

Properties of Some Cast Polyurethane Rubbers Prepared from Poly- ϵ -caprolactone Polyols and Diisocyanates

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Synopsis

Polyurethanes were prepared by a one-step method from poly- ϵ -caprolactone (PCL) diols, diisocyanates, and a triol crosslinking agent (either PCL triol or trimethylolpropane). The influence of composition on mechanical properties was examined. In some formulations the elastomeric properties were lost by crystallization of the PCL segments. The occurrence and rate of crystallization were influenced by the composition and factors such as hydrolytic degradation and oil swelling. In one series of polymers the susceptibility to crystallization could be predicted from the composition. These materials showed melting and glass transitions when examined by differential scanning calorimetry and thermomechanical analysis. The molecular weight of the PCL diol had a greater influence on the glass transition temperature than the diol concentration.

INTRODUCTION

A soft durable rubber was required for a textile machine, and in a preliminary investigation¹ a cast polyurethane prepared by a one-step method from a mixture of poly- ϵ -caprolactone (PCL) polyols and tolylene diisocyanate performed well. Consequently, these polymers were investigated in detail. This type of polyurethane differs significantly in composition, properties, and method of manufacture from most PCL polyurethanes mentioned in the literature.²⁻⁷ Most of the latter²⁻⁴ are thermoplastic types that are not crosslinked and incorporate low molecular weight difunctional chain extenders. The few reports⁵⁻⁷ on cast (i.e., thermosetting) PCL polyurethanes used a two-step preparation: a prepolymer was first prepared from the PCL polyol and diisocyanate and later crosslinked, usually with diamines such as 4,4'-methylenebis-2-chloroaniline. The only one-step cast PCL polyurethane reported⁴ was not crosslinked.

This paper describes a systematic investigation of the influence of composition on the properties of cast polyurethanes prepared in a one-step reaction of diisocyanate, PCL diol, and PCL triol crosslinking agent with 1:1 hydroxyl-isocyanate stoichiometry. Our particular interest was in soft rubbers with high strength. However, our results should assist generally in the selection of formulations with other properties.

EXPERIMENTAL

Full details of the methods for casting and testing the rubbers have been given before.¹ All samples were cured for 16 hr at 110°C. The PCL polyols shown

in Table I were used as received from Union Carbide. The tolylene diisocyanate (TDI) used was a 65:35 mixture of the 2,4- and 2,6-isomers.

Differential Scanning Calorimetry (DSC)

DSC experiments were performed under nitrogen with a Perkin-Elmer DSC-1B instrument scanning at 8°C/min from -83°C. The samples tested had been stored after curing for between 2 and 18 months at 20°C.

In some experiments crystallinity was destroyed by heating samples in the instrument to 60°C and then cooling with liquid nitrogen. After approximately 5 min the sample temperature had dropped to -83°C, and heating was recommenced.

The glass transition temperatures (T_g) reported here are the lowest temperatures at which the slope changed in the DSC trace. The melting transition temperatures (T_m) reported are taken from the peaks of endothermic transitions between 20° and 60°C.

Thermomechanical Analysis (TMA)

The Perkin-Elmer TMS-1 thermomechanical analyzer was used in its penetration mode with a Perkin-Elmer UU-1 temperature controller. Analyses were carried out under nitrogen at a scan rate of 10°C/min. The samples tested had been stored after curing between 4 and 18 months at 20°C. The quenched samples were first heated in the instrument to 150°C, removed and dropped into liquid nitrogen, and then immediately reanalyzed. The T_g reported is the lowest temperature at which there was a change in slope of the displacement trace, which occurred at the same position as the start of a peak in the corresponding derivative trace. The T_m was taken as the peak of the derivative displacement curve in the +20 to +60°C region. The temperatures of the transitions from TMA corresponded within 5°C to those from the DSC experiments.

The melting of crystalline samples was more distinct in TMA than DSC, but melting transitions in the rubbers were only observed with DSC. Glass transitions of the rubbers were clearer in TMA than DSC, but in crystalline samples they were more distinct in DSC.

TABLE I
PCL Polyols Used

Designation	Type	\bar{M}_n^a
PCP 0200	diol	530
PCP 0210	diol	830
PCP 0230	diol	1250
PCP 0240	diol	2000
PCP 0260	diol	3000
PCP 0300	triol	540
PCP 0301	triol	300
PCP 0310	triol	900

^a From the manufacturer's literature.

