

Structure-Property Relationships in Thermoplastic Elastomers III. Segmented Polyacetal-Polyurethanes

BAOBEI XU, D. N. KHANNA, C. PETER LILLYA, and JAMES C. W. CHIEN* *Department of Chemistry, Department of Polymer Science and Engineering, Materials Research Laboratories, University of Massachusetts, Amherst, Massachusetts 01003*

Synopsis

Dihydroxy-terminated polyacetals had been synthesized from aldehydes and glycols and used as soft segments to obtain segmented polyurethane block copolymers. For soft segment $\geq 1700 M_n$, the T_g ranges from -48 to -58°C and is insensitive to the structures of diisocyanate and chain extender. The T_g of PacPU with $1350 M_n$ polyacetals is raised to -38°C , and none was observed for shorter polyacetal chains. The copolymers can be synthesized to have a broad range of mechanical properties, such as modulus from 0.5 to 130 MPa, stress at break from 0.7 to 21 MPa, and elongation at break from 66 to 1300% through the variation of the constituents and composition. The rheologic properties are only slightly dependent on temperature for symmetrical diisocyanates but quite temperature sensitive with asymmetric diisocyanate copolymers. The polyacetals are selected to build in acid-catalyzed thermal decomposition of the thermoplastic elastomers. The extreme acid sensitivity of the polyacetal block is buffered in the copolymers.

INTRODUCTION

Block copolymers,¹ especially the segmented types, are quite amenable to molecular engineering. Our research has been directed toward establishing basic structure-property relationships for a variety of thermoplastic elastomers having contrasting physical, chemical, and mechanical properties, such as tough versus soft, thermally stable and unstable, low versus high melt viscosity, low and high T_g , and amorphous versus crystalline hard segment. We have reported structure-property relationships of segmented polyether polyurethanes¹ and their thermochemistry.² The soft polyether segment is thermally more stable than the hard polyurethane segment and is insensitive toward acid-catalyzed decomposition. In this paper we report the synthesis of a novel polyacetal soft segment that has the designed degradative characteristics and a wide range of physical and mechanical properties.

EXPERIMENTAL

Materials

Butyraldehyde was purchased from Fisher Scientific Co.; diethylene glycol and other aldehydes were from Aldrich Chemical Co. The aldehydes were treated with sodium carbonate, dried with sodium sulfate, and distilled

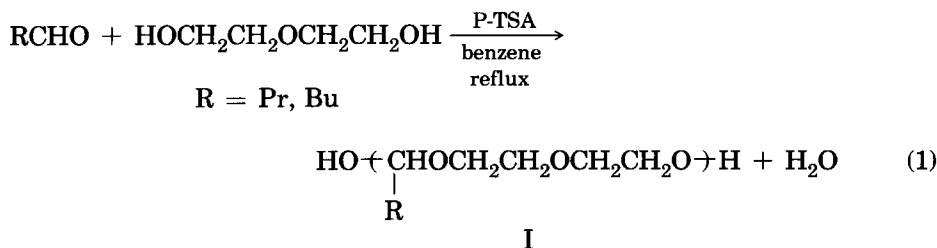
*To whom correspondence should be addressed

twice before use. Diethylene glycol was dried with a molecular sieve and distilled before use. *p*-Toluene sulfonic acid was purchased from MCB, 4,4'-diphenyl methane diisocyanate (MDI) from Mobay Chemicals, 2,4-toluene diisocyanate (TDI) from Sigma Chemicals, and 2,6-toluene diisocyanate (TDI') from Aldrich Chemicals were all distilled in vacuo before use. The purity of TDI and TDI' were checked by infrared (IR) absorption³ at 910 and 781 cm^{-1} , respectively. bis-2-Hydroxyethylisophthalamide (BI) and bis-2-hydroxyethylterephthalamide (BT) were synthesized by aminolysis of the isophthalate and terephthalate esters, respectively, with 2-aminoethanol [BI, MP 138–140°C; analysis found (theoretical): C, 56.80 (57.13); H, 6.54 (6.39); N, 11.38 (11.11); BT, MP 232–233°C; analysis: C, 56.98 (57.13); H, 6.60 (6.39); N, 11.23 (11.11)].

