New Perfluoropolyether Soft Segment Containing Polyurethanes

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SYNOPSIS

New segmented polyurethanes (FPU) with perfluoropolyether (PFPE) blocks have been synthesized by a two-step process. In the first step, a fluorinated isocyanate end-capped prepolymer has been obtained by reaction of a fluorinated macrodiol with alicyclic diisocyanates in the presence of solvent. The following chain extension has been carried out by reaction of the prepolymer with short hydrogenated polyols giving a polymeric matrix. Tensile properties, dynamical–mechanical (DMA), and calorimetric (DSC) analyses have been evaluated, and relationships between chemical structure and final properties are established. These polymers show unusual low-temperature elastomeric behavior, due to the low glass transition (T_g) of the continuous fluorinated phase. In general, with respect to traditional polyurethanes (HPU), thermal stability and chemical resistance are strongly improved by the effect of the highly inert fluorinated chains. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polyurethane elastomers are a class of polymeric materials showing a wide range of interesting physical and mechanical properties such as tensile properties, thermal behavior, hardness, and surface characteristics. This versatility makes them useful for application in many different fields.

The drawbacks of polyurethane elastomers are their low thermal stability, due to the presence of weak urethane bonds. Thermal stability is further reduced by the presence of allophanate and biuret groups coming from side reactions.[1,2] Besides, polyurethanes containing polyester soft blocks have rather poor chemical resistance, expecially in strong acid and basic environments.[3] Moreover, many high technological industries are looking for new materials combining good tensile properties with unusual low-temperature elastomeric behavior and superior chemical resistance.

Recently, new studies have been reported in the scientific literature describing surface and bulk structures of polymers containing fluoroalkylenic

blocks;[4-7] other recent contribution reports on the synthesis of fluorine containing segmented poly-(urethane-urea)s for new-blood compatible materials.[8] All these fluorine-containing polymers are obtained by using low molecular weight difunctional fluoromonomers, showing good compatibility vs. the hydrogenated counterpart, so they can upgrade some properties of conventional materials, but they do not decrease the polymer T_g.

Therefore, it is a very interesting possibility of employing high molecular weight fluorinated building blocks in order to obtain new fluorinated polyurethanes, combining the chemical resistance of fluorinated structure with unusually low T_g and superior elastomeric performances. The aim of this study was the synthesis of a new class of polyurethane elastomers showing superior performances compared to commercially available hydrogenated polyurethanes (HPU).

This goal has been pursued using, as a soft phase, a fluoropoly(oxyalkylene)diol 1 (Fig. 1); in fact, the presence of this fluorinated block, having a very low T_g ($< -115°C$), allows, in principle, obtaining a polymeric structure having very good elastomeric behavior even at an unusually low temperatue, together with high hydrolytic and thermal stability.

$$CH_3OC(O)CF_2O(CF_2CF_2O)_p(CF_2O)_qCF_2C(O)OCH_3$$

(p/q = 0.8 - 1.2)

2 (Z DEAL)

$$HOCH_2CF_2O(CF_2CF_2O)_p(CF_2O)_qCF_2CH_2OH$$

2a (Z DOL)

$$H(OCH_2CH_2)_nOCH_2CF_2O(CF_2CF_2O)_p(CF_2O)_qCF_2CH_2O(CH_2CH_2O)_nH$$

(n = 1 - 2)
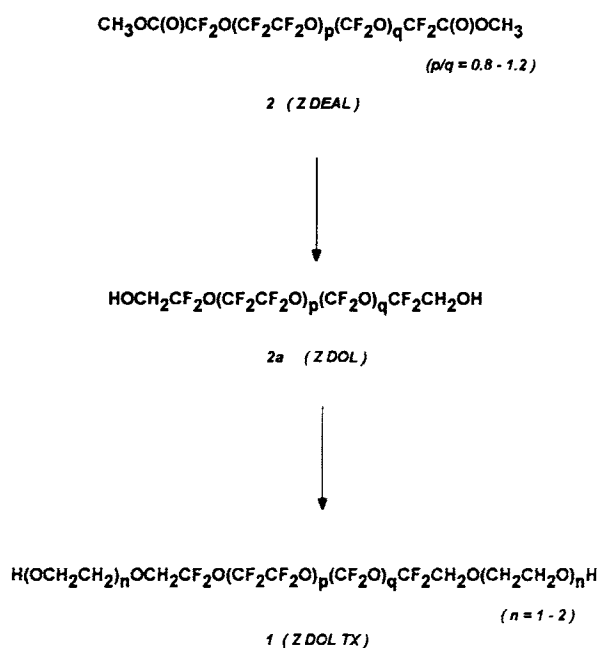
1 (Z DOL TX)

Figure 1   Synthesis of fluorinated macroglycols.

Figure 2   Hydrogenated comonomers.

EXPERIMENTAL

Materials

Fluoropoly(oxyalkylene)diol **1** is a commercially available product (Fomblin ZDOLTX®, by Ausimont), synthesized by reduction of the corresponding diester **2** (Fig. 1),[9] and subsequent base-catalyzed addition to ethylene oxide.[10] This macromer is a oligomeric mixture of products, constituted by a random distribution of —CF_2CF_2O— (C2 unit), —CF_2O— (C1 unit), end capped by ethoxylated units —$CH_2O(CH_2CH_2O)_nH$, characterized by: M_w/M_n = 1.6–2.0, C2/C1 = 0.8–1.2, n = 1–2, M_n = 2000–4500. The difuncional content is higher than 95% and is present less than 5% of monofunctional molecules, in which one OH end group is substituted with a perhaloalkyl segment (CF_2XO— or CF_2XCF_2O, where X = F, Cl). This product was dried under vacuum at 90°C for 2 h.

