

## Polyurethanes Derived from Caprolactone Polyesters and Diamines\*

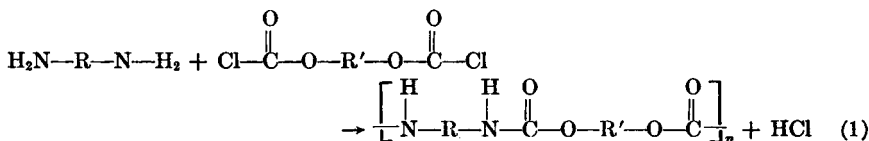
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### Synopsis

Thermoplastic, light-stable polyurethanes have been prepared by the interfacial polycondensation of secondary diamines with the bischloroformates of polyester diols derived from  $\epsilon$ -caprolactones. A straight-line relationship was obtained from a logarithmic plot of inherent viscosity versus  $\bar{M}_n$ . The effect of some structural variations on the properties of the polyurethanes is discussed. These variations included the molecular weight of the polyester diol, the initiator used in preparing the polyester diol, the introduction of a methyl substituent on the caprolactone ring, and the structure of the diamine. Polyurethanes prepared from polyester diols of  $\bar{M}_n$  from 2000-4000 are opaque, stiff materials which undergo a melting transition at 40-50°C. characteristic of the polyester component. Polyurethanes which are flexible and translucent at room temperature are obtained either by using a low molecular weight polyester diol or a copolyester diol containing >25% methyl  $\epsilon$ -caprolactone. The polyurethanes described are soluble in several common solvents and can be cold-drawn to produce material of high tensile strength. Thermal studies using DTA and TGA show an exothermic reaction starting above 300°C. Rapid weight loss beginning at 300-330°C. and leveling off near 500°C. accounted for 85-90% of the total sample and is attributed to decomposition of the polyester chains.

### INTRODUCTION

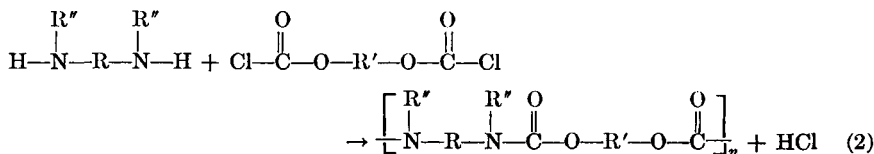
The preparation of polyurethanes by the reaction of diamines with the chloroformates of diols or polyols was first developed in Germany during World War II.<sup>1</sup> This method, represented by eq. (1), has not found widespread industrial application or been as extensively studied as the familiar reaction of diisocyanates with diols.<sup>2</sup> The formation of by-product HCl imposes certain limitations on the use of this system and



in particular makes it unsuitable for casting procedures. In conjunction with the interfacial polymerization technique, however, the method

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offers some advantages. Polyurethanes can be prepared which are difficult to obtain by melt polymerization due to high melting points and attendant decomposition. The low temperature and the absence of the characteristic isocyanate side reactions leading to allophanate, urea, and biuret formation should make possible the synthesis of more nearly linear, unbranched polyurethanes. Furthermore, this reaction offers access to certain structures not available via the diisocyanate route, notably polyurethanes with no residual hydrogen on the urethane nitrogen. Such polyurethanes may be prepared by the reaction of secondary diamines with glycol bischloroformates as shown in eq. (2).



The preparation of polyurethanes from secondary diamines and low molecular weight glycol bischloroformates<sup>3</sup> or diphenol bischloroformates<sup>4</sup> by the interfacial polycondensation technique at room temperature has been studied. Polyurethanes from certain polyether bischloroformates and secondary diamines have also been reported.<sup>5,6</sup>

This paper presents a study of the synthesis and characterization of previously unreported linear polyurethanes by the interfacial polycondensation of secondary diamines with the bischloroformates of polyester diols derived from  $\epsilon$ -caprolactones.