Solvent dimethylformamide (DMF) from Fischer Scientific was dried with a molecular sieve and distilled in the presence of TDI under vacuum before use. The catalyst dibutyltindilaurate (BTL) was purchased from Alfa Products.

Synthesis of Polyacetal

Polyacetals (Pac) were synthesized by the following scheme:



Equimolar amounts of valeraldehyde, diethylene glycol, and 10^{-4} mol equivalent of *p*-TSA in benzene were reacted in a three-necked flask equipped with a mechanical stirrer, Dean Stark trap, and condenser. After about 48 h of refluxing, 90–94% of the theoretical yield of water was eliminated. The reaction mixture was washed with aqueous alkali solution and then with water to neutrality. After drying with Na_2SO_4 , the lower boiling compounds were removed by distillation under reduced pressure with a yield of 82–90%. Number-average molecular weight, M_n , was determined by the Karl-Fisher method⁴ to be 1350–1900. The properties of various polyacetals are given in Table I.

Synthesis of Polyacetal Polyurethanes

The segmented polyacetal polyurethanes were synthesized from polyacetals derived from either butyraldehydes ($M_n = 750$) or valeraldehyde ($M_n = 1350$ –1900) using the following reactions.

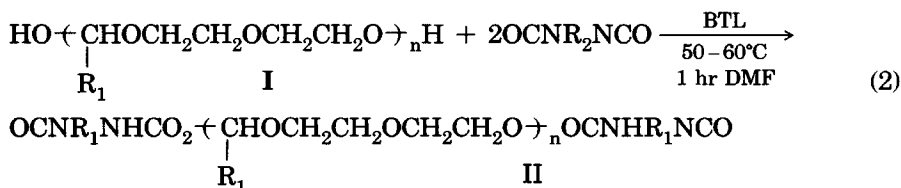



TABLE I
 Synthesis and Properties of Polyacetals^a

R — C $\begin{matrix} \text{O} \\ // \\ \text{H} \end{matrix}$	Reaction time (h)	Yield (%)	M_n		$[\eta]^d$ (dL g ⁻¹)	T_g (°C)
			GPC ^b	End group ^c		
H	20	96	1,300	1,290	0.15	-43
CH ₃ CH ₂ —	48	22	1,200	1,160	0.13	-77
CH ₃ CH ₂ CH ₂ —	48	33	750	720	0.10	-84
(CH ₃) ₂ CH—	48	35	870	708	0.065	-76.4
CH ₃ CH ₂ CH ₂ CH ₂ —	48	82–90 ^e		1,350–1,900		-74 to -76.8
(CH ₃) ₂ —CH—CH ₂ —	20	95	2,000	1,900	0.13	-58
	20	80	940	820	0.074	-51

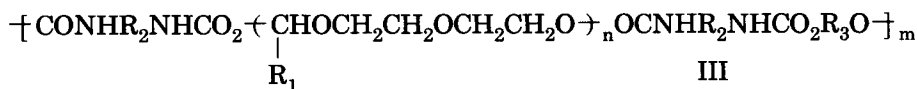
^a All with diethylene glycol.

^b *N*-methylpyrrolidone solvent.

^c Karl-Fischer method using LiAlH₄.

^d Intrinsic viscosity in DMF.

^e Range of values for different preparations.



Polyacetal, 10 g, was dropped into the DMF solution of diisocyanate; the molar ratio between polyacetal and diisocyanate was 1:2; 1 drop of dibutyltin dilaurate was added as catalyst. The reaction proceeded at 50–60°C for 1 h in N₂ atmosphere, then the DMF solution of the chain extender was added. The second step reaction was run at either room temperature or 50–60°C for 4 h. The reaction mixture was then casted on a Teflon sheet, and the solvent was removed at 80°C and 1 torr overnight. The PacPU yield is about 95%.

