time in THF solution. An experiment without it resulted in no methanol-precipitated material after 7 days using **1c** and **2**.

IR Spectra. The infrared spectra of these materials exhibit the complete disappearance of the NCO peak at

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(11) Munk, P. *Introduction to Macromolecular Science*; John Wiley & Sons: New York, 1989; p 111.

Table I. Coupling Constants in the ^{1}H NMR Spectra of Diols 1a–c[a]

diol	peak	J_{HH}, Hz	J_{HF}, Hz
1a (C_7 diol)	d	6.4	18.9
	e		
	g	7.1	
	h	6.4	
1b (C_9 diol)	d	6.3	18.8
	e		
	g	6.9	
	h	6.3	
1c (C_{11} diol)	d		
	e		
	g	7.1	
	h	6.4	

[a] Dashes represent coupling constants which could not be measured due to multiple peaks or line broadening.

Table II. ^{13}C–^{19}F Coupling Constants for Diols and Polyurethanes

	peak	J_{CF}, Hz (multiplicity)
1a (C_7 diol)	b	19.9 (d)
	d	21.2 (t)
	f	4.7 (t)
	g	8.8 (d)
1b (C_9 diol)	b	18.6 (d)
	d	21.0 (t)
1c (C_{11} diol)	b	19.7 (d)
	g	8.4 (d)
3	b	23.2 (d)
	d	23.2 (t)
5	b	20.6 (d)
	d	27.0 (t)
7	b	23.2 (d)

2280 cm^{-1}.[12] For both C_9 and C_{11} polyurethane the expected broad C–F stretching region is present, at 950–1400 cm^{-1}. Other peaks are assigned as follows:[13] 1710, $\nu_{C=O}$; 2865, $\nu_s(CH_2)$; 2940, $\nu_{as}(CH_2)$; 3340 (broad), ν_{NH}, ν_{OH}.

^{1}H NMR Spectra. *Diols.* The proton NMR spectra and assignments in Figure 1 give insight into the structural details of the polyurethane prepared via Scheme I. Lower field and resolution spectra have been reported previously for the diisocyanate[3] and **1a**.[5]

Diols **1a–c** exhibit an OH singlet in the δ 1.5–1.8 region. Peaks d, e, g, and h represent CF_2CH_2, $CF(CF_3)CH_2$, $CF(CF_3)CH_2CH_2$, and $CF_2CH_2CH_2$, respectively. The coupling constants associated with these four multiplets, given in Table I, indicate that d is coupled with h (J_{HH} 6.3–6.4 Hz), and e with g (J_{HH} 6.9–7.1 Hz).

The high-resolution NMR data allow a detailed analysis of the compositions of **1a–c**. Previous analysis of the iodide precursors[6] leads to the expectation that diol **1a** consists of $HOCH^{h}_{2}CH^{d}_{2}(CF_2)_4CF_2CF(CF_3)CH^{e}_{2}CH^{g}_{2}OH$ (C_7–I) plus a small amount of $HOCH^{h}_{2}CH^{d}_{2}(CF_2)_4CF(CF_3)CF_2CH^{d}_{2}CH^{h}_{2}OH$ (C_7–II). Our spectra show that the g triplet in **1a** is only slightly lower in area than h. If the diminished peak area of the g triplet is attributed to the presence of C_7–II, the relative areas indicate the C_7–I and C_7–II percentages, respectively, are 98.4 and 1.6.

An examination of the spectra for the C_7, C_9, and C_{11} diols in Figure 1B,D,F shows the steady growth of g and e peaks due to CH_2's adjacent to $-CF(CF_3)-$ and the steady diminution of d and h peaks due to CH_2's adjacent to $-CF_2-$. These data support the continued dominant addition of the perfluoropropenyl group in such a way as to place a $CFCF_3$ group at the terminus of the chain. Thus, assuming that the C_9 diol consists mainly of C_7–I and C_{10}–I ($HOCH^{g}_{2}CH^{e}_{2}CF(CF_3)CF_2(CF_2)_4CF_2CF(CF_3)CH^{e}_{2}CH^{g}_{2}OH$) and ignoring contributions from C_7–II and small amounts of higher oligomers, a molecular mass for C_9 diol of 475 g/mol may be calculated. Baum[5] determined the molecular weight of the C_9 diol (540) by quantitative ^{1}H and ^{19}F NMR spectroscopy. The latter value was used in polyurethane synthesis. We conclude that higher oligomers (and isomers) account for our low value.