## EXPERIMENTAL

### Materials

$\epsilon$ -Caprolactone (ECL) and methyl  $\epsilon$ -caprolactone (MECL) were obtained from Union Carbide Chemicals Co., and were purified by vacuum distillation after refluxing over 4,4'-diphenylmethane diisocyanate (MDI) to remove water and free carboxylic acid. The glycols 1,4-butanediol, 1,3-butanediol, 2-butene-1,4-diol, trimethylolpropane monoallyl ether, and neopentyl glycol were obtained from commercial sources. The first four were distilled before use, a center cut being retained. The crystalline neopentyl glycol was used as received. The diamines and the catalysts were obtained from commercial sources and used as received. Reagent grade solvents were used.

### Polyesters from Caprolactones

A series of polyesters was prepared by the ring-opening polymerization of ECL and MECL at 170°C. by using an initiator diol and either dibutyltin dilaurate or tetrabutyl titanate as catalyst, by the method described by Young and co-workers.<sup>7</sup> Acid and hydroxyl numbers were determined by established methods<sup>8</sup> and the molecular weight calculated on assuming difunctionality.

### Preparation of Bischloroformates

The phosgenation procedure used was adapted from published procedures.<sup>9,10</sup> Due to the toxicity of phosgene, this reaction must be carried out in an efficient fume hood. The apparatus consisted of a 3-liter flask fitted with a stirrer, low-temperature thermometer, addition funnel with pressure-equalizing side arm, gas inlet tube leading to the bottom of the flask, and a gas exit tube. The evolved gases were led through a drying tube and a series of traps containing 10% aqueous sodium hydroxide to a sink drain where they were washed down with water. A phosgene cylinder mounted on a balance was connected by Tygon tubing through a trap and flowmeter to the gas delivery tube.

A typical run using 2000 molecular weight polyester was conducted as follows. Dry methylene chloride (800 ml.) was cooled in the reaction flask to  $-70^{\circ}\text{C}$ . by a Dry Ice-acetone bath, while protected with a drying tube. Phosgene (215 g., 2.17 mole) was admitted from the weighed cylinder. A solution of caprolactone polyester (PECL) (800 g., 0.4 mole) in 1200 ml. methylene chloride was added from the dropping funnel over a period of 3-4 hr. During this time the temperature was allowed to rise slowly to about  $-10^{\circ}\text{C}$ . When all the polyester solution had been added, the cooling bath was removed and the solution allowed to stand overnight. Excess phosgene, HCl, and solvent were removed by aspirator vacuum while heating on a water bath. The residue was dissolved in benzene and adjusted to the desired volume for subsequent polymerization. The bischloroformates were not routinely isolated, but selected samples were analyzed for chlorine and for chloroformate. The chloroformate analysis was performed by a modification of a standard method used for isocyanate analysis.<sup>8</sup>

### Interfacial Polymerization

The procedure used as standard for most of the polyurethanes discussed in this paper was adapted from published reports.<sup>3,11</sup> A benzene solution containing 0.2 moles of PECL bischloroformate in 1200 ml. was added quickly to 900 ml. aqueous solution containing 0.22 moles piperazine and 0.45 moles sodium hydroxide in a stainless steel beaker with rapid stirring with a Dispersator stirrer (Premier Mill Corp., Reading, Pa.) controlled by a variable transformer. The whole mass thickened and in a matter of minutes could no longer be mixed. The polymer was then freed from salts and excess piperazine by dissolving in 4 liters of acetone and precipitated by pouring into 12 liters of water. The process was repeated twice more before drying the polymer in a vacuum oven at  $65^{\circ}\text{C}$ .