The MW of the polyurethanes was determined by a Waters Associates gel permeation chromatograph. Tetrahydrofuran or *N*-methylpyrrolidone was used as solvent. The calibration curve was made with a series of standard polystyrene. The results of PacPU synthesis are listed in Table II.

Preparation of Nitrogen-Substituted Polyurethane⁵

Polyurethane, 5 g Pac(7.5)-TDI-BI (1:2:1), was dissolved in 15 mL of DMF, and a suspension of 0.48 g NaH in 5 mL DMF was added dropwise at -5°C. As hydrogen gas was evolved and the color of the solution turned to green, 0.36 g of C₂H₅Br was added and stirred for 1 h at 0°C. The reaction mixture was poured into distilled water; the precipitated polymer was washed thoroughly with water, then dried at 50°C and 1 torr overnight; 3.12 g of a soft and somewhat sticky polymer was obtained. The product has $M_n = 12,100$

TABLE II
Polyacetal Polyurethane Synthesis and Some Properties

Copolymers	Reaction condition						GPC (THF)			DP	Appearance
	Step 1		Step 2		BC ^b	M _n	M _w	DP			
	Temperature (°C)	Time (hr)	Temperature (°C)	Time (hr)							
Pac(7.5)-TDI-BI	50-60	2	50-60	4	Yes	14,900	26,900	1.81	Not sticky, no elasticity		
Pac(7.5)-TDI-BD	50-60	2	50-60	4	Yes	17,800	42,300	2.38	Slightly sticky, elastic material		
Pac(7.5)-MDI-BD	50-60	2	50-60	4	Yes	13,900	25,000	1.80	Not sticky, no elasticity, low strength		
Pac(7.5)-MDI-BT	50-60	2	50-60	4	Yes	14,200	27,700	1.95	Not sticky, less elasticity		
Pac(7.5)-TDI-BT	50-60	2	50-60	4	Yes	11,900	26,000	2.20	Not sticky, less elasticity		
Pac(7.5)-MDI-BT	50-60	2	50-60	4	Yes	23,800	40,100	1.68	Flexible, no elasticity, good strength		
Pac(19)-MDI-BT	50-60	1	50-60	4	No	11,800	40,100	1.82	Sticky, elastic material		
Pac(19)-TDI-BT	50-60	1	RT	4	Yes	6,000	9,900	1.65	Viscous liquid		
Pac(19)-TDI-BT	50-60	1	RT	4	Yes	11,200	15,500	1.35	Very sticky material		
M-BT ^a	—	—	RT	4	Yes	33,000 ^b	45,000	1.36	Hard, brittle, solid		
Pac(19)-TDI-BT	50-60	1	RT	4	Yes	10,400 ^c	14,000	1.38	Not sticky, elastic material		
Pac(19)-MDI ^e	50-60	1	—	—	Yes	18,200	25,800	1.42	Viscous liquid		

^a Pac(7.5)-TDI-BI corresponds of Pac of 750 MW from butyraldehyde, 2 mol of TDI and 1 mol of BI; all copolymers in this table have the 1:2:1 mol ratios of reactants; Pac(19) is 1900 MW soft segment from valeraldehyde.

^b With or without benzoyl chloride (BC).

^c *N*-methyl pyrrolidone is the solvent for GPC.

^d Hard segment only polymer.

^e Soft segment polymer only.

and $M_w = 24,000$; its IR spectrum is the same as the parent polyurethane, except with a reduced NH absorption at 3300 cm^{-1} .

Instrumental Techniques

TGA was obtained with a Perkin Elmer TGS-II instrument using about 5 mg sample, with a nitrogen flow rate of 0.08 mL min^{-1} and $20^\circ\text{C min}^{-1}$ heating rate. DSC curves were obtained with a Perkin Elmer DSC-II instrument at a $20^\circ\text{C min}^{-1}$ heating rate.

Dynamic rheologic properties were measured with a RD 7700 spectrometer using 2.5 cm diameter parallel disks, 10% strain at 10 rad s^{-1} .