Ethylacetate was distilled and kept under molecular sieves. 1,4-butandiol **3** (BDO, by Aldrich) and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol **4** (TMP, by Fluka) were dried under vacuum at 70°C for 2 h. Trans-1,4-cyclohexane diisocyanate **5** (CHDI, by Du Pont) was distilled under vacuum, 4,4 methylenbis(cyclohexylisocyanate) **6** (H12MDI, by Mobay), and 4,4 methylenebis(phenylisocyanate) (MDI, by ICI) were used as received (Fig. 2).

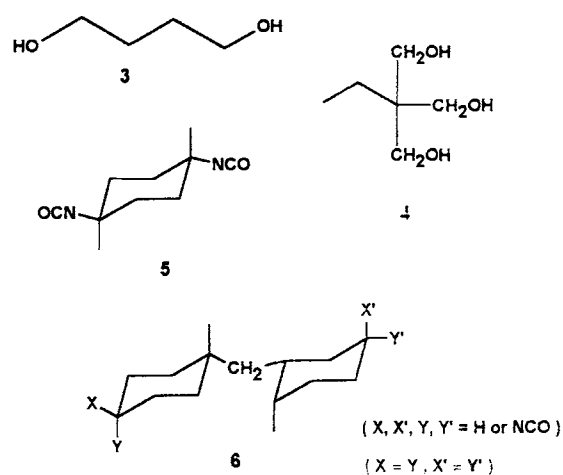Polycaprolactonediols 2000 M_w and 1250 M_w (PCL, by Interox), poly(oxytetramethylene)diol

2000 M_w (PTMEG, by Aldrich), and poly-(butadiene)diol 2800 M_w (PBD, by Aldrich) were dried under vacuum at 80°C for 2 h.

Fluorinated Polymer Synthesis

All fluorinated polymers were prepared using a two-step polymerization technique. The prepolymer synthesis (first step) was carried out in solvent; the chain extension and or crosslinking (second step) was completed in bulk condition.

First Step

An excess of diisocyanate (equivalent ratio between diisoyanate and fluorinated macromer: 5), with re-

Table I   Reagent's Density

Product	Density (g/mL)	Temperature (°C)
ZDOLTX-1200	1.74	25
ZDOLTX-1550	1.76	25
ZDOLTX-1750	1.77	25
ZDOLTX-2100	1.78	25
ZDOLTX-2260	1.79	25
PCL-625[a]	1.08	40
PCL-1000[a]	1.08	40
PTMEG-500[a]	0.97	40
PTMEG-1000[a]	0.97	40
PBD-1000[a]	0.90	25
CHDI[a]	1.12	70
H12MDI[a]	1.07	25
MDI[a]	1.19	50
BDO[a]	1.02	40
TMP	1.09	60

[a] From technical bulletin.

Table II   Polymer Compositions

Samples H12MDI-Based	Equivalent Ratio ZDOLTX/H12MDI/ BDO/TMP	ZDOLTX eq wt	Hard Phase (vol %)	M_c[a]
H-2260-19	1 : 2 : 0.5 : 0.5	2260	18.6	10250
H-2100-20	1 : 2 : 0.5 : 0.5	2100	19.7	9630
H-1750-23	1 : 2 : 0.5 : 0.5	1750	22.6	8225
H-1200-30	1 : 2 : 0.5 : 0.5	1200	29.5	6000
H-2100-15	1 : 1.5 : 0.5 : 0	2100	14.9	/
H-2100-20b	1 : 2 : 1 : 0	2100	19.7	/
H-2100-24	1 : 2.5 : 0.75 : 0.75	2100	24.0	6665
H-2100-28	1 : 3 : 1 : 1	2100	27.8	5165

Samples CHDI-Based	Equivalent ratio ZDOLTX/CHDI/ BDO/TMP	ZDOLTX eq wt	Hard Phase (vol %)	M_c[a]
C-2100-14	1 : 2 : 0.5 : 0.5	2100	14.0	9300
C-1750-16	1 : 2 : 0.5 : 0.5	1750	16.3	7635
C-1750-16b	1 : 2 : 1 : 0	1750	16.3	/
C-1550-18	1 : 2 : 0.5 : 0.5	1550	19.7	7035
C-1200-22	1 : 2 : 0.5 : 0.5	1200	21.8	5635

[a] Average molecular mass between chemical crosslinks.

spect to the defined stoichiometry, was dissolved in ethyl acetate (100 vol. of solvent for 100 g of fluorinated macromer). In the case of H12MDI, a proper amount of catalyst (dibutyltin dilaurate 0.006% eq. catalyst/NCO × 100) was added and the solution was refluxed under nitrogen.

The fluorinated macromer **1** was fed dropwise in 3 h. The reaction mixture was then refluxed for another 2 h, then the solvent was eliminated by distillation.

The reaction was completed at 80°C in 2 h, then the prepolymer mass was degassed under vacuum. The free diisocyanate was eliminated by distillation and solvent extraction with cyclohexane and the equivalent weight of the NCO end-capped prepolymer was determined by titration.

Second Step

In the second step, if the stoichiometry is not matched, the proper amount of free diisocyanate can be added; then the chain extender **3** (BDO) or a mixture of chain extender/crosslinker **4** (TMP) was fed, up to a final NCO/OH ratio of 1.05–1.00. The reaction mass was vigorously stirred for 2–3 min under vacuum and then cast in a mold and put in a press to complete the curing (24 h at 130°C).

The reaction was monitored by IR analysis looking at the disappearance of the isocyanate absorption band (2260 cm^{-1}).

Hydrogenated Polymer Synthesis

The hydrogenated polymers, described for comparison in the present work, were prepared by a two-step bulk reaction without a catalyst. The cast-molded samples were formed starting from a temperature approximately 20°C higher than the highest DSC endotherm, then annealed at 130°C for 24 h.