## RESULTS AND DISCUSSION

The ring-opening polymerization of  $\epsilon$ -caprolactone proved to be a rapid convenient method of obtaining polyesters with nearly complete hydroxyl termination. The average molecular weight could be varied as desired

TABLE I  
 Polyester Diols from Caprolactones

Lactone	Initiator	$n_D^{20}$	$\bar{M}_n$ (by endgroup analysis)	M.p., °C.	$[\eta]$ , dl./g. <sup>a</sup>
ECL	1,4-Butanediol	1.4558	520	33	0.031
		1.4584	1040	47	0.048
		1.4600	2010	53	0.080
		1.4606	2780	59	0.102
		1.4607	4400	62	0.135
ECL	2-Butene-1,4-diol	1.4613	2080	55	0.080
ECL	1,3-Butanediol	—	1940	50	0.082
ECL	Trimethylol propane monoallyl ether	1.4607	2000	53	0.074
ECL	Neopentyl glycol	1.4594	2020	48	0.080
MECl	1,4-Butanediol	1.4578	2080	Liquid	0.064
MECl 50%	1,4-Butanediol	1.4587	2195	Liquid	0.071
ECL 50%					
MECl 25%	1,4-Butanediol	1.4594	1960	Paste	0.074
ECL 75%					

<sup>a</sup> Viscosities were determined with a Ubbelohde dilution viscometer in toluene at 30°C. over a concentration range from 2 g. to 0.5 g./100 ml. The intrinsic viscosity  $[\eta]$  was obtained by extrapolating a plot of  $\eta_{sp}/c$  versus  $c$  to zero concentration.

by adjusting the monomer/initiator ratio. In addition, changing the type of initiator or substituents on the caprolactone ring allowed for further structural variations. The polyester diols used in this study are described in Table I. The use of polyester diols derived from  $\epsilon$ -caprolactone in preparing polyurethanes by reaction with diisocyanates has been previously reported.<sup>12-14</sup>

The bischloroformate derivatives of the polyester diols were prepared by reaction with excess phosgene at low temperatures to minimize the competing reaction of chloroformate with an additional hydroxyl group to form a carbonate structure. The bischloroformates which were isolated resembled the polyester diols in appearance and physical properties and decomposed slowly on standing in air with evolution of HCl.

The formation of polyurethanes by the interfacial polycondensation method involves the reaction of an aqueous solution of diamine and acid acceptor with the bischloroformate in an organic solvent immiscible with water. The importance of a number of reaction variables in the interfacial process has been discussed in detail, particularly for the case of polyamides.<sup>15,16</sup> Similar work with polyurethanes from short-chain glycol bischloroformates and diamines has also been reported.<sup>3,17</sup> Some of the variables examined were the concentration of reactants, the choice of acid acceptor and the organic solvent.

Although most of the polyurethanes reported in this study were prepared under the standard set of conditions outlined in the Experimental section, several runs were made in which these parameters were systematically

TABLE II  
Effect of Reaction Conditions on Polyurethane Properties<sup>a</sup>

Piperazine concn., mole/l.	Bischloro- formate concn., mole/l.	Acid acceptor	Solvent	Yield, %	$\eta_{inh}^b$
0.367	0.300	NaOH	Benzene	84	1.09
0.367	0.250	"	"	74	0.85
0.367	0.167	"	"	65, 72	0.87, 0.93
0.367	0.083	"	"	64	0.71
0.367	0.033	"	"	67	1.20
0.330	0.167	"	"	76	1.00
0.250	0.167	"	"	81	1.05
0.100	0.167	"	"	71	0.86
0.050	0.167	"	"	85	1.57
0.367	0.167	Na <sub>2</sub> CO <sub>3</sub>	"	76	1.01
0.367	0.167	Et <sub>3</sub> N	"	70	0.22
0.367	0.167	NaOH	Methylene chloride	95	0.96
0.367	0.167	"	Toluene	—	0.98

<sup>a</sup> All reactions were conducted at a diamine/bischloroformate mole ratio of 1.1:1, a total volume of 550 ml., and were stirred with a Dispersator (Premier Mill Corp., Reading, Pa.).