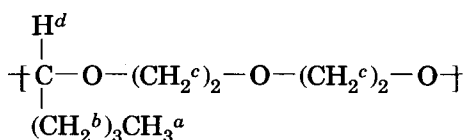
An Instron Tester was used to measure the mechanical properties of solvent casted copolymer film. Residual DMF was removed by evacuation at $70\text{--}80^\circ\text{C}$, $<1\text{ torr}$ for more than 24 h. The strain rate was 10 cm sec^{-1} .

RESULTS AND DISCUSSION

Synthesis

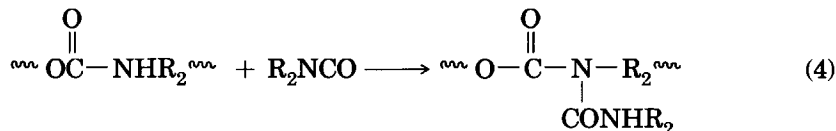
The MW of polyacetal synthesis is determined primarily by the stoichiometry of the reactants and efficiency of removal of the by-product, water. The latter was achieved by distillation of the azeotrope. In the case of the butyraldehyde-water azeotrope, it has a boiling point of 68°C , which is lower than 69.4°C for the benzene-water azeotrope. This resulted in a low MW polyacetal ($M_n = 750$). Attempts with parabutyraldehyde did not increase the MW.

The boiling point of valeraldehyde-water azeotrope is 83°C . Higher MW polyacetal can be obtained than butyraldehyde because of the more complete elimination of water. The ratio of aldehyde to glycol was 1:1. ^1H NMR spectra for the valeraldehyde-diethylene glycol polyacetal have peaks at δ (ppm): $H^a = 0.91$, $H^b = 1.40$, $H^c = 3.60$, and $H^d = 4.56$ in the correct intensity ratio for



The IR spectra of MDI end-capped polyacetal of valeraldehyde-DEG has the expected N-H stretching band at 3300 cm^{-1} , the N=C isocyanate vibration at 2260 cm^{-1} , the band at 1730 cm^{-1} for the C=O of isocyanate, and a 1600 cm^{-1} band for the carbonyl stretching of the urethane group. The IR spectra of the corresponding TDI capped soft block is like this except there are two urethane C=O bands at 1600 and 1620 cm^{-1} because of the two different urethane linkages with the 2,4-TDI. The spectra of the 1:2:1 copolymers of Pac-TDI-BI and the Pac-MDI-BD polymers have an N-H band at 3300 cm^{-1} , doublet C=O bands at 1710 and 1730 cm^{-1} , and doublet urethane C=O bands at 1600 and 1620 cm^{-1} . However, in the case of the former polymer, there is an additional intense absorption at 1650 cm^{-1} , which may be construed as absorptions due to allophenates.

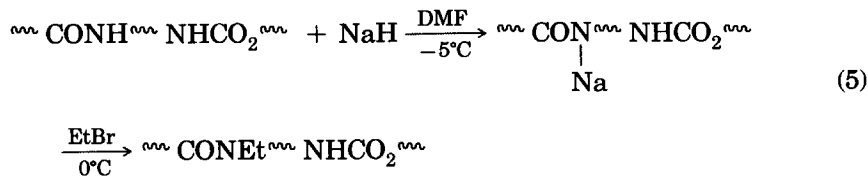
The main side product of polyurethane synthesis is the allophenates found by the following reaction, particularly at high conversion⁶:



The presence of allophenate can be detected by its characteristic 1640 cm^{-1} IR band.⁷ However, this assignment may not always be valid, as Hocker⁸ observed no 1640 cm^{-1} absorption in polymers containing allophenate groups. It is unlikely that the 1650 cm^{-1} absorption band in Pac-TDI-BI (1:2:1) polymer is assignable to allophenate because this absorption is absent in the spectra of Pac-MDI-BD (1:2:1) polymer. Instead, the 1650 cm^{-1} absorption may be best attributed to the C=O vibration of the aromatic amide of BI.