RESULTS AND DISCUSSION

Crystallization of the Polycaprolactone Segments

The materials prepared from the PCL diol/triol mixtures and diisocyanates were mostly clear transparent rubbers of hardness about 60 Shore A (nos. 1–12, 14–18, 20, 29, and 30, Table II). However, some formulations (nos. 13, 19, 21, 31–33, 35 and 36) were hard (~90 Shore A) and opaque, but after being warmed at 50°C for 5–10 min softened to clear rubbers. The change in hardness and opacity was considered to be due to crystallization of the PCL part of the polymer or, in polyurethane terminology, the “soft” segments. The parent PCL diols melted below 50°C (Table III), whereas PCL homopolymer MW 41,000 melts at 60°C.² Polyurethanes can also become hard and opaque by crystallization of the “hard” urethane and urea segments,* but it was necessary to heat at much higher temperatures to destroy the crystallinity.^{3,8} Thermoplastic PCL polyurethanes can also crystallize^{2,3} but only if derived from the diol MW = 3000 and not from lower molecular weight diols. The more pronounced crystallization observed here was attributed to the high proportion of PCL diol (usually above 80% by weight) in the reaction mixture.

Polycaprolactone Melting Transitions in DSC and TMA Experiments

Thermal analysis showed (e.g., Fig. 1) multiple PCL melting transitions which were usually more pronounced in TMA than DSC. The positions of the melting peaks were below the melting points of the PCL diols (Table III). There was no relationship between the position of these melting peaks and either the molecular weight or the concentration of the PCL diol in the reaction mixture. The intensities of the melting peaks, but not their positions, depended on the thermal history of the sample. This was most apparent in cycling experiments in which, after being heated above the melting transition, the sample was cooled to –83°C. When the sample was heated again, the melting peak was absent or less intense. In two cases (nos. 27 and 33) there was a DSC crystallization exotherm in the cooling step.

Some of the rubbers that were clear, with no visual signs of crystallization, showed small DSC melting transitions (Table III). Melting transitions have also been observed in other rubbery polyester polyurethanes.⁹

Factors Influencing Crystallization

Various factors influenced the occurrence and rate of crystallization. It was more convenient to monitor crystallization by measuring the hardness than by thermal analysis. After the crystallinity had been destroyed by heating, the time for different formulations to reharden varied enormously and depended on their thermal history and composition. Increasing the heating temperature used to destroy crystallinity lengthened the time for subsequent recrystallization. After

* In this paper the term “hard segment” has been used for the urethane groups plus the diisocyanate backbones. This definition differs from that used by some authors^{2,8} who have restricted “hard segments” to the part of the polymers derived from low molecular weight chain extenders plus diisocyanates. According to this definition none of the polymers studied here (except no. 26) would contain any hard segments.