Polymer Characterization

All polymers were obtained as slabs (2 or 12 mm thickness) by the casting process; the samples were conditioned 2 weeks at room temperature before testing. The designations H, C, and M have been used to describe the ZDOLTX/H12MDI/ BDO+TMP, ZDOLTX/CHDI/BDO+TMP, and ZDOLTX/MDI/BDO systems, respectively. The designations PCL, PTMEG, PDMS, PIB, and PBD have been used to describe the following hydrogenated polyurethanes PCL/MDI/BDO, PTMEG/ MDI/BDO, PDMS/MDI/BDO, PIB/MDI/BDO, and PBD/MDI/BDO. The number immediately
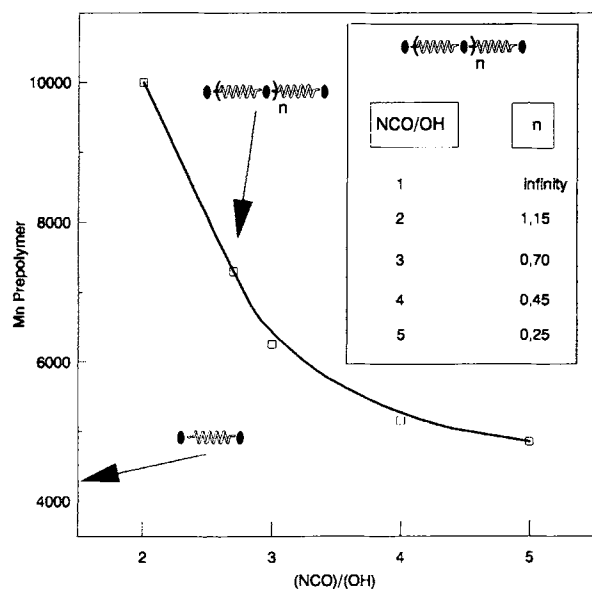
Figure 3 Relationship between reagents equivalent ratio (NCO/OH) and fluorinated prepolymer growth.

following the system name refers to the soft chain equivalent weight, while the last number following the dash refers to the hard phase content (volume percentage, calculated on the base of composition and reagents density, according to data reported in Table I).

IR

The IR measurements were made using a spectrometer IR FT Nicolet 20SX, with a miniature diamont navel cell P/N 2500 for polymeric material analysis.
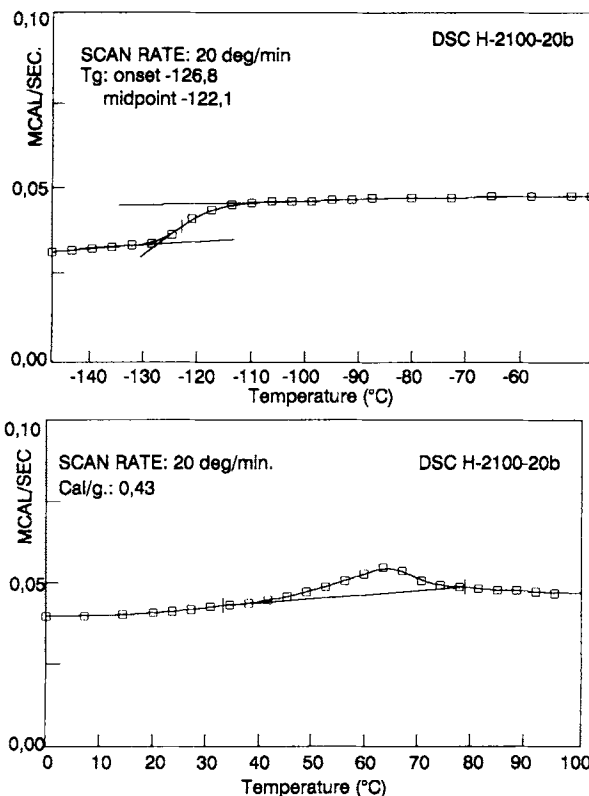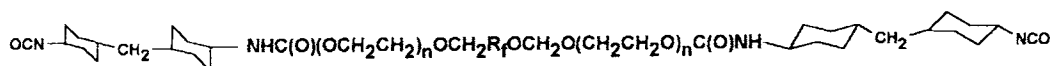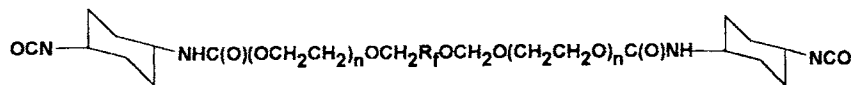

Figure 5 DSC analysis of H12MDI-based fluorinated polymer (H-1750-24).

DSC

Differential scanning calorimetry was carried out using a Perkin–Elmer DSC 2 Instrument, n-hexane, p-nitrotoluene, and indium calibrated. Melting temperatures were measured on heating runs from

7   (H12MDI based fluorinated prepolymer)

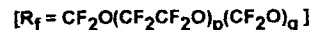8   (CHDI based fluorinated prepolymer)

$$[R_f = CF_2O(CF_2CF_2O)_p(CF_2O)_q]$$

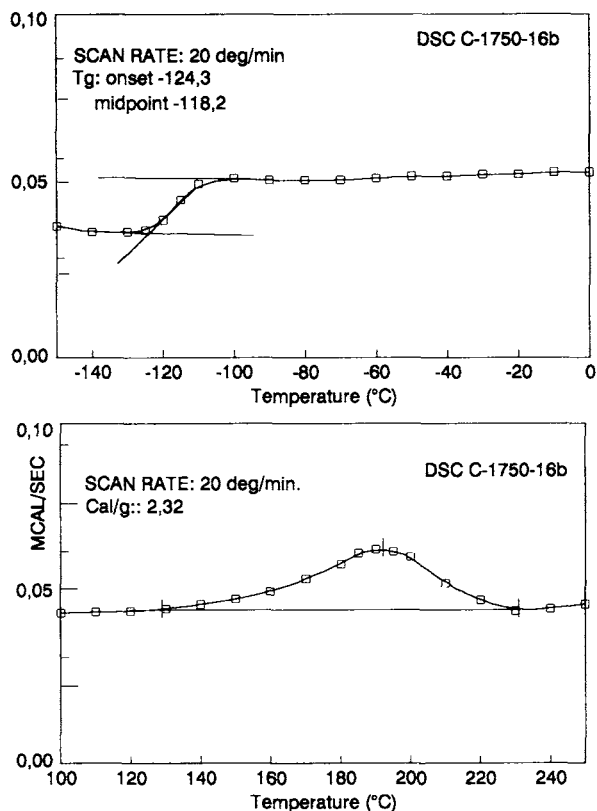**Figure 4** NCO end-capped prepolymer structures.