Gel formation can occur during reaction 2 or 3, depending upon the particular reactants. The probable cause is a trace amount of polyfunctionality in the polyacetal. Gel formation can be prevented by the addition of a trace amount of benzoyl chloride, a technique of restoring stoichiometric balance that is well known for condensation polymerizations. If the added benzoyl chloride overcompensates the stoichiometric imbalance, then it can significantly lower the MW. Some of the very low MW copolymers in Table I may be attributed to this effect, such as one of the TDI products. The effect of benzoyl chloride also supports the absence of allophenate formation, which could cause gelation.

The PacPU with some of the hydrogen atoms on the nitrogen are replaced with ethyl groups by the reaction



The derivative is a very soft material, due partly to reduced hydrogen bonding interactions¹ and the presence of ethyl groups, both would detract from the formation of crystalline domains.

Thermal Decompositions and Acid-Catalyzed

In the previously reported polyether polyurethanes,¹ the polyurethane hard segment decomposes between 200 and 300°C before the polyether soft segment decomposes above 400°C . The present copolymers also undergo two-stage decompositions, as shown by the data in Table III and the two TGA peaks in Figure 1.

For the pure soft segment Pac(19), the first derivative TGA peak is at 343°C ; the hard segment alone MDI-BI polymer has the peak at 292°C (Fig. 1c). End capping of the polyacetal definitely increases its thermal stability; the Pac(19)-MDI has T_{50} and TGA peaks (Fig. 1a) that are 66 and 47°C

TABLE III
TGA Data of Polyacetal Polyurethane

Copolymer (1:2:1)	Wt% of hard segment	T_{50}^a (°C)	TGA peaks (°C) ^b		H^+ induced ^c (wt. loss %)
			1	2	
Pac(19)	0	314		343	98.0
Pac(7.5)-TDI-BI	44.4	311	298	340	31.4
Pac(7.5)-TDI-BD	36.9	317		339	41.0
Pac(7.5)-MDI-BD	44.0	315	Not clear	340	38.0
Pac(7.5)-MDI-BI	50.1	337		348	
Pac(7.5)-MDI-BT	44.4	306	310	Not clear	
Pac(7.5)-MDI-BT	50.1	318	304	330	
MDI-BI	100	309		292	
Pac(19)-MDI	11.6	380		390	39.9
Pac(19)-TDI-BI ^d	24.0	315	308	340	
Pac(19)-MDI-BI	28.4	338	316	366	32.0
Pac(19)-TDI-BI ^e	24.0	314	Not clear	340	
Pac(19)-TDI'-BI	24.0	344	303	375	
Pac(15)-MDI-BI	33.4	—	—	—	33.4

^a Temperature for 50% weight loss.

^b Obtained by first derivative of TGA curve.

^c Acid-catalyzed isothermal decomposition at 200°C for 20 min. in the presence of 1% ethyl tosylate

^d $M_n = 13,300$.

^e $M_n = 6000$.

higher than Pac(19), respectively. Under idealized situations, the segmented block copolymers should undergo two-stage decomposition with peaks at 292 and 390°C. Such is not the case; Table III shows that, in general, the two TGA peaks lie between the two limits. This may be partly attributable