An analogous calculation using the ^{1}H g:h ration for the C_{11} diol gives a much lower value (537 g/mol) than that of Baum (660 g/mol). This is because of the increasing contribution of higher oligomers (C_{13} and higher) which have spectra indistinguishable from the C_{10} diol.

Polyurethanes. All three polyurethanes exhibit two broad singlets in the δ 1.3–1.6 region due to the central four methylenes of the hexamethylene unit. The remaining CH_2N resonance occurs as a multiplet at δ 3.2. For the ethylene protons, a broad multiplet is found at δ 2.5 (d and e), while a multiplet at δ 4.3 is assigned to g and h. The same e:d and g:h area ratio trends discussed for the diols above are in evidence. The NH peak (i) of the polyurethanes appears at δ 4.9. This is consistent with the position of this peak in ethyl *N*-ethylcarbamate ($CH_3CH_2OC(O)NHCH_2CH_3$) in the same solvent (δ 4.75).[14]

An NMR spectrum of the solvent alone as well as solutions of the polymers contains a peak at δ 1.6–1.7. This peak is therefore ascribed to an impurity, probably water, in the $CDCl_3$. This peak becomes more prominent in the order $C_7 < C_9 < C_{11}$ due to decreasing polymer solubility with increasing fluorocarbon segment mass. The small, broad peak at δ 5.1–5.2 in Figure 1E,G remain unassigned. Viscosity broadening and the presence of multiple species precluded the determination of spin–spin coupling constants in the polymers.

^{13}C NMR Spectra. Carbon-13 NMR spectra are presented in Figure 2 with assignments. Hexamethylene diisocyanate exhibits the expected three peak aliphatic region (a, c, and e) and an isocyanate peak at 121.89 ppm. The minor peaks in the spectrum are due to impurities. Both the diol and polyurethane spectra in Figure 2 provide striking evidence of the increasing $-CF(CF_3)CH_2-$ to $-CF_2CH_2-$ ratio noted above in the series **1a–c**. In these spectra the b carbons are split by a neighboring CF into a doublet (J_{CF} = 19–23 Hz), and the d carbons by CF_2 into a triplet (J_{CF} = 21–27 Hz) (Table II). The f (J_{CF} = 4.7 Hz) and g (J_{CF} = 8–9 Hz) carbons experience long-range coupling by fluorine. The trend from C_7 to C_{11} in both the diols and the polyurethanes is toward higher b:d and g:f peak ratios. In fact, in the limited number of scans obtained on the C_{11} diol and polyurethane, the d and f peaks are absent. Furthermore, while two C=O singlets are seen in the C_7 polyurethane [155.92 ppm, adjacent to $-OCH_2CH_2CF_2-$, and 155.85 ppm, adjacent to $-OCH_2CH_2CF(CF_3)-$], only a singlet at 155.83 is observed in C_9 and C_{11}. In these two polyurethanes, most of the carbonyls are adjacent to $-OCH_2CH_2CF(CF_3)-$.

Molecular Weight. Number average (M_n) and weight average (M_w) molecular weights of the current series of polymers were estimated utilizing gel permeation chro-

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(12) Pouchert, C. J. *The Aldrich Library of Infrared Spectra*, 2nd ed.; Aldrich Chemical Co.: Milwaukee, WI, 1975; p 462H.

(13) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; John Wiley & Sons: New York, 1981.

(14) Pouchert, C. J.; Campbell, J. R. *The Aldrich Library of NMR Spectra*; Aldrich Chemical Co.: Milwaukee, WI, 1974, Vol III; p 116A.