TABLE II
Mechanical Properties of Polycaprolactone Polyurethane Rubbers

No.	Polycaprolactone		Ratio diol/ triol by wt	Diisocyanate by conc., pphr	Additive conc., pphr	Crystal- lization ^a behavior	Hard- ness, Ha	Tensile strength, N/mm	Elongation, %	Tear strength, N/mm		Modulus, N/mm ²	
	Diol	Triol								Die B	Die C	100%	300%
1	PCP 0200	PCP 0300	4	TDI (27)		none	65	20.2	750	10.5		1.5	3.3
2	"	"	7	TDI (26)		none	50	6.5	450	13.3	17.5	2.0	4.0
3	"	"	7	TDI (26)	Nipsil (7)	none	53	9.5	350	17.8	19.1	3.2	8.4
4	"	"	10	TDI (25)		none	53	5.3	1200	9.2	12.0	0.8	1.1
5	0210	trimethylol- propane	16	TDI (24)		none	66	9.7	550			1.7	3.6
6	"	PCP 0300	4	TDI (21)		none	61	9.7	550	9.6	15.5	1.3	3.3
7	"	"	4	MDI (30)		none	65	9.7	500		12.8	1.8	4.1
8	"	"	4	HDI (20)		none	58	2.5	400		14.5	1.2	2.2
9	"	"	10	TDI (19)		none	55	10.8	1150	10.1	17.3	0.9	1.4
10	"	0300	2.4	TDI (19)		none	59	3.5	500	10.3	13.9	1.5	2.8
11	0230	0300	8	TDI (15)		none	54	10	1100	18.2	21.0	1.1	1.8
12	"	"	10	TDI (15)		slow	56 (62)	13.4 (13.4)	1100 (900)	(15.8)		0.9 (1.3)	1.7 (2.1)
13	PCP 0230 + 0240 (1:3)	"	8	TDI (13)		fast	55 (88)	>12.1 (21.1)	>1000 (900)	(30.0)	(42.0)	1.0 (4.1)	1.8 (5.7)
14	" (1:2)	trimethylol- propane	19	TDI (16)		none	64	12.0	700	10.0	21.1	1.5	3.0
15	PCP 0240	trimethylol- propane	20	TDI (15)		slow	62 (72)	(14.4)	(700)	(10.7)	(26.6)	(1.7)	3.0
16	"	PCP 0301	4	TDI (20)		none	67	3.9	250	7.2	7.4	1.9	
17	"	0300	4	TDI (14)		none	64	6.8	450	6.7	17.7	1.6	3.1
18	"	"	4	TDI (14)	Daltogard PR (1)	slow	55 (67)	8.9 (13.5)	850 (950)	(15.9)	(35.3)	1.2 (1.7)	2.2
19	"	"	4	TDI (14)	Ultrasil (8)	slow	69 (90)	8.0	500	16.5	25.5	2.2	5.4

20	"	"	4	TDI (22)	64	2.5	200	10.6	9.9	1.4
21	"	"	4	TDI (14)	55 (94)	4.6 (7.2)	650 (500)	(12.5)	(14.9)	1.0 (4.0)
22	"	"	6	TDI (13)	53 (76)	>13.0	>900 (700)	(36.7)	(32.9)	1.0 (2.9)
23	"	"	8	TDI (12)	46 (92)	>25.0	>1600 (700)	(33.8)	14.7	1.0 (4.5)
24	"	"	10	TDI (10)	30 (94)	>3.6 (18.9)	1450 (1150)	(58.9)	(41.2)	1.7
25	"	0310	3	TDI (12)	55 (90)	8.6	600	(64.4)	(64.4)	0.3 (5.6)
26	"	" + 1,4-butanediol (22:1)	64	TDI (19)	64 (91)	>19.0	>1450 (>1100)	(43.8)	14.6	(4.4)
27	PCP 0260	trimethylol-propane	19	TDI ^b (11)	35 (95)	(>26)	1350 (1000)	(73.2)	(41.2)	0.9 (4.0)
28	"	"	19	TDI (13)	60 (93)	6.4	750 (500)	(80.0)	(80.0)	0.2 (9.1)
29	PCP 0260	PCP 0300	2	TDI (17)	65	(25.3)				0.4
30	"	"	3	TDI (14)	62	14.4				1.3 (5.2)
31	"	"	4	TDI (12)	58 (88)	(15.3)				1.9
32	"	"	4	TDI (12)	64 (92)	2.3	550 (350)	(18.9)	6.9	1.8
33	"	"	4	TDI (12)	64 (92)	3.8		(22.5)	11	
34	" + Desmo-phen 1900U ^c (4:1)	0310	19	TDI (7)	51 (79)	(7.8)	(1150)	(70.2)	(101)	(3.3)
35	PCP 0240	Daltorol	8	TDI (8)	40 (93)	11.8	>1100	(7.3)	7.9	0.5
36	"	castor oil BP	4	TDI (11)	50 (80)	(12.1)	>1000	(7.3)		0.9

Figures in parentheses refer to properties of crystalline materials.

^a None = no opacity or increase in hardness observed after one year at 20°C; slow = took more than one week at 20°C to show opacity and increase in hardness; fast = took less than one week at 20°C to show opacity and increase in hardness.

^b Isocyanate hydroxyl ratio = 0.8:1.

^c Poly(propylene oxide)diol MW = 2000.