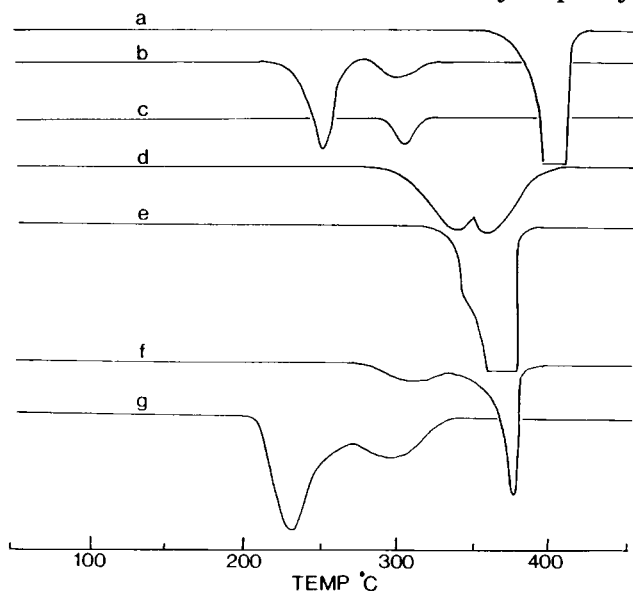


Fig. 1. First derivative of TGA curves for (a) MDI-end-capped Pac(19) with 11.6% hard segment; (b) same as (a) with 1% EtOTs; (c) MDI-BI with no soft segment; (d) Pac(7.5)-MDI-BI (1:2:1) 50% wt% hard segment; (e) Pac(19)-MDI-BI (1:2:1) 28.4% wt% hard segment; (f) Pac(19)-TDI'-BI (1:2:1) 24 wt% hard segment; (g) same as (e) with 1% EtOTs.

to imperfect microphase separation in the PacPU copolymers, but there is mixing-in-domain and/or domain mixing. This is supported by the sensitivity of thermal stability to the copolymer composition. For instance, as the hard segment content decreases, the polymer becomes more thermally stable. In Figure 1d of Pac(7.5)-MDI-BI (1:2:1) (50% hard segment), the TGA peaks are found at 336 and 360°C for the hard and soft segments, respectively. At lower hard segment content of 28% for Pac(19)-MDI-BI (1:2:1) (Fig. 1e), the two peaks at 347 and 366°C nearly merged. In this copolymer there may be little if any separate hard segment domain. If this hypothesis is correct, then there should also be an effect from the structure of diisocyanate. This is indeed the case. Copolymers containing the asymmetric 2,4-TDI either have lower decomposition temperatures or have one of the two TGA peaks too weak to be resolved. In the case of both symmetrical 2,6-TDI' and MDI, copolymers containing the former have the two TGA peaks approaching the limit values of the model soft and hard segments (compare Figs. 1e and 1f). This may mean better microphase separation in the 2,6-TDI' copolymers. There is apparently not a significant dependence on molecular weight. Thus, the two samples of Pac(19)-TDI-BI (1:2:1) denoted d and e in Table II, have M_n of 6000 and 13,300 but the same hard/soft composition. They have very similar TGA curves.

In the presence of 1% of ethyl tosylate, which is a precursor for *p*-TSA, the polyacetal soft segment is decomposed completely at 200°C in 20min. This acidolysis is buffered to slower rates in copolymers or MDI endcapped Pac(19).

Glass Transition

Polyacetals have very low T_g , which is insensitive to MW. The values of T_g determined by DSC for polyacetals having M_n values of 750, 1350, 1500, and 1900 are -76.0, -75.7, -74.1, and -76.8°C, respectively. This is raised by mere end capping; for instance, Pac(19)-MDI has $T_g = -55.8^\circ\text{C}$. Microphase separation is not expected for end-capped polyacetals, but polar interaction between end groups is apparently sufficient to lower the chain mobility. Table IV shows that the PacPu polymers all seem to have the

TABLE IV
 T_g of PacPu Copolymers

Copolymer	T_g (°C)	Copolymer	T_g (°C)
Pac(19)-MDI-BI (1:2:1)	-47.6	Pac(18)-TDI-BT (1:2:1)	-54.9
Pac(19)-MDI-BI (1:3:2)	-50.2	Pac(18)-TDI-BT (1:3:2)	-55.7
Pac(19)-MDI-BI (1:4:3)	-58.1	Pac(18)-TDI-BT (1:4:3)	-58.1
Pac(19)-MDI-BI (1:6:5)	-57.0	Pac(17)-MDI-BT (1:2:1)	-53.5
Pac(19)-TDI-BI (1:2:1)	-55.0	Pac(17)-MDI-Q (1:2:1)	-50.0
Pac(19)-TDI'-BI (1:2:1)	-50.4	Pac(17)-MDI-BD (1:2:1)	-50.8
		Pac(17)-MDI-BI (1:2:1)	-50.1

same T_g between -48 and -58°C . There is no definite trend of T_g dependence on hard segment content, or the nature of the isocyanate and the chain extender. Though the T_g of Pac with 1700–1900 MW do not show significant differences, there is definitely a limit on soft segment chain length below which the low-temperature T_g cannot be seen. This is true for the copolymer series with 750 MW polyacetal. In fact, even with soft segment MW of 1350, the Pac(13.5)-MDI-BI(1:2:1) has T_g raised to -37.9°C . The results suggest that the critical soft segment length is about eight repeat units.