Figure 6 DSC analysis of CHDI-based fluorinated polymer (C-1750-18).

25°C to 250°C (10°C/min), while T_g values were determined by heating (20°C/min) from −160°C to 20°C.

DMA

Dynamic mechanical data were obtained using a Torsionautomat Brabender according to ASTM D 2236B.

Tensile Properties

Uniaxial stress–strain and ultimate properties measurements were made using a Instron dynamometer Mod. 1185 at a speed of 500 mm/min according to ASTM D 412 D.

Compression Set

Specimen: cylinder 12.5 mm diameter × 12 mm height; deformation: compressive, lambda = 0.75 (25%); testing temperature: from −75 up to 23°C.

Surface Tension Measurement

Surface tension was evaluated through contact angle measurements, with a series of liquid having different gamma-LC (from 21.7 mN/m for isopropanol up to 48.5 mN/m for ethylene glycol).

The experimental cos θ related to surface tension fit a simple linear expression and, consequently, it is possible to calculate the surface tension of the tested polymer by extrapolation of the straight line to cos θ = 1.

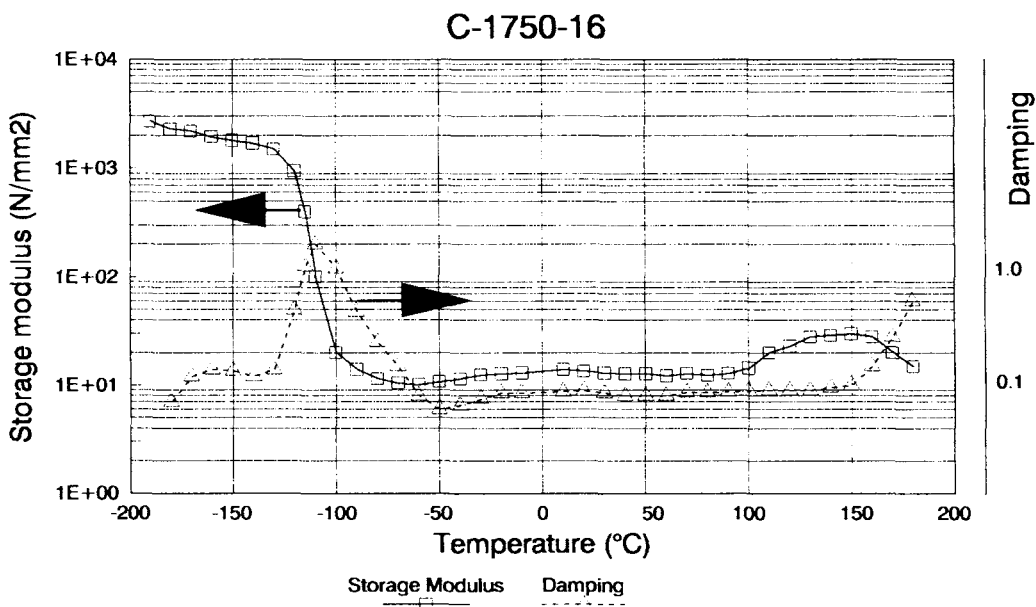**Figure 7** Dynamic mechanical spectrum of fluorinated polymer (C-1750-18).

Table III Tensile Properties at 23°C and 135°C

Samples H12MDI-Based	Temp. (°C)	Hard Phase (vol %)	Hardness (Shore A)	Modulus 20% (MPa)	Modulus 100% (MPa)	Tensile at Break (MPa)	Elongation at Break (%)
H-2260-19	23	18,6	65	6,5	3,2	6,2	470
H-2100-20	23	19,7	68	6,3	3,1	6,1	390
H-1750-23	23	22,6	73	10,0	5,0	8,3	259
	135			1,4	0,6	1,3	250
H-1200-30	23	29,5	89	21,0	5,8	12,2	363
	135			0,9	0,4	0,6	130
H-2100-15	23	14,9	52	3,5	1,5	4,7	479
H-2100-20b	23	19,7	70	6,5	3,5	10,0	554
H-2100-24	23	24,0	72	7,1	3,9	9,1	427
	135			0,6	0,3	1,1	540
H-2100-28	23	27,8	78	10,4	6,3	10,6	240
	135			0,3	0,7	0,9	151

| Samples CHDI-Based	Temp. (°C)	Hard Phase (vol %)	Hardness (Shore A)	Modulus 20% (MPa)	Modulus 100% (MPa)	Tensile at Break (MPa)	Elongation at Break (%)
C-2100-14	23	14,0	74	10,1	3,8	6,5	329
	135			5,4	1,9	2,5	235
C-1750-16	23	16,3	85	19,5	6,4	8,4	316
	135			8,5	2,3	2,9	292
C-1550-18	23	17,9	85	18,7	6,9	9,0	250
	135			13,7	3,3	4,0	219
C-1200-22	23	21,8	89	26,0	7,9	10,0	100
	135			15,0	/	5,0	48

RESULTS AND DISCUSSION

Following the procedure outlined in the experimental part, a series of segmented polyurethanes, containing PFPE blocks, was synthesized; the composition of the polymers is shown in Table II.