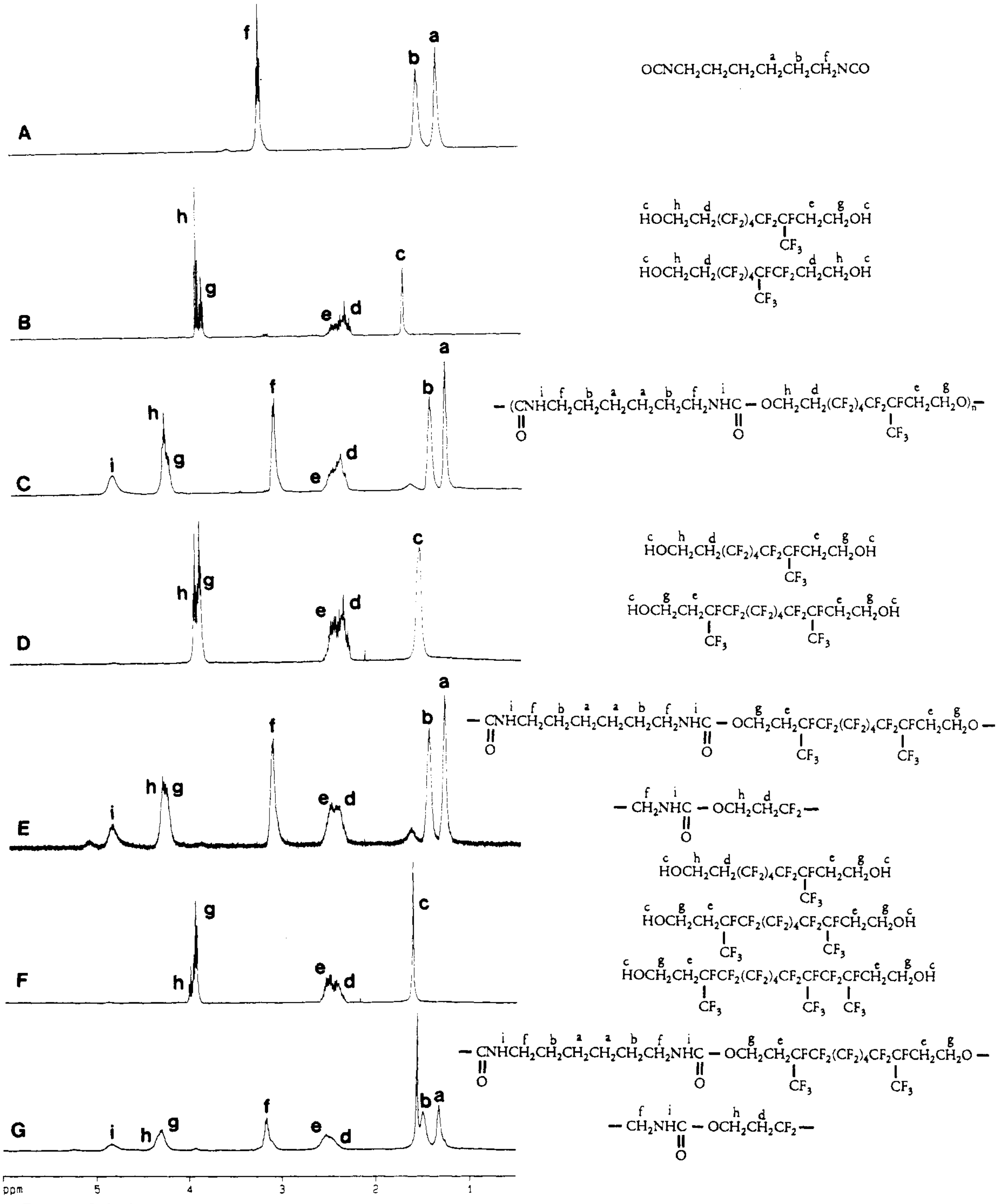

Figure 1. Proton NMR spectra in chloroform-*d*: A, HDI (**2**); B, C_7 diol (**1a**); C, bulk C_7 polyurethane (**3**); D, C_9 diol (**1b**); E, bulk C_9 polyurethane (**5**); F, C_{11} diol (**1c**); G, bulk C_{11} polyurethane (**7**).