Seefried et al.¹⁰ studied the T_g of polyurethanes using dynamic mechanical measurements. They found that the polymers derived from 2,4-TDI have T_g that increases with increasing hard segment, whereas there is no comparable dependence for the corresponding MDI copolymers. In our copolymers, those synthesized with 2,4-TDI and MDI have comparable T_g . This may be because the chain extenders we used are the more rigid BT and BI, which tend to reduce the effect reported by Seefried et al., who used the flexible BD as the chain extender.

We were unable to observe any transition other than T_g , including the melting transition, which was found for polyether polyurethane¹¹ and other polyurethanes.¹² There is apparently extensive mixing of soft and hard segments in the domain boundaries,¹² or mixing of segments in their respective domains¹ so that there is no significant microphase separation. Wide-angle x-ray analysis showed only a diffuse maximum at $2\theta = 20.5^\circ$, suggesting the absence of any crystalline domain.

Rheologic Properties

The rheologic properties seem to be sensitive to the diisocyanate, as might be expected. Table V compares them for copolymers comprised of the same polyacetal and chain extender but with different diisocyanates. The polymers containing the symmetrical 2,6-TDI or MDI have moduli G' and G'' , which are only slightly affected by temperature changes from 50 to 100°C . In marked contrast, these properties were decreased two to three orders of magnitude with the increase of 50° in temperature. Schneider et al.¹³ reported extensive domain mixing in the 2,4-TDI polyurethanes but less mixing for the 2,6-TDI systems. Seefried et al.¹⁰ concluded that the symmetry of the diisocyanate influences the degree of order in the hard segment domain.

TABLE V
Rheologic Properties of PacPU Copolymers

Copolymer	Temperature ($^\circ\text{C}$)	η^* (poise)	G' (dynes cm^{-2})	G'' (dynes cm^{-2})
Pac(19)-MDI-BI (1:2:1)	50	3.1×10^6	4.9×10^6	4.6×10^5
	100	6.7×10^4	2.7×10^6	1.4×10^6
Pac(19)-TDI-BI (1:2:1)	51	1.0×10^6	6.2×10^6	1.2×10^6
	100	6.4×10^4	9.2×10^6	4.3×10^5
Pac(19)-TDI-BI (1:2:1)	50	5.8×10^4	2.9×10^6	5.0×10^5
	100	7.2×10^2	1.1×10^2	7.2×10^3

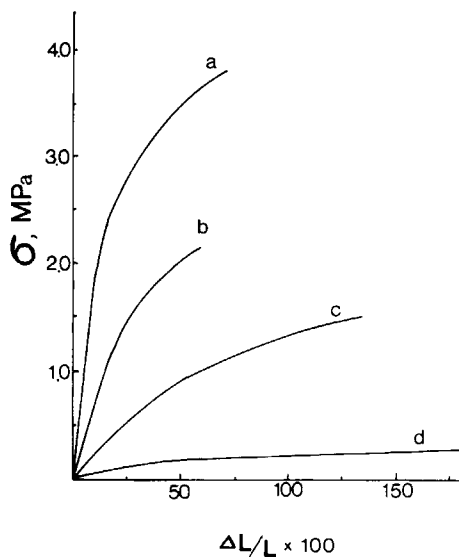


Fig. 2. Influence of chain extender on the stress-strain curve of (a) Pac(17)-MDI-BT (1:2:1); (b) Pac(17)-MDI-Q; (c) Pac(17)-MDI-BD (1:2:1); (d) Pac(19)-MDI-BI (1:2:1).