<sup>b</sup> Determined at 30°C. at a concentration of 0.5 g./100 ml. in toluene.

varied. The effect on yield and inherent viscosity of variations in the concentration of the reactant solutions and in the type of solvent and acid acceptor are shown in Table II. In all cases the ratio of amine groups to chloroformate groups was maintained at 1.1:1, the total volume of reactants was 550 ml., and the stirrer control was kept at the same setting. The values reported for the yield are based on the amount of polyester diol used and are approximate due to the difficulty of obtaining quantitative recovery of the sticky polymer during repeated precipitations. The final yield of dry polymer ranged from 65 to 95% and tended to be higher with increasing concentration of the bischloroformate solution. The inherent viscosity determined in toluene at 30°C. on solutions containing 0.5 g. polymer/100 ml. ranged from 0.71 to 1.57 with one exception; a value of 0.22 was obtained when triethylamine was used as the acid acceptor. Although no direct relation between solution concentration and inherent viscosity was observed, the highest viscosities were obtained at the lowest piperazine concentration in the one series and at the lowest bischloroformate concentration in the other. Operating at very low concentrations of both components, apart from the difficulty in handling large volumes, may result in competition from the hydrolysis of the chloroformate groups, especially at high pH values.<sup>16</sup> The effect of variation of organic solvent and of acid acceptor was also examined in a few experiments.

A relationship between viscosity and molecular weight was obtained for the series of linear polyurethanes prepared from 2000 molecular weight PE-

TABLE III  
Comparison of Inherent Viscosity with Intrinsic Viscosity  
for Randomly Selected Polyurethanes from Polycondensation<sup>a</sup>

$[\eta]^b$	$\eta_{inh}$ (0.5 g./100 ml.) <sup>c</sup>	Difference
0.55	0.55	0
0.49	0.49	0
0.55	0.54	-0.01
0.98	0.98	0
1.00	1.11	+0.11
0.97	0.97	0
0.87	0.93	+0.06
1.60	1.54	+0.06
0.26	0.27	+0.01
0.25	0.25	0
0.16	0.17	+0.01
1.02	1.05	+0.03
0.69	0.69	0
0.64	0.67	+0.03
1.32	1.30	-0.02
0.65	0.69	+0.04
1.09	1.09	0
0.92	0.95	+0.03
1.03	1.02	-0.01
1.24	1.24	0

<sup>a</sup> The polyurethanes were all prepared by the reaction of diamines with the bischloroformates of caprolactone polyester diols. The polyester diols were prepared using various initiator diols, and were of various molecular weights.

<sup>b</sup> Determined in Ubbelohde dilution viscometer at concentrations ranging from 2.0 to 0.2 g./100 ml. in toluene at 30°C. and extrapolation of a plot of  $\eta_{sp}/c$  versus  $c$  to zero concentration.

<sup>c</sup> Calculated from the value for  $\eta_{sp}/c$  at a concentration of 0.5 g./100 ml. as read from the plot of  $\eta_{sp}/c$  versus  $c$  used for determination of  $[\eta]$ .

CL and piperazine. The inherent viscosity measured at a specific concentration is sometimes used as a convenient approximation of the intrinsic viscosity.<sup>18</sup> A comparison of the intrinsic viscosity with the inherent viscosity determined at a concentration of 0.5 g./100 ml. for a number of polyurethanes prepared by the method described in this study is shown in Table III. These data confirm that for this family of polyurethanes the inherent viscosity so obtained is a good approximation for the intrinsic viscosity and it was so used throughout this investigation. Number-average molecular weights  $\bar{M}_n$  were determined with a Shell-Stabin automatic osmometer, toluene or tetrahydrofuran being used as the solvent. A log-log plot of inherent viscosity versus  $\bar{M}_n$  formed the straight line relationship shown in Figure 1, which can be expressed by the equation:

$$\eta_{inh}(0.5 \text{ g./100 ml.}) = 4.08 \times 10^{-4} M^{0.71} \quad (3)$$

Although these molecular weights were determined on unfractionated polymers, the straight-line relationship indicates that the distribution in each case was probably similar and a useful relation was obtained.