matography (GPC). Since the specific refractive increments (dn/dc) of these polymers in THF solution are very low (<0.01 mL/g),[15] high concentration solutions of the polymers (about 2–3 wt %) were used to enhance the signals, and the resulting chromatograms were smoothed by the method of Fourier transform convolution.[16]

The molecular weight was determined using polystyrene standards as references. Typical values for the weight and number average molecular weights of these polymers are shown in Table III. The average molecular weights given in Table III were calculated from weight fraction distribution curves shown in Figure 3. The weight fraction distributions for polymers based on C_7 diol and HDI, exemplified by curve A, indicate that both the molecular weight and polydispersity of the polymers are in satisfactory ranges. The weight fraction distribution curves for polymers based on C_9 diol and HDI, curves B and C, however, represent only the lower ends of the ranges of the molecular weights. This is because gelation occurred during polymerization, and a portion of the product, being cross-linked, was not amenable to GPC measurements.

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(15) This value was obtained by comparing spectra for polystyrene and the current polyurethanes at the same concentration.

(16) We used programs included in *Mathematica* to perform this operation; Wolfram, S. *Mathematica: A system for doing mathematics by computer*, 2nd ed.; Addison-Wesley Publishing Co., Inc.: Redwood City, CA, 1991; p 679.

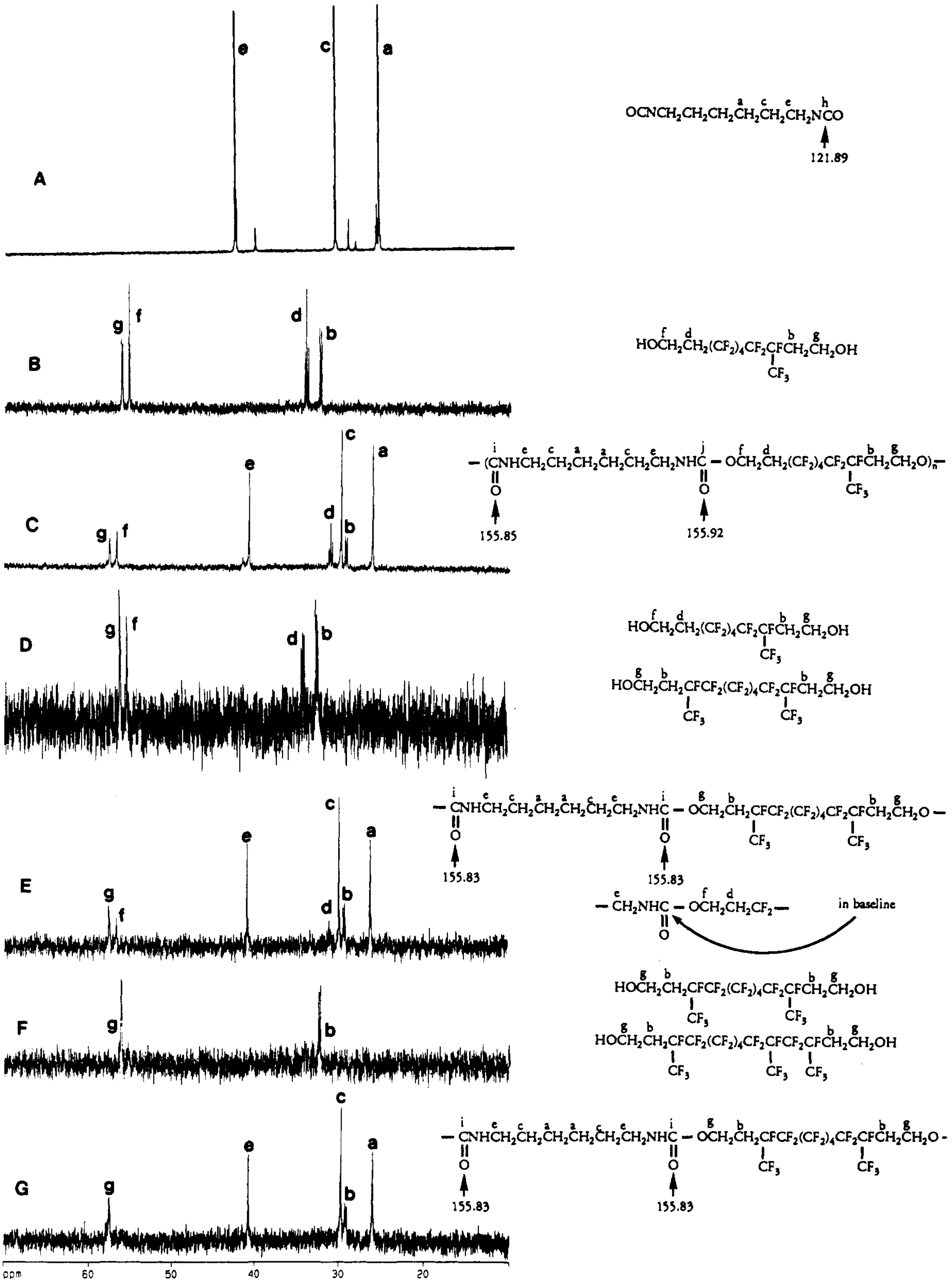

Figure 2. Proton-decoupled fluorine-coupled ^{13}C NMR spectra in chloroform-*d*: A, HDI (**2**); B, C_7 diol (**1a**); C, bulk C_7 polyurethane (**3**); D, C_9 diol (**1b**); E, bulk C_9 polyurethane (**5**); F, C_{11} diol (**1c**); G, bulk C_{11} polyurethane (**7**). The aliphatic (three most intense) peaks in A have been clipped.