The macromer **1**, due to the presence of a hydrogenated segment (the ethoxylated unit) between the fluorinated chain and hydroxyl functional end group, shows a reactivity close to that of a hydrogenated primary alcohol.

The first step (i.e., the reaction of diisocyanate with **1** to give the prepolymer) is the most critical because of the strong difference between the reagents in terms of density and solubility.

The key point, in order to successfully carry out the synthesis, is to work in a homogeneous medium to reduce the prepolymeric chain growth, which would give the following long sequences:

$$— (PFPE — I)n —$$
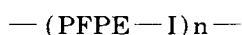
(where PFPE = ZDOLTX and I = diisocyanate)

In fact, the presence of these long perfluoropoly-ether–isocyanate copolymeric blocks causes the following undesirable effects: (1) a broadening of soft-phase length distribution giving, consequently, a less regular polymeric network; (2) a reduction of the extent of hard-phase segregation in the polymer because a short diisocyanate unit coupling two soft segment units is not phase separated.[11] For these reasons, it is not advisable to operate in bulk conditions: in this case, a significant chain growth is observed because the reaction, in spite of the defined NCO excess, is diffusion controlled. Fair to good solutions of macromer **1** with alicyclic diisocyanates are obtained in the presence of polar solvents (ketones or esters). Moreover, improved compatibility can be achieved by dropwise addition of the fluorinated reagent to the diisocyanate solution, because the NCO end-capped prepolymer is more compatible with hydrogenated counterparts, thus increasing the overall compatibility.

The prepolymer growth depends also on the stoichiometry.[12] In Figure 3, some data are reported about the relationship between the equivalent ratio (NCO/OH) and the prepolymer M_n, as determined by end-group titration after free isocyanate removal.
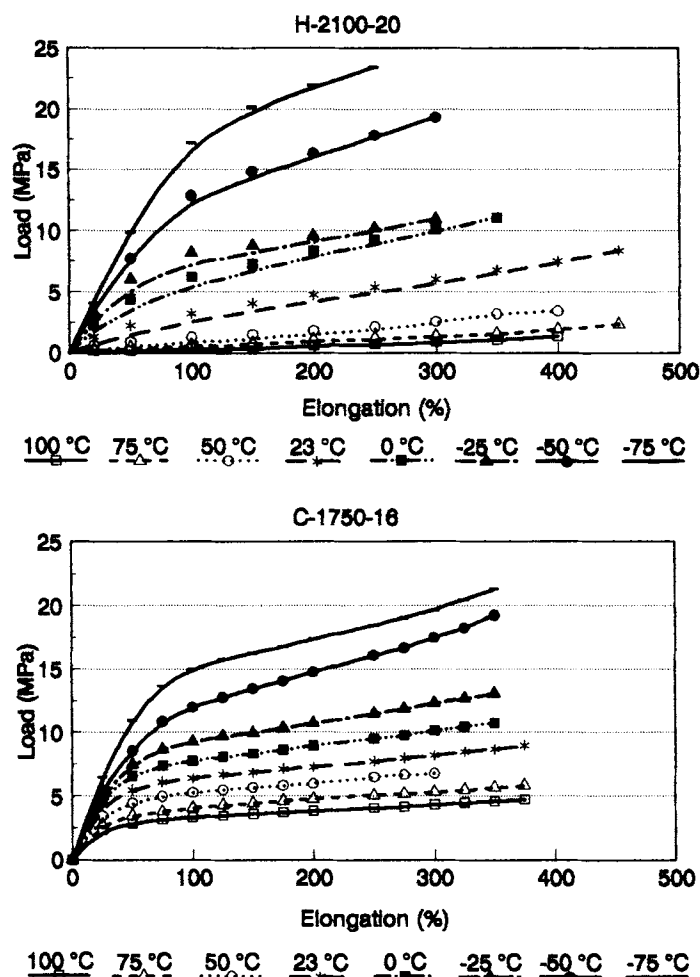
Figure 8   Relationship between temperature and tensile properties retention: comparison between H12MDI- and CHDI-based fluorinated polymers.

These data show that the prepolymer, when the equivalent ratio is equal or larger than 5, is mainly constituted by the three blocks structure I—Z—I; the lower the equivalent ratio, the larger is the prepolymer growth.

The FT IR and ^{19}F, ^{1}H NMR analysis are in good agreement with the three blocks structure I—Z—I (for NCO/OH $\geq$ = 5) (Fig. 4).

The thermal behavior of CHDI- and H12MDI-based fluorinated polyurethanes are evaluated by DSC analyses, as shown in Figures 5 and 6.

In order to eliminate possible disturbance of crystallization due to the use of a mixture of difunctional and trifunctional chain extender, this comparison is made with linear polymers based on BDO alone. Nevertheless, the same trend is observed for all the considered fluorinated polymers, independently of the composition of the chain extender/ crosslinker mixture.

The glass transition of the soft phase is always very low and roughly the same for all polymers. The T_g of the final polymer is very close to the value of the starting fluorinated macrodiol, and it appears to be quite independent on the moiety. All that clearly suggests that a high degree of phase separation must be present in the polymer network; otherwise, the reagent's nature and the polymer composition should strongly affect the T_g values.[13-16] This result is not surprising, because the solubility parameters of perfluoropolyether chains are quite different from the corresponding parameters of high polar hydrogenated blocks. Therefore, the perfluorinated chains tend to be present as a well segregated soft phase, thus maintaining the original and typical properties of the PFPE structure.