^d Poly(ethylene adipate) polyol.¹

TABLE III
 Transitions in Thermal Analyses of Polycaprolactone Polyurethanes

No. ^a	Polyol molecular weight (wt % of diol in polymer)		$T_g, ^\circ\text{C}$		$T_m, ^\circ\text{C}$		Remarks
	Diol	Triol	DSC	TMA	DSC	TMA	
1R	530 (59)	540 (15)	-21	-20	—	—	—
2R	530 (65)	540 (9)		-17	—	—	—
3R	530 (59)	540 (9)	-21		49		contains 10% Nipsil
4R	530 (68)	540 (7)	-22	-21, +8	—	—	—
5R	830 (72)	134 (5)	-35		42	—	—
6R	830 (63)	540 (15)	-31	-28	30, 51	—	—
7R	830 (56)	540 (14)	-24	-54, -20	39, 54	—	MDI in place of TDI
8R	830 (64)	540 (16)	-49	-53	45	—	HDI in place of TDI
9R	830 (73)	540 (7)	-35		33	—	—
10R	830 (57)	900 (24)	-30		39, 48	—	—
11R	1250 (75)	540 (9)	-44		41, 47	—	—
12C	1250 (78)	540 (8)	-43		49	—	—
13C	1250 (20) + 2000540 (10) (59)		-47		36, 50	—	—
14R	1250 (27) + 2000134 (4) (53)		-48		21, 50	—	—
15C	2000 (81)	134 (4)	-52	-46	57	35, 42	—
16R	2000 (64)	300 (16)	-43		49	—	—
17R	20C0 (68)	540 (17)	-50	-49	—	—	—
18C	2000 (68)	540 (17)	-41		39, 48		contains 1% Daltogard
19C	2000 (63)	540 (16)	-45	-44	35, 47	45	contains 10% Ultrasil
20R	2000 (63)	540 (16)	-55	-49	50, 48	—	MDI in place of TDI
21Q	2000 (68)	540 (17)	rubber -55	-54	—	—	HDI in place of TDI
21C	2000 (68)	540 (17)	cryst -55	-49	37, 49	37, 45, 48	exotherm 215°C
22C	2000 (75)	540 (13)	-52	-49	32, 50	31, 43	—
23Q	2000 (78)	540 (10)	rubber -59	-57			—
23C	2000 (78)	540 (10)	cryst -55	-57	38, 49	34, 43	—
24C	2000 (81)	540 (8)	-63	-57	47	50	—
25C	2000 (66)	900 (22)	-51		55		—
26C	2000 (75) + (90) — (4)		-47		55		MDI
27Q	3000 (85)	134 (4)	-51	-51, -26	58	50	—
27C	3000 (85)	134 (4)		-43, -11	49, 56	30, 45, 48	—
28C	3000 (82)	134 (4)	-52		40, 52		—
29R	3000 (55)	540 (28)	-49	-43			—
30R	3000 (64)	540 (21)	-54	-48	28	43	—
31C	3000 (70)	540 (18)	-46	-54	23, 35, 49	38, 43	—
32C	3000 (64)	540 (16)		-52		45	contains 10% Ultrasil
33C	3000 (89)	900 (5)	-51		45, 51		—
34C	3000 (55) + 2000540 (18) (14)		-50		31, 42		20% polycaprolactone replaced by Desmophen 1900U
35	2000 (81)	FW = 711 (10)	-54		48		11% polycaprolactone replaced by Daltorol PRI

No. ^a	Polyol molecular weight (wt % of diol in polymer)		T_g , °C		T_m , °C		Remarks
	Diol	Triol					
			DSC	TMA	DSC	TMA	
36	2000 (80)	933 (10)	-54		31, 46		20% polycaprolactone replaced by castor oil
<i>Pure Diols</i>							
	530 (100)	—	-36		28, 41		
	830 (100)	—	-35		41, 46		
	1250 (100)	—	-60		33, 57		
	2000 (100)	—	b		53, 59		
	3000 (100)	—	b		37, 67		

^a R = No observable crystallization after one year at 20°C; C = observable crystallization; Q = crystalline samples melted then quenched (forming a rubber).

^b No glass transition observed above -83°C.

cooling from 60 to 20°C some formulations crystallized in less than 1 hr (nos. 27 and 33, Table II), whereas others took several months to show signs of crystallization. In a few cases crystallization was incomplete after two years (nos. 15 and 22), with a translucent material of intermediate hardness (75 Shore A) being formed.