Curves D and E in Figure 3 are weight fraction distributions for polymers based on C_{11} diol and HDI. The curves indicate these polymers have polydispersities at the expected level ($M_w/M_n \approx 2$) and molecular weights somewhat less than polymers based on C_7 diol and HDI. The lower molecular weight is a bias caused by gelation as in the case of polymers based on C_9 diol and HDI. Comparing curves B and C with D and E, one can notice that in polymers based on C_9 diol and HDI, cross-linking involves almost all molecules of molecular weight more than 40 000, while in polymers based on C_{11} diol and HDI, molecules of comparable molecular weight do not always cross-link. The reasons for this lower threshold for cross-linking in the former are not known. On the other hand,

Table III. Typical Values of Glass Transition Temperatures and Average Molecular Weights for Polymers 3–7[a]

polymer	T_g, °C	M_w	M_n	M_w/M_n
3	18.2	54 300	34 300	1.6
4	22.0	11 900	9 800	1.2
5	18.7	20 000	16 600	1.2
6	26.5	43 000	22 300	1.9
7	20.4	39 400	21 800	1.8

[a] T_g measured with DSC, molecular weights with GPC.

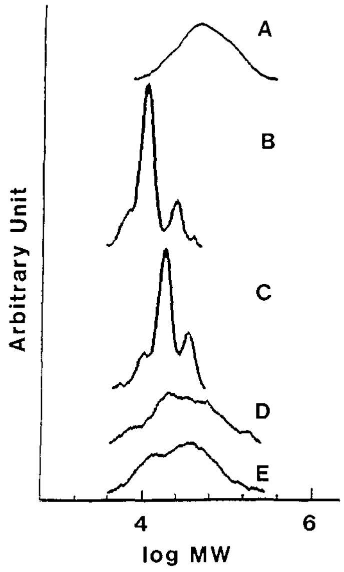

Figure 3. Weight fraction distribution curves, derived from GPC chromatograms, for polymers: A, polyurethane based on C_7 diol and HDI, polymerized in bulk; B, polyurethane based on C_9 diol and HDI, polymerized in THF solution; C, polyurethane based on C_9 diol and HDI, polymerized in bulk; D, polyurethane based on C_{11} diol and HDI, polymerized in THF solution; E, polyurethane based on C_{11} diol and HDI, polymerized in bulk.

molecular weights of these two types of polymers both appear to be of multimode distribution. This type of distribution could occur if during the polymerization the catalyst was not uniformly distributed and the reaction proceeded locally at different rates. The localization of reaction could be caused by high viscosity of the diols exacerbated by the rapid progress of the polymerization reaction. Intrinsic viscosities of polymers based on C_7 diol and HDI in THF have been measured, and a Mark–Houwink–Sakurada type correlation between intrinsic viscosity and viscosity-average molecular weight was reported previously.[3] We did not attempt to established similar correlations for polymers based on C_9 and C_{11} diols, because of limited data.