On the contrary, the melting temperature of the hard phase is quite different, and it is strongly de-
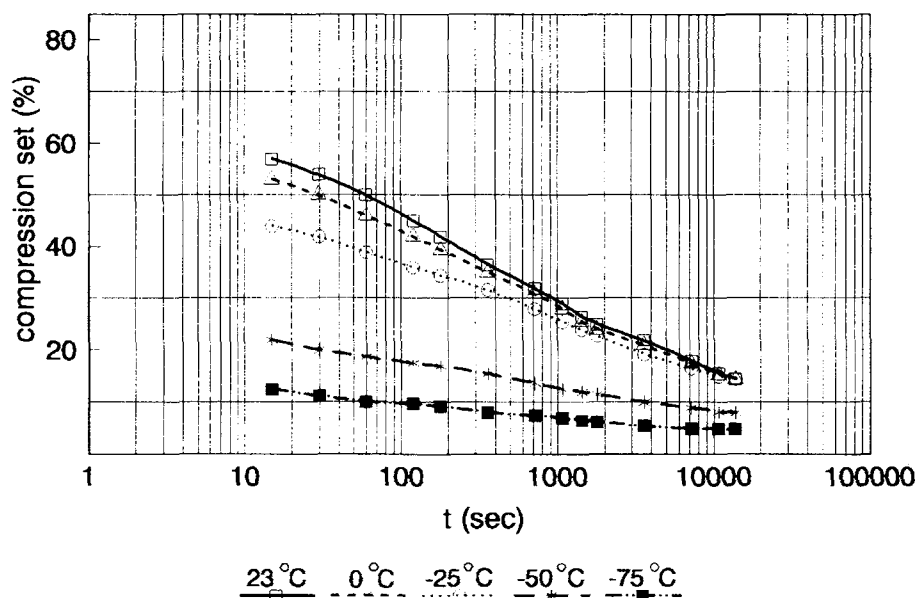
C-1750-16

Figure 9   C-1750-18: compression-set as a function of temperature and time.

pendent on the isocyanate structure and the hard-phase content.

Unlike conventional segmented PUs, in which melting phenomena are found only for a hard-phase content higher than 25%,[17-19] fluorinated polyurethanes (FPUs) present significant endothermic phenomena even at very low hard-phase content (< 20%). This is particularly true in the case of the CHDI-based FPU.

In this case, the melting temperature is much higher than the melting temperature of the corresponding H12MDI-based polymer (190°C vs. 65°C): this suggests that, in the case of the CHDI-based

polymer, a better organized hard phase must be present.

In fact it must be considered that, while CHDI is present only in the *trans* form, the H12MDI is a mixture of three isomers (*cis-cis, cis-trans*, and *trans-trans*).

For this reason, the presence of a well-ordered hard phase is possible only in the case of isomerically pure CHDI; on the contrary, the mixture of isomers of H12MDI is a barrier to the formation of well-organized hard microdomains. This will largely affect not only the thermal behavior, but also the mechanical properties of the polymers.

Table IV   Tensile Properties of Polyurethane Copolymers at Different Temperatures

		Room Temperature				Other Temperature				
Samples[a]	T_g (°C)	$T - T_g$ (°C)	M100% (MPa)	T_b (MPa)	E_b (%)	Test temp. (°C)	$T - T_g$ (°C)	M100% (MPa)	T_b (MPa)	E_b (%)
1) PLC-1000-23	−40	63	3	50	480	23	63	3	50	480
2) PTMEG-1000-23	−70	93	2–3[b]	20–40[b]	400–800[b]	0	70	3	47	600
3) PDMS-1000-25[c]	−120	143	4	5	170	−50	70	11	16	240
4) PIB-1700-27[c]	−57	80	8	13	270	3	60	9	19	340
5) PBD-1000-28	−75	98	5	8	190	/	/	/	/	/
6) H-2100-20b	−120	143	4	10	550	−50	70	14	23	300
7) M-1750-23	−120	143	5	10	460	−50	70	15	25	310

[a] Sample nomenclature described in text.
[b] Strongly dependent on aging conditions.
[c] From ref. 20.

Table V   Melting Temperature as Function of Soft Phase

Samples	Hard Phase MDI + BDO (% vol)	Melting Temperature (°C)
PCL-625-31	31	114
PCL-1000-26	26	116
PTMEG-500-33	33	100
PTMEG-1000-20	20	107
PTMEG-1000-24	24	116 (main peak), 188
PBD-1000-23	23	221
M-1750-21[a]	21	218
C-1750-16b[b]	16	190

[a] MDI-based FPU.
[b] CHDI-based FPU.

Dynamic mechanical analyses (Fig. 7) are in good agreement with DSC data: the storage modulus drops at a temperature corresponding to the T_g of the soft fluorinated continuous phase ($-115/-120°C$), and two damping peaks are present at the T_g and T_m transitions.

The presence of a ordered hard phase gives a significant contribution to the physical crosslink of the material;[20] so it could be easily predicted that the CHDI-based polymers will better maintain the mechanical properties at high temperature than the corresponding H12MDI-based polymers. This be-

havior is clearly confirmed by the comparison of the tensile properties at 23 and 135°C (Table III).

Because the fluorinated blocks represent the continuous phase of these new materials, the polymers should display some of the outstanding typical properties of the perfluoropolyethers building blocks. In fact, based on DMA and tensile properties, these FPU could cover a very large temperature range of elastomeric behavior (from $-75°C$ up to 135°C), performing as elastomers still at very low temperature (Fig. 8). Also, compression-set data, obtained by testing the deformation recovery as a function of temperature and time, are unusually good (Fig. 9).

In the last few years, other low T_g polyurethane elastomers, based on soft segment, different from conventional polyether or polyester macrodiols, have been introduced.[21] These polymers, based on polyisobutylene (PIB), polybutadiene (PBD), and polydimethylsiloxane (PDMS) blocks, show superior hydrolytic stability and reduced water permeability. Moreover, they offer improved low-temperature flexibility even if, in some cases, they have a poor oxidative stability. All these new structures present an increased degree of phase separation; this is not surprising, because they do not have significant soft segment–hard segment hydrogen bonding.