Mechanical Properties

PacPU segmented block copolymers can be synthesized to have a broad range of mechanical properties. Some of the stress-strain curves are shown in Figures 2 and 3. These properties at break and the moduli are summarized in Table VI. For very similar soft segments of M_n from 1700 to 1900, the molecular structures of the diisocyanate and the chain extender have a profound effect on the mechanical strength of the material. For a given diisocyanate, the toughness decreases in the order of symmetrical amide BT, bis(2-hydroxyethyl)hydroquinone Q, nonrigid BD, and asymmetric BI. The 1:2:1 copolymer with asymmetric 2,4-TDI and BI is liquidlike; the strength increases with the symmetrical 2,6-TDI' and BT. The modulus of the Pac-MDI-BI polymers increases at first with the hard segment content

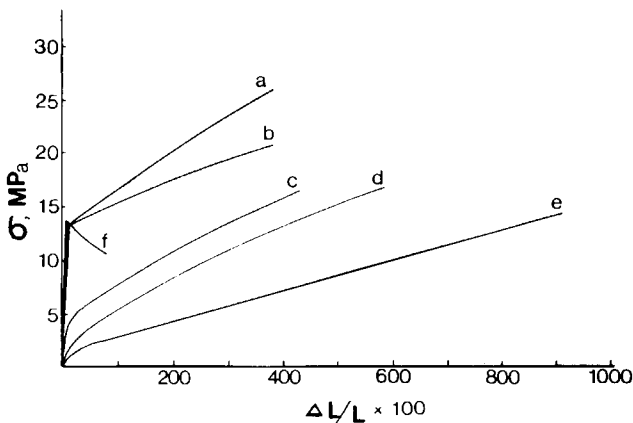


Fig. 3. Stress-strain curves for two series of PacPU copolymers: (a) Pac(18)-TDI-BT (1:4:3); (b) Pac(19)-MDI-BI (1:4:3); (c) Pac(19)-MDI-BI (1:3:2); (d) Pac(18)-TDI-BT (1:3:2); (e) Pac(18)-TDI-BT (1:2.5:1.5); (f) Pac(19)-MDI-BI (1:6:5).

TABLE VI
Mechanical Properties of PacPU Copolymers

Copolymer	Hard segment (wt %)	σ_y^a (MPa)	σ_b^b (MPa)	ϵ_b^c (%)	E^d (MPa)
Pac(17)-MDI-BT (1:2:1)	30.7		3.7	70.6	18.2
Pac(17)-MDI-Q (1:2:1)	29.1		2.2	65.9	7.1
Pac(17)-MDI-BD (1:2:1)	25.8		1.5	145	2.8
Pac(19)-MDI-BI (1:2:1)	28.4	0.13	0.8	1300	0.46
Pac(19)-MDI-BI (1:3:2)	39.8	5.5	16.4	429	21.2
Pac(19)-MDI-BI (1:4:3)	48.0	12.9	20.6	378	129
Pac(19)-MDI-BI (1:6:5)	59.2	13.5	11.0	83.6	71.6
Pac(17)-TDI-BI (1:2:1)	26.1	0.07	— ^e	—	—
Pac(18)-TDI-BT (1:2.5:1.5)	31.1	1.9	14.3	907	11.1
Pac(18)-TDI-BT (1:3:2)	36.3	4.5	16.7	586	12.7
Pac(18)-TDI-BI (1:4:3)	44.7	13.2	25.9	385	86.1
Pac(19)-TDI-BI (1:2:1)	24.0		0.7	90	4.2

^a Yield stress.

^b Stress at break.

^c Extension at break.

^d Modulus.

^e Does not break.

and then decreases after the latter exceeds 50%. This may be due to mixing of segments into the hard domain. The same seems to be true for the 2,4-TDI-BT system even though materials with very high hard segment content were not prepared.

The copolymers have elongation from 63 to 1300% and modulus from 0.5 to 129 MPa. A similarly large range of yield and break stress were found for the PacPu materials.

Acknowledgment

This work was supported by a grant from ONR.

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Received May 15, 1985

Accepted June 15, 1985