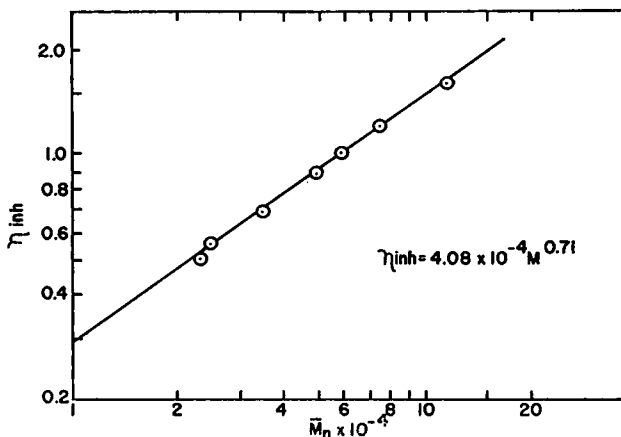


Fig. 1. Relationship between inherent viscosity and  $\bar{M}_n$  for polyurethanes derived from PECL and piperazine.

### Properties of Polyurethane

The linear polyurethane obtained by interfacial polymerization of piperazine with the bischloroformate of 2000 molecular weight PECL which had been initiated with 1,4-butanediol was taken as the reference standard for comparison of structural variations. The polyurethane was a tough, opaque, stiff, white material at room temperature which softened and became clear and flexible at about 40–50°C. Differential thermal analysis indicated this to be a first-order, melting transition. The polymer was soluble at a concentration of 18 g./100 ml. in acetone, methylene chloride, and benzene, but was essentially insoluble in methanol, water, and petroleum ether. Stress-strain data were obtained with an Instron tester at a crosshead speed of 6 in./min. on 0.5 × 6 in. samples which were die-cut from pressed sheets. On extension the polyurethane reached a yield point at about 10% elongation, after which cold-drawing occurred, resulting in an ultimate elongation of about 2000%. Nielsen,<sup>19</sup> in a discussion of the cold-drawing phenomenon, has described the types of polymers and the conditions usually associated with it. Both crystalline and amorphous polymers are known to cold-draw. Due to accompanying thermal gradients and large changes in cross-section, the significance of ultimate properties, such as tensile strength at break, is uncertain. Thus, based on the original cross-sectional area, the tensile strength of the polyurethane described above was 2000–3000 psi. However, when the cross-section of drawn samples was used for calculation, tensile strength at break was 10,000–12,000 psi. Because of the cold-drawing tendency of most of these polyurethanes, stress-strain data were not used for characterization.

Several series of polyurethanes were prepared with the use of the same reaction conditions, but with varying structure of the reactants. The reactants and the properties of the polyurethanes obtained are summarized

TABLE IV  
Effect of Reactant Structure on Polyurethane Properties

Polyester diol			Polyurethane properties					
Mol. wt. <sup>a</sup>	ECI, %	MECL, %	Initiator	Diamine	Softening point, °C.	$\eta_{inh}^b$	$\bar{M}_n^c$	Description
500	100	—	1,4-Butanediol	Piperazine	25	0.88	73,000 <sup>d</sup>	Transparent, flexible
1000	"	—	"	"	44	0.99	55,000	Opaque, less flexible
2000	"	—	"	"	49	0.87	49,000	Opaque, stiff
2800	"	—	"	"	57	0.80	45,000	"
4400	"	—	"	"	54	0.57	28,500	"
2000	"	—	2-Butene-1,4-diol	"	47	0.87	—	"
2000	"	—	Trimethylol propane monoallyl ether	"	45	0.60	—	"
2000	"	—	1,3-Butanediol	"	48	0.51	—	"
2000	"	—	Neopentyl glycol	"	43	0.51	—	"
2000	—	100	1,4-Butanediol	"	25	0.79	—	Transparent, flexible
2000	50	50	"	"	25	0.60	—	"
2000	75	25	"	"	25	1.03	—	"
2000	100	—	"	2-Methylpiperazine	47	0.60	—	Opaque, stiff
2000	"	—	"	<i>N,N'</i> -Dimethyl-hexamethylene-diamine	47	0.24	—	Granular, hard
2000	"	—	"	Hexamethylene-diamine	52	0.43	—	Opaque, stiff