The following changes to the composition facilitated crystallization:

1. Increasing the molecular weight of the PCL diol.
2. Increasing the concentration of PCL diol in the formulations. Three ways to do this were (a) to add less triol, (b) to add less than the stoichiometric amount of diisocyanate, and (c) to replace the PCL triol by trimethylolpropane.

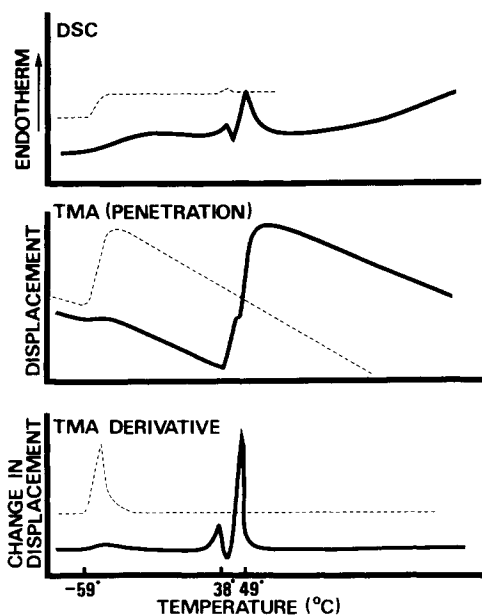


Fig. 1. Thermal analysis of PCL polyurethane no. 23. Solid line = crystalline sample; broken line = same material immediately after crystallinity destroyed by heating above the melting transitions.

3. Adding the carbodiimide antihydrolysis agent, Daltogard PR (ICI).
4. Adding fumed silica filler.
5. Changing from TDI to MDI or HDI.

In Figure 2 the polymers derived from TDI are arranged according to composition and their crystallization behavior is noted. From this, the susceptibility to crystallization could be predicted. The dividing line between crystalline and rubbery formulations would be different if other diisocyanates or hydroxyl isocyanate stoichiometries were considered.

As hydrolytic degradation (in water at 50°C or in an 80% R.H., 50°C atmosphere) proceeded, samples that were initially rubbery began to crystallize. A similar effect has been noted recently with thermoplastic polyester polyurethanes.¹⁰ We have observed (unpublished results) that swelling with certain oils also facilitated crystallization.

Attempts to produce very soft rubbers by introducing fewer, more spaced crosslinks resulted in harder materials since these changes facilitated crystallization. It was possible to produce rubbers of 30 Shore A hardness (e.g., no. 24, Table II), but these crystallized very rapidly. The softest rubber that did not crystallize at room temperature had a hardness of 50 Shore A (no. 2, Table II).

Several ways to inhibit crystallization were examined. Blending of PCL diols of MW 1250 and 2000 (nos. 13 and 14) had little effect. Replacement of 20% of the PCL diol by a poly(propylene oxide glycol) (MW 2000, no. 34) did not prevent crystallization but reduced the strength. Replacement of some of the polyol by other polyester polyols was examined in view of reports^{2,11} that PCL has high compatibility with other polymers. However, in the cases studied with castor oil (no. 36) or a poly(ethylene adipate) polyol (no. 35), it appeared that at least 25% of the PCL would need to be replaced. Castor oil slowed down crystallization more than the adipate polyol did.

Mechanical Properties of the Elastomers

Attempts to relate mechanical properties to composition were complicated since the concentration of both diol and diisocyanate as well as molecular weights

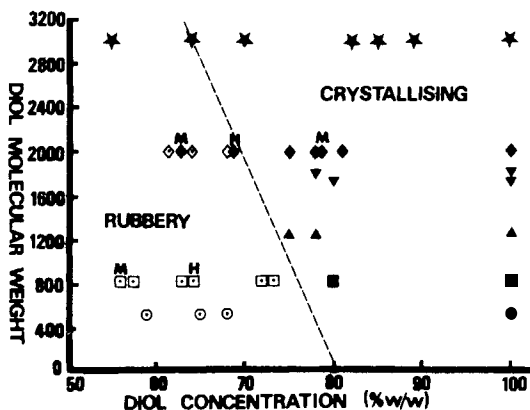


Fig. 2. Effect of PCL diol concentration on the tendency to crystallize. Samples to the right of the broken line (except no. 14) crystallized. Diol MW: (○) 530; (◻) 830; (Δ) 1250; (▽) 1250/2000; (◇) 2000; (★) 3000. M = MDI used as chain extender; H = HDI used as chain extender; TDI was used as chain extender in all other cases.