A drawback of these PBD-, PIB-, and PDMS-based polyurethanes comes from the tensile properties (tensile at break and tear resistance) and toughness that are lower than conventional polyether- and polyester-based polyurethanes.
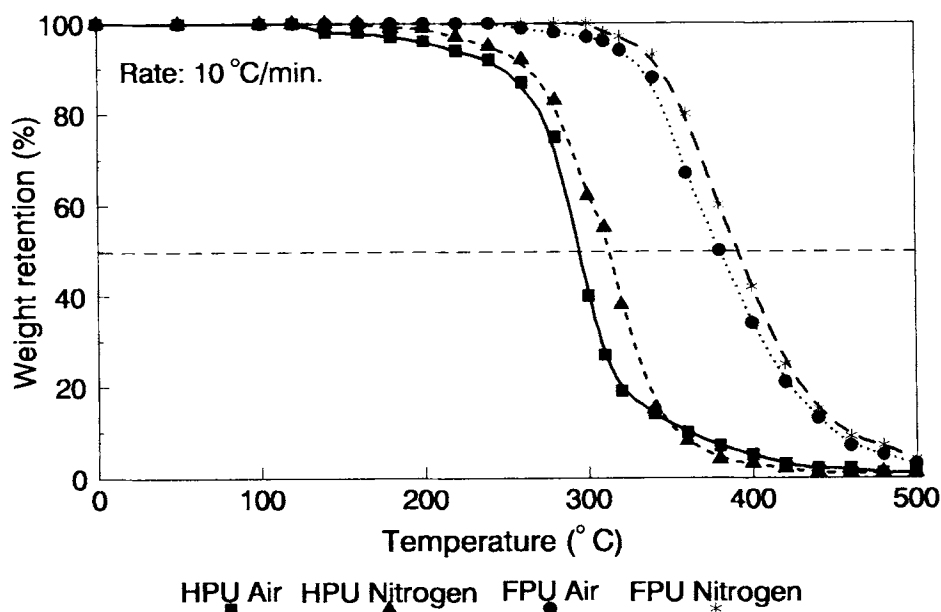

Figure 10   TGA analysis: comparison between hydrogenated and fluorinated polyurethanes.

Table VI   C-1750-16—Chemical Resistance

Chemical Treatment			Volume Change (vol %)	Tensile Properties (% Retention)			
Chemical Agent	Temp. °C	h		100% strength MPa	Ultimate Strength MPa	Elong. at Break %	HPU[a]
1. Reference	—	—	—	5.0	8.3	259	
2. 3% H_2SO_4	70	24	+0.9	102	109	100	A/B
3. 30% H_2SO_4	70	24	+0.02	109	99	84	C
4. 10% NaOH	70	24	+0.45	100	86	75	B
5. 60% NaOH	70	24	−0.08	111	98	81	C
6. Isottane	70	24	+11.7	74	84	96	B
7. Toluene	70	24	+24.2	28	48	113	C
8. Olive oil	135	24	+0.08	111	113	98	B
9. Mineral oil	135	24	+1.45	97	109	109	A/B
10. ASTM No. 3 oil	135	24	+4.0	93	107	103	B
11. ASTM Fuel C	70	24	+22.0	33	41	102	B/C
12. H_2O	85	96	+2.0	100	100	89	B/C

[a] A = Little or no effect; B = minor to moderate effect; C = complete destruction.

It has shown that segmented polyurethane elastomers present tensile properties strongly dependent on temperature:[22] the more distant the test temperature from the soft phase T_g, the lower will be the modulus and the tensile strength. In fact, the tensile behavior reflects the viscoelastic state of the material at the test conditions.

Starting from this consideration, it has been noted[23] that the poorer values of modulus and tensile at break of nonpolar soft segment-based polyurethanes are at least partly attributable to the very low T_g of the soft phase. This evidence suggests comparing PU's properies at equivalent values of $T - T_g$.

Table IV reports such a comparison, in which tensile properties at room temperature and at equivalent value of $T - T_g$ of FPUs, conventional PUs, and nonpolar-based PUs are shown.

In order to minimize the contribution of other important factors that could largely influence the tensile performances, this comparison was carried out among thermoprocessable polymers characterized by: (1) the same hard-phase composition: all polymers, except where noted, are based on MDI
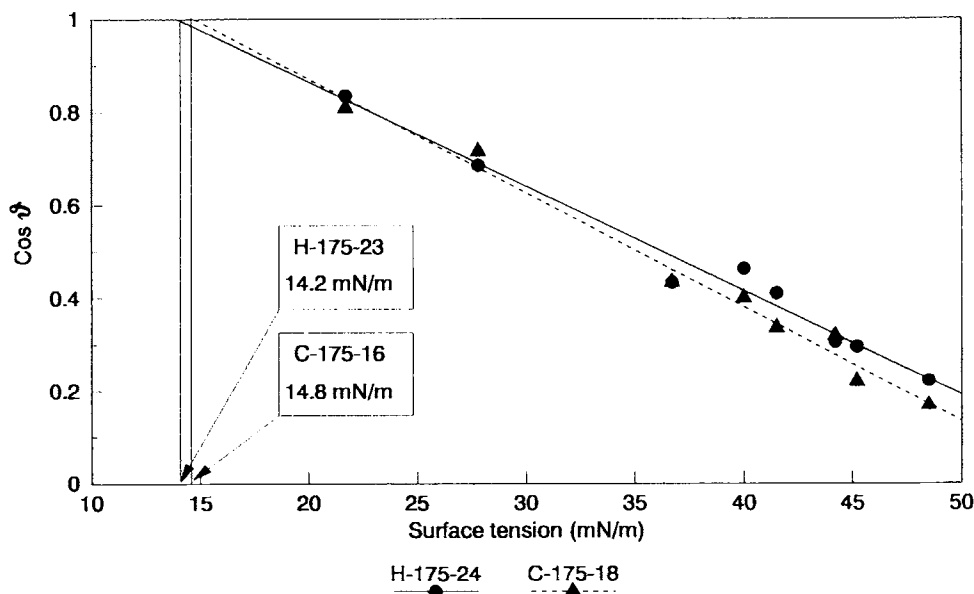

Figure 11   Surface tension of H12MDI- and CHDI-based fluorinated polyurethanes.

and BDO; (2) similar hard-phase content; (3) similar soft-segment chain length (if defined as numbers of atoms along the main chain); and (4) same thermal treatement.