Elemental Analysis. Elemental analysis (for C, H, F, and I, using methods which differentiate between the two halogens) of diols **1a–c** indicates (Table IV) that 0.84% of the end groups in **1a**, 0.53% in **1b**, and 0.52% in **1c** are iodides remaining from the conversion of the diiodo alkane precursors to diols **1a**, **1b**, and **1c**. In a step-growth polymerization, this limits the molecular weight of the resulting materials. As an approximation, the stoichiometric imbalance[17] $r = N_{OH}/N_{NCO}$ can be used in a calculation of maximum possible DP and M_n, where N_{OH} is the number of moles of OH end groups, N_{NCO} the number of moles of NCO end groups, DP the number-average degree of polymerization, and M_n the number-average molecular weight. For completion of reaction (extent of reaction $p = 1$), DP and M_n are 237 and 72 000 g/mol for the C_7 polyurethane, 376 and 133 000 g/mol for the C_9 polyurethane, and 384 and 159 000 g/mol for the C_{11} polyurethane, respectively. These M_n values are higher than those obtained above via gel permeation chromatography probably because of the use of polystyrene GPC standards, differences in the extent of reaction, and the presence of cross-linked material excluded from the injected GPC samples.

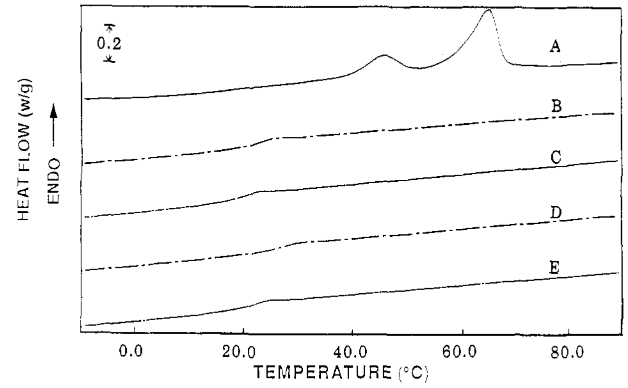

Figure 4. DSC traces for polymers: A, polyurethane based on C_7 diol and HDI, polymerized in bulk; B, polyurethane based on C_9 diol and HDI, polymerized in THF solution; C, polyurethane based on C_9 diol and HDI, polymerized in bulk; D, polyurethane based on C_{11} diol and HDI, polymerized in THF solution; E, polyurethane based on C_{11} diol and HDI, polymerized in bulk.

Table IV. Elemental Analyses of Diols 1a–c

		calcd	found
1a (C_7 diol)	C	30.02	29.87
	H	2.29	2.12
	F	60.42	60.59
	I	0.00	0.48
1b (C_9 diol)	C	28.94	29.87
	H	1.87	1.91
	F	63.40	63.18
	I	0.00	0.25
1c (C_{11} diol)	C	28.04	28.19
	H	1.53	1.34
	F	65.69	65.42
	I	0.00	0.20

Thermal Properties. Typical DSC traces for this series of polymers are shown in Figure 4. Polymers based on C_7 diol and HDI, **3**, show interesting thermal behavior. The glass transition region, between 10 and 25 °C, appears to be diminished compared with the two melting peaks. The melting peaks, located at about 46 and 67 °C, respectively, exhibit time-dependent variations in position and height. A detailed analysis of the thermal properties of these polymers has been reported separately.[3] DSC traces for polymers based on C_9 diol and HDI, **4** and **5**, and C_{11} diol and HDI, **6** and **7**, indicate no melting phenomena, and the glass transitions for these polymers occur at temperatures between 15 and 30 °C. Values for the T_g of polymers **3–7** are listed in Table III.