of both diol and triol were varied in the formulations studied. Considerations of the extent of crosslinking gave the simplest interpretation of the mechanical properties. Increased crosslinking slightly raised the modulus and hardness but reduced the tensile strength and elongation (samples 17 and 22–24 in Table II). Changing the molecular weight of the triol had little effect on the mechanical properties. In contrast to crosslinking, the addition of silica filler had a significant effect at low extensions (e.g., samples 2 with 3, 17 with 19, and 31 with 32). Silica increased the hardness, tensile strength, modulus, and tear strength but had little effect on the elongation.

In several cases other diisocyanates were used instead of TDI. With the PCL diol MW 830, changing from TDI (no. 6) to MDI (no. 7) increased the strength (a trend found^{2c} in thermoplastic PCL polyurethanes), but changing to HDI gave a softer weaker rubber (no. 8). With the PCL diol MW 2000 (nos. 17, 20, and 21) the MDI material was weaker, whereas the HDI material was softest but had intermediate tensile properties.

Effect of Crystallization on Mechanical Properties

The hardness, modulus, and tear strength of the crystalline materials were higher before the crystallinity was removed by heating at 50°C. However, crystallization did not change the ultimate tensile strength and elongation.

In tensile tests the crystalline materials showed necking with a soft, transparent neck. In addition, at very high strains some materials (e.g., nos. 24 and 27) showed strain-induced crystallization in the extended material. After extension the rubbery materials recovered completely, whereas the crystalline materials recovered only partially. However, if the extended crystalline samples were heated at 50°C in the absence of any stress, they recovered their original dumbbell shape within a short time.

All the rubbers, including those with DSC melting transitions in the thermal analysis (Table III), had the same mechanical properties when measured immediately after heating at 50°C or measured after storage for over two years at 20°C. This indicates that the partial crystallization of the soft segments in some rubbers did not have a reinforcing effect.

Swelling in Organic Solvents

The swelling of the rubber samples in xylene (Fig. 3) and dimethylformamide (Fig. 4) showed the expected effects of crosslinking. Swelling was greater in dimethylformamide than xylene, and reducing the molecular weight of the PCL diol increased this difference. Increasing the urethane concentration and hence polarity (e.g., by reducing the molecular weight of the PCL diol) reduced the swelling in both solvents. The extent of swelling for different diisocyanates was in the order HDI > TDI > MDI. The addition of silica filler did not change the swelling. Crystalline materials became clear after swelling in these solvents.

Polycaprolactone Glass Transition Temperatures

PCL glass transitions were shown in both DSC and TMA experiments. The glass transition temperatures (T_g) determined by DSC and TMA were within experimental error and independent of the thermal history of the samples. Crystallization, however, broadened the glass transition (e.g., Fig. 1). Crystal-

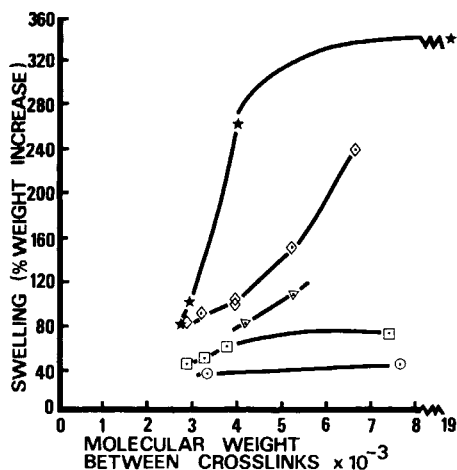


Fig. 3. Effect of composition on the extent of swelling in xylene. Molecular weight between crosslinks calculated according to ref. 18. For a description of symbols see Fig. 2.

lization has been reported to increase T_g in some thermoplastic PCL polyurethanes^{2a} and in a high molecular weight PCL homopolymer.¹¹

The T_g values were influenced by the composition. With different diisocyanates the order of T_g values was MDI > TDI > HDI with polymers derived from the PCL diol MW 830, but there was little difference with the polymers based on PCL diol MW 2000. A lower T_g was expected with the HDI polymer due to the greater flexibility of the hexamethylene chain compared with aromatic rings.^{9,12} Some thermoplastic PCL polyurethanes have higher T_g for TDI than MDI which was attributed to different extents of phase separation.²