<sup>a</sup> Approximate value. See Table I for description of individual polyesters.

<sup>b</sup> Determined at 30°C., 0.5 g./100 ml. in toluene.

<sup>c</sup> Determined with Shell-Stabin automatic osmometer.

<sup>d</sup> This value may be high due to some diffusion through the membrane.



in Table IV. The results of these structural variations are discussed in the following sections.

### Effect of Polyester Molecular Weight

Polyurethanes were prepared from a series of polyester diols with molecular weights ranging from 500 to 4400. Reducing the molecular weight of the polyester diol has the effect of increasing the concentration of the reactive groups and, consequently, of the urethane linkages in the final polymer. This normally would result in a higher softening or melting temperature due to increased interchain hydrogen bonding.<sup>20</sup> However, in the present case, the substituted urethane linkages do not contribute such hydrogen bonding. Under these circumstances the polyurethane properties are more dependent on the character of the polyester chain portion. The lower molecular weight polyester diols used were liquids and hence had the effect of lowering the softening temperature of the polyurethane. Thus, the polyurethane derived from a 500 molecular weight polyester diol was a clear, flexible material at room temperature, while the polyurethanes from higher molecular weight polyesters were opaque and comparatively stiff. The temperature at which these became clear and flexible is recorded in the table as the softening point. The inherent viscosities and molecular weights from osmometry were in agreement with the relationship shown in Figure 1. The molecular weight of the polyurethane tended to decrease somewhat with increasing molecular weight of polyester.

### Effect of Polyester Initiator

Polyesters prepared using a number of branched and unsaturated diol initiators were used to prepare linear polyurethanes by reaction with piperazine. All the polyurethanes from polyesters of  $\bar{M}_n = 2000$  were similar to that from the polyester with 1,4-butanediol, previously described. The degree of branching provided by the initiator diols was not sufficient to overcome the crystallization of the long polyester chains, and the softening points were not significantly lowered. Functional groups or cross-linking sites may be introduced into the polymer, however, by selection of a suitable initiator.

An unexpected difficulty was encountered when initiators having vicinal hydroxyl groups or hydroxyl groups adjacent to ether oxygen were used. Included in this group of diols were ethylene glycol, 1,2-propanediol, dipropylene glycol, and poly(propylene glycol). Caprolactone polyester prepared from these initiators consistently failed to give high molecular weight polyurethanes after phosgenation and interfacial reaction with piperazine. The reason for this behavior is not known.

### Effect of Methyl-Substituted Polyester

A series of polyurethanes was prepared from polyester diols ( $\bar{M}_n = 2000$ ) derived from methyl  $\epsilon$ -caprolactone (MECL) and copolymers of MECL

with unsubstituted caprolactone. The presence of the methyl-substituted segments on the polyester chain even in a 25% concentration resulted in polyurethanes which did not crystallize at room temperature. Inherent viscosities indicated that these were of the same molecular weight range as the crystalline polymers obtained from unsubstituted PECL.