This observations lead to the conclusion that other factors different from hard-phase composition or content and soft chain length must be taken into account in order to justify the strong different tensile behavior at room temperature, as clearly evidenced by the reported data.

At the same time, the values of the modulus and the tensile at break, at equivalent value of $T - T_g$ show that the polyurethanes based on apolar soft segment (hydrogenated, siloxane-based, and fluorinated) give close performances (modulus: 9–15 MPa, tensile at break: 16–25 MPa); on the other hand, the polymers based on soft segments, more compatible with respect to polar hard chains (polyether- or polyester-based polymers), are quite different from the previous class (modulus: 3, tensile at break 43–50).

It cannot be neglected that a contribution to tensile behavior could result from a possible soft-phase crystallization (in the case of PTMEG- and PCL-based polymers), thus making difficult a generalization about ultimate properties (tensile and elongation at break); but, at the same time, crystallization must have an opposite effect on modulus with respect to the observed general lower values for polyether- or polyester-based PU.

So, based on the experimental data, and taking into account the above considerations, it seems that we are in the presence of two classes of polymeric structures, at constant $T - T_g$ and hard-phase content, characterized by the polarity of the soft phase, regardless of their chemical nature. Materials with higher modulus, typical of "apolar" soft phase-based polyurethanes, belong to the first class, while materials with lower modulus, with significant strain hardening phenomena, typical of "polar" soft phase-based polyurethanes, belong to the second one.

It is widely accepted that many of the final properties of block polymers can be attributed to phase separation of the hard segments into domains dispersed in the matrix of soft segments; these domains reinforce the elastomeric matrix as filler particles.[24-27]

Domains dimension and crystallinity depend on the structure of comonomers, hard-phase content, compatibility between hard and soft phases, synthetic procedure, and thermal history. It seems reasonable that compatibility could be a key factor in explaining the above-mentioned differences, because the lack of compatibility between soft and hard

phase could force the hard-phase segregation, giving larger and better organized hard domains. This hypothesis seems to be confirmed by a comparison of calorimetric behavior of polyurethanes based on apolar or polar soft phase. In Table V, the melting temperatures of the hard phase of different classes of polyurethanes based on MDI + BDO are reported. These values confirm that the apolar soft phase-based polymers, even if with a significant lower hard-phase content, present a crystalline phase with higher melting temperature.

Thermal stability is another very important property for polymeric materials that must be taken into account for final use.

It is well known that the weak bond in the polyurethanes is the urethane group.[1] Other decomposition reactions involve the soft phase, particularly if ether groups are present: the CH_2 groups adjacent to ethero atoms are very sensitive to thermo-oxidative degradation. In fact, PTMEG-based polyurethanes undergo, at high temperature, an extensive decomposition.

Therefore, it is reasonable to expect that PFPE-containing polyurethanes, in spite of the presence of urethane weak groups, can offer some advantages in comparison with conventional polyurethanes as far as thermal stability is concerned; in fact, the soft fluorinated chain is "per se" highly thermally stable.

This assumption is confirmed by comparative TGA analyses between traditional and fluorinated H12MDI-based polyurethanes (Fig. 10). It is evident the superior thermal stability of the fluorinated network ($T°_{50\%} = 382°C$, vs. 290°C, in air).

Finally, the barrier effect of fluorinated chains strongly improves the chemical resistance of polymers. Chemical aging tests indicates that, in general, no significant effects come out after chemical treatment, even in very drastic conditions (Table VI).

These results are in good agreement with preliminary tests showing that the polymeric surface is essentially perfluorinated. In fact, surface tension measurements of FPU polymers, obtained through contact angle methodology with a series of solvents having different surface tension, confirm that the surface is completely fluorinated: the critical gamma values, 14–15 mN/m compared to 30–32 mN/m for hydrogenated PU, are close to the typical values of the perfluorinated chain itself (Fig. 11). The very low surface energy of the highly flexible PFPE chain is an effective driving force to preferentially orient the perfluorinated chains to the surface.[28]

This is a general outstanding property of perfluoropolyether-based polymers. In fact, the fluorinated segments, due to their thermodynamic in-

compatibility with the hydrogenated moiety, low surface energy, and high flexibility, present an unusually high tendency to segregate and to self-orient toward the surface. Unlike these PFPE-based PUs, the other fluorinated polyurethanes described in the litterature[4-8] do not give a self-segregated fluorinated phase because of the low molecular weight and reduced chain flexibility of fluorinated counterpart; for this reason they act like conventional chain extenders, being bonded to very polar hard groups.

CONCLUSIONS

From the results and discussion in the foregoing sections, the following main conclusions can be derived:

1. FPU with different hardness and tensile properties can be produced by conventional two-steps polymerization of fluorinated macrodiols with conventional diisocyanates and chain extenders/crosslinkers
2. These PFPE-based segmented polyurethanes show a high degree of fluorinated soft-phase segregation.
3. The presence of a low T_g ($-120°C$) perfluoropolyether chain in the polymeric network assures a very good maintenance of elastomeric behavior and dimensional recovery after load removal, even at a very low temperature ($-75°C$).
4. The fluorinated chains, "per se" highly thermally stable, strongly improve the thermal stability of materials. At the same time, chemical resistance, even in very drastic conditions, is very good, thanks to the barrier effect of fluorinated moiety.
5. Based on surface tension measurements, the fluorinated comonomers are usually enriched at the surface.

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