The crosslink density (i.e., concentration of triol) had little effect on T_g , but T_g generally (Fig. 5) decreased with increasing molecular weight of PCL diol. This trend has also been noted with uncrosslinked thermoplastic PCL^{2,7} and

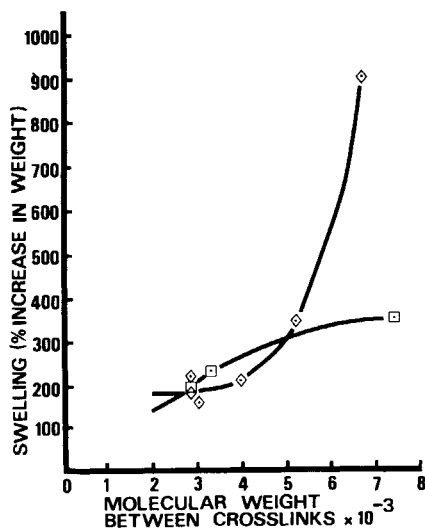


Fig. 4. Effect of composition on the extent of swelling in dimethylformamide. For a description of symbols see Fig. 2.

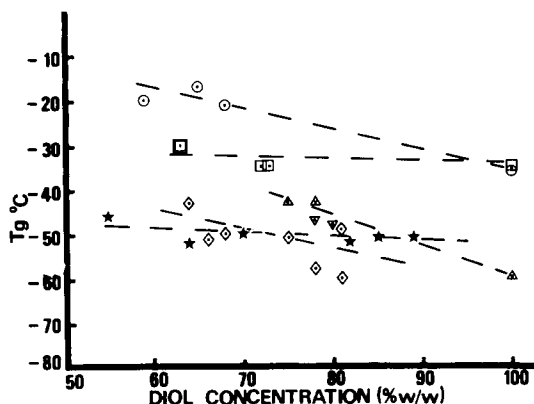


Fig. 5. Effect of composition on glass transition temperature (determined by DSC). Broken lines relate polymers from a particular diol. For description of symbols see Fig. 2.

adipate¹² polyurethanes. Normally with linear polymers, T_g increases with molecular weight. However, in polyurethanes the ends of the diol chains are anchored by urethane bonds, and so these chains become more flexible with increasing molecular weight of the diol and T_g falls.^{2a} Increasing the concentration of urethane groups (i.e., reducing the proportion of diol in the reaction mixture) would also be expected to increase T_g as the thermal transitions associated with the "hard" segments (i.e., urethanes) occur at higher temperatures. Such an effect was found^{2b} with thermoplastic polyurethanes derived from PCL diol MW 830; whereas with PCL diol MW 2100, T_g increased only at very high "hard" segment concentrations, and this was attributed to different degrees of phase separation. In the present case it is difficult to separate the effects of diol molecular weight and urethane concentration, since an increase in diol molecular weight is inevitably accompanied by a reduction in the weight content of urethanes in order to maintain 1:1 isocyanate-hydroxyl stoichiometry. If polyurethanes from one particular diol molecular weight are compared (dotted lines in Fig. 5), T_g did not greatly change in the range of diol compositions studied. Consequently, it was concluded that T_g was influenced more by the molecular weight of the PCL diol than by the urethane concentration.

The only polymer that showed another transition between the melting transitions and 240°C was no. 21 derived from HDI. It was not possible to say if this was a "hard" segment transition or decomposition.

Microstructure of Polycaprolactone Polyurethanes

Phase separation of "hard" and "soft" segments is considered to have an important influence on polyurethane properties; "hard" phases are embedded in a rubbery matrix, resulting in high strength and modulus.^{2,8,13} Even though polyurethane phase separation is widely accepted, it has been unequivocally established only in a few cases, mainly with uncrosslinked thermoplastic types including some PCL types.² There is much less evidence for phase separation in crosslinked polyurethanes, e.g., in polybutadiene^{14,15} and polyether¹⁶ types. Electron microscopy of an MDI-based PCL prepolymer crosslinked with polyols suggested phase separation.¹⁷