### Effect of Various Diamines

Although most of the polyurethanes investigated were prepared with piperazine, the study was extended to include a few other diamines for comparison. No significant difference was observed on substituting 2-methylpiperazine for piperazine. *N,N'*-Dimethylhexamethylenediamine gave a granular solid product with a low viscosity. The molecular weight of this material as determined with the Mechrolab vapor pressure osmometer was 4350, indicating that an average of only two polyester units were joined together. The use of a diprimary amine, hexamethylenediamine (HDA), resulted in a polyurethane very similar in appearance to the piperazine-containing polymer but which had a somewhat lower inherent viscosity.

The results of structural variations indicate that the crystalline polyester chain segments and the substituted aliphatic urethane linkage are predominantly responsible for the polymer properties. As long as the character of the polyester or the urethane linkage was not significantly changed, variations in polyester molecular weight, initiator structure, or diamine structure did not greatly affect the polyurethane properties. More drastic changes in the polyester chain, such as methyl substituents, or changes in the urethane linkage, such as the presence of an aromatic group, did change the characteristics of the final polyurethane.

### Color Stability of Polyurethanes

The tendency for polyurethanes from aromatic diisocyanates to turn yellow on exposure to light has been a factor limiting their use in some applications. The relationship of color stability to structure has been the subject of a number of investigations. Infrared and ultraviolet spectra have been offered as evidence that color formation results from an ultraviolet-initiated autoxidation of the aromatic ring to a quinoid structure.<sup>21</sup> Polyurethanes from aliphatic diisocyanates<sup>22</sup> and from diisocyanates in which the aromatic ring was separated from the isocyanate group by alkylene groups<sup>23</sup> have been reported to have improved color stability and weatherability. Beachell and Ngoc Son noted yellowing of tolylene diisocyanate (TDI) in oxygen or in nitrogen, which occurred more rapidly with ultraviolet exposure.<sup>24</sup> These workers attributed some yellowing, especially on heating, to the formation of carbodiimides from degradation products. Beachell has also suggested that the improvement in color stability of urethane foams by treatment with reagents such as monoisocyanates, reported by Wilson,<sup>25</sup> is probably due to the reaction with free amine groups. Such amine endgroups have been found to influence the rate of decomposi-

tion even in *N*-substituted urethanes.<sup>17</sup> Polyurethanes prepared from caprolactone polyesters and secondary diamines, such as those described in this study, have neither aromatic groups nor urethane hydrogens. These materials did not turn color after many months exposure to light. A more drastic Fadeometer test showed no changes after 60 hr. of exposure but could not be continued due to softening of the sample. Visual comparison of the polyurethanes prepared by reaction of PECL bischloroformate with piperazine and with hexamethylenediamine indicated little difference in the stability of these materials to light. Polyurethanes prepared by the reaction of PECL with TDI, however, undergo quite rapid yellowing under the same conditions. These qualitative observations suggest that the presence of urethane hydrogens may not be detrimental to color stability unless activated by an adjacent phenyl group.

### Thermal Stability of Polyurethanes

The initial thermal degradation of polyurethanes normally proceeds via urethane scission to isocyanate and hydroxyl components<sup>24,26</sup> Tobolsky has shown by stress relaxation studies that polyurethanes without urethane hydrogens are more resistant to scission since the above reaction path is blocked.<sup>27</sup>

In the present study the thermal stability of some representative polyurethanes has been examined by differential thermal analysis (DTA) and thermogravimetric analysis (TGA). Thermograms for the temperature range 20–200°C. in the air are shown in Figure 2. The opaque polyurethanes prepared from 2000  $\bar{M}_n$  PECL and the PECL itself show an endothermic peak in the 45–50°C. region. This is a first-order melting transition characteristic of the polyester segments. The translucent flexible polyurethanes prepared from PMECL or from PECL of low  $\bar{M}_n$  have no melting transition in this region. DTA thermograms are compared with the weight loss determined by TGA at temperatures above 200°C. in