Mechanical Properties. Mechanical properties were examined with an Instron tester. Samples were prepared in two ways: compression molding at 100 °C and solution casting from 10% solution in THF. The results are shown in Figure 5 and summarized in Table V. The C_7-HDI polymer **3** has high Young's modulus and shows a yield peak, while polymers based on C_9 and C_{11} diols behave elastically. For a given polymer, the compression-molded

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[17] Odian, G. *Principles of Polymerization*, 2nd ed.; John Wiley & Sons: New York, 1981; p 83.

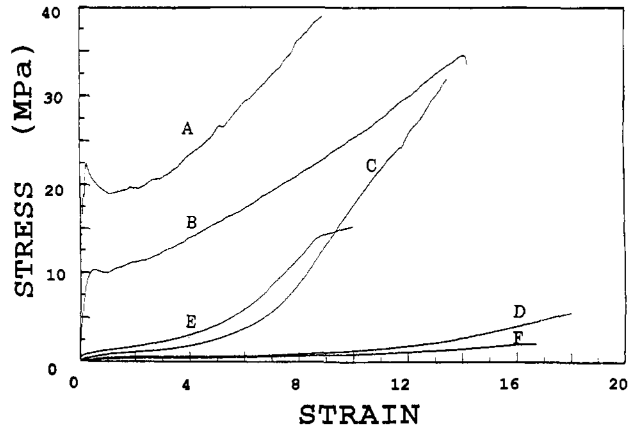

Figure 5. Stress–strain curves for polymers: A, polyurethane based on C_7 diol and HDI, compression-molded film; B, polyurethane based on C_7 diol and HDI, solvent-cast film; C, polyurethane based on C_9 diol and HDI, compression-molded film; D, polyurethane based on C_9 diol and HDI, solvent-cast film; E, polyurethane based on C_{11} diol and HDI, compression-molded film; F, polyurethane based on C_{11} diol and HDI, solvent-cast film.

Table V. Mechanical Properties of the Fluorinated Polyurethanes[a]

sample	Young's modulus (MPa)	strain at break
A	248	8.9
B	56.3	14.2
C	8.63	13.4
D	0.82	18.0
E	11.8	10.0
F	1.14	16.7

[a] Strain rate: 1.67 min^{-1}. A: polymer based on C_7 diol and HDI, compression-molded film. B: polymer based on C_7 diol and HDI, solvent-cast film. C: polymer based on C_9 diol and HDI, compression-molded film. D: polymer based on C_9 diol and HDI, solvent-cast film. E: polymer based on C_{11} diol and HDI, compression-molded film. F: polymer based on C_{11} diol and HDI, solvent-cast film.

film has higher tensile strength, while the solvent cast film has higher strain at break.

Young's moduli for polymers based on C_7 diol, 248 MPa for compression molded films and 56.3 MPa for solvent cast films, reflect the semicrystalline morphology of the material. The evolution of such morphology has been studied using time-dependent DSC and IR techniques, and its effects on the mechanical properties of the polymer by a combined calorimetrical mechanical analysis.[3] The results show that ordered-domain increases are correlated with increases in the extent of intermolecular hydrogen bonding. Applying the same analysis to polyurethanes based on C_9 and C_{11} diols, changes were not observed in the extent of intermolecular hydrogen bonding after 4 weeks at room temperature. As discussed in a previous section DSC traces revealed no melting phenomena in these materials consistent with a lack of ordered domains.

The small insoluble gel portions in polymers based on C_9 and C_{11} samples were not removed before preparation of compression-molded samples. Cross-linking due to the presence of gel could account for the stiffening of these films when the strain reached about 6 as shown in Figure 5 (curves C and E).