In the present study there is no definitive evidence for phase separation. The main factors¹⁶ that inhibit phase separation are present, e.g., crosslinks, low-

temperature processing, the use of TDI rather than the symmetrical MDI,^{2c,16} the low urethane concentration, the known^{11,13} compatibility of PCL with other polymers, the possibility of hydrogen bonding between the ester carbonyl groups and the urethane groups, and also the use of a one-step rather than prepolymer synthesis which might be expected to produce a more random structure. On the other hand, the occurrence of crystallization might be related to phase separation. The only evidence suggesting phase separation is the T_g data. With PCL diols MW 830 and 3000, the T_g was essentially independent of the diol concentration (Fig. 5). Such evidence has been used elsewhere^{2b} to indicate phase separation, but it may not be valid here as the "hard" segment concentration is low.

CONCLUSIONS

The influence of composition on the physical properties of a type of poly- ϵ -caprolactone polyurethane has been investigated systematically. The polymers were prepared in one step by reaction of a mixture of a diisocyanate, PCL diol, and a triol which was either a PCL triol or trimethylolpropane. The isocyanate-hydroxyl stoichiometry was kept at 1:1, but the crosslink density was varied. Other variations examined were the diisocyanate structure and the molecular weight of the PCL diol and triol.

A significant feature of this type of polymer was the crystallization of the polycaprolactone segments in some formulations which resulted in loss of elastomeric properties. Softer materials tended to crystallize more readily than harder ones. It was also possible to predict which formulations would crystallize. Crystallization could thus be avoided by changing the composition.

In certain applications crystallization would be a significant limitation, particularly since it was facilitated by partial hydrolysis and oil swelling, situations commonly encountered with such polyurethanes in service. Also, for other applications, poor low-temperature performance might be expected due to the high T_g (up to -20°C in some formulations). Formulations with the lowest tendency to crystallize generally had highest T_g .

References

1. G. B. Guise and G. C. Smith, *J. Macromol. Sci. Chem.*, to appear.
2. (a) C. G. Seefried, J. V. Koleske, and F. E. Critchfield, *J. Appl. Polym. Sci.*, **19**, 2493 (1975); (b) **19**, 2503 (1975); (c) **19**, 3185 (1975).
3. F. E. Critchfield, J. V. Koleske, and R. A. Dunleavy, *Rubber World*, **164**, 61 (August 1971).
4. K. W. Rausch and A. A. Sayigh, *Ind. Eng. Chem., Prod. Res. Dev.*, **4**, 92 (1965).
5. G. Magnus, *Rubber Age*, **97**, 86 (July 1965).
6. R. A. Dunleavy and F. E. Critchfield, *Rubber World*, **156**, 53 (June 1967).
7. N. E. Rustad and R. G. Krawiec, *Rubber Age*, **105**, 45 (November 1973).
8. N. S. Schneider, C. S. Paik Sung, R. A. Matton, and J. L. Illinger, *Macromolecules*, **8**, 62 (1975).
9. R. R. Aitken and G. M. F. Jeffs, *Polymer*, **18**, 197 (1977).
10. D. W. Brown, R. E. Lowry, and L. E. Smith, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.*, **19**, 822 (1978).
11. J. V. Koleske and R. D. Lundberg, *J. Polym. Sci. Part A-2*, **7**, 795 (1969).
12. K. Onder, R. H. Peters, and L. C. Spark, *Polymer*, **13**, 133 (1972); **18**, 155 (1977).
13. S. B. Clough and N. S. Schneider, *J. Macromol. Sci. Phys.*, **2**, 553 (1968).
14. R. R. Lagasse, *J. Appl. Polym. Sci.*, **21**, 2489 (1977).

15. Y. Minoura, S. Yamashita, H. Okamoto, T. Matsuo, M. Izawa, and S.-I. Kohmoto, *J. Appl. Polym. Sci.*, **22**, 1817 (1978).
16. T. L. Smith, *Polym. Eng. Sci.*, **17**, 129 (1977).
17. S. C. Kim, D. Klemperer, K. C. Frisch, W. Radigan, and H. L. Frisch, *Macromolecules*, **9**, 258 (1976).
18. B. E. Brokenbrow, D. Sims, and J. Wright, *Rubber J.*, **153**(6), 48 (1971).

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