Surface Properties. Advancing contact angles of water and methylene iodide on surfaces of the polymers were examined. Contact angles at both sides of the profile of a sessile drop were measured; each value reported in Table VI is the average of at least sixteen readings. The contact angle of water, θ_{H_2O}, on PTFE obtained with our instrument was 109.5° and that of methylene iodide, $\theta_{CH_2I_2}$, was 80.2°; both are within the range of the literature values.[18] The solid surface free energy was calculated from the cosine of the contact angles of the two test liquids using a method suggested by Owens and Wendt:[18]

Table VI. Contact Angles and Surface Energies of Fluorinated Polymers[a]

polymer	θ_{H_2O} (deg)	$\theta_{CH_2I_2}$ (deg)	γ_s^d (ergs/cm^2)	γ_s^h (ergs/cm^2)	γ_s (ergs/cm^2)
PTFE	109.5	80.2	16.9	0.5	17.4
3	93.4	55.1	30.0	1.5	31.5
5	95.7	66.0	23.5	2.0	25.5
7	95.7	64.1	24.7	1.8	26.5

[a] PTFE: polytetrafluoroethylene. 3: polyurethane based on C_7-diol and HDI. 5: polyurethane based on C_9-diol and HDI. 7: polyurethane based on C_{11}-diol and HDI.

$$1 + \cos\theta = 2\sqrt{\gamma_s^{o}}(\sqrt{\gamma_{1o}}/\gamma_{1v}) + 2\sqrt{\gamma_s^{h}}(\sqrt{\gamma_1^{h}}/\gamma_{1v}) \quad (1)$$

$$\gamma_{1v} = \gamma_1^{d} + \gamma_1^{h} \quad (2)$$

$$\gamma_s = \gamma_s^{d} + \gamma_s^{h} \quad (3)$$

In eqs 1–3, γ_{1v} is the surface free energy of the liquid, γ_1^d denotes the component due to dispersion forces, and γ_1^h the component due to hydrogen bonding and dipole–dipole interactions. γ_s is the surface free energy of the solid, γ_s^d its dispersion force component, and γ_s^h the hydrogen bonding and dipole–dipole interaction component. The surface free energies for water and methylene iodide used in the calculation are literature values.[18] For water, γ_1^d is 21.8 ergs/cm^2, and γ_1^h 51.0 ergs/cm^2, while for methylene iodide, γ_1^d is 49.5 ergs/cm^2, and γ_1^h 1.3 ergs/cm^2.

Using Owens and Wendt's method, the surface free energy for polyethylene is 33.2 ergs/cm^2, polytetrafluoroethylene, 19.1 ergs/cm^2, and polyhexafluoropropylene, 12.8 ergs/cm^2.[19] Polar segment containing polymers, such as poly(methyl methacrylate) and poly(hexamethylene adipamide), have surface free energies higher than 40 ergs/cm^2.[19] Surface free energies of the fluorinated polyurethanes reported herein range between 25.5 and 31.5 ergs/cm^2. These data are consistent with surfaces consisting of both hydrocarbons and perfluorohydrocarbon segments. Ratner and co-workers have studied the surface compositions of polyurea–urethanes containing fluorinated chain extenders with angular-dependent X-ray photoelectron spectroscopy (XPS).[8,20] They did not observe surface enrichment of fluorine in their systems except when the chain extender was a perfluoroether oligomer.

The higher surface free energy value of 31.5 ergs/cm^2, is associated with polymers based on C_7 diol with a fluorocarbon content at 58 wt %. When the fluorocarbon content increases to 64 wt % as in polymers based on C_9 diol the surface free energy decreases to 25.5 ergs/cm^2. Further increase in fluorocarbon content (C_{11} diol polymer 7) does not result in decrease in surface free energy.

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Conclusions

Polyurethanes derived from fluorinated diols **1a–c** and HDI can be prepared under mild conditions. The surface free energy values fall between those for polyolefins and polyperfluoroolefins. Increased average fluorocarbon chain length leads to lower surface free energy, while the mechanical properties decrease due to the loss of ordering in structure.

The surface free energy data suggest that despite the increased average fluorocarbon chain length of the C_9 and C_{11} diols, the surface composition is similar to the bulk. We conclude that the desired phase separation of longer fluorocarbon segments at the surface was not achieved. We are currently working on soft segments with longer chains of low surface energy to achieve the surface phase segregation of this component that we believe is required for a minimally adhesive surface.

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