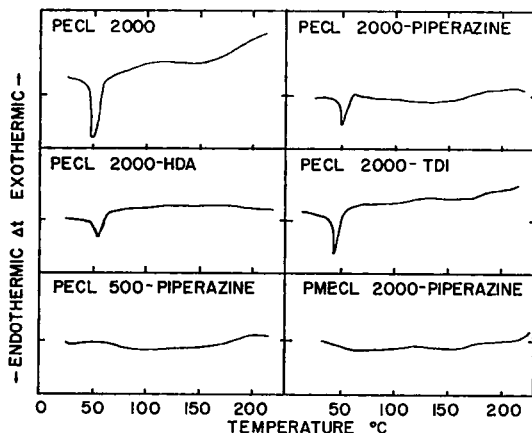


Fig. 2. DTA thermograms (0–200°C.) for PECL 2000 and for several polyurethanes.

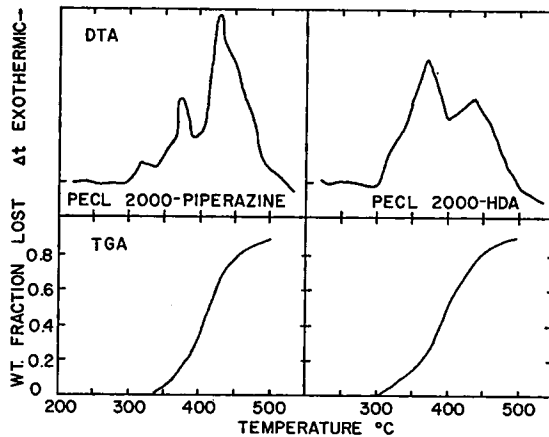


Fig. 3. DTA and TGA thermograms (200–500°C.) for polyurethane derived from PECL 2000 and piperazine or hexamethylenediamine.

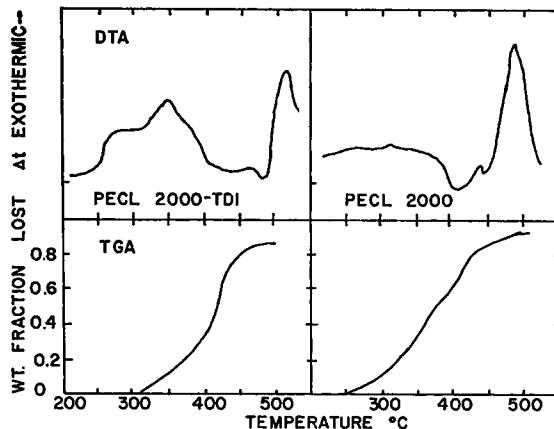


Fig. 4. DTA and TGA thermograms (200–500°C.) for PECL and for a polyurethane derived from PECL and TDI.

Figures 3 and 4. The polyurethane from PECL–piperazine has a smaller exotherm below 400°C. than does the polyurethane from PECL–hexamethylenediamine. Weight loss began at 300°C. for the PECL–HDA polymer and at 330°C. for the PECL–piperazine polymer. In both cases the most rapid weight loss occurred at 400°C. coinciding with the DTA endotherm in this region. The TGA curves leveled off near 500°C. after 85–90% weight loss. A comparative experiment with a PECL–TDI polyurethane resulted in a similar weight-loss curve but the exothermic reaction began at a lower temperature (250°C.). This may be a result of the activating effect of the phenyl group adjacent to the urethane. Slade and Jenkins<sup>28</sup> in studies on crosslinked polyurethanes attributed the initial exothermic reaction to oxidation and the endothermic region to depoly-

merization. In the case of the polyester itself, a broad exothermic region extends from 200–300°C. Weight loss begins at 250°C. and appears to proceed in two stages, ultimately leveling off at 450°C.

Thus, it appears that although stability in the region 250–300°C. is enhanced by the absence of urethane hydrogens activated by adjacent phenyl groups, the major decomposition and weight loss occurring at higher temperatures is characteristic of the polyester chain rather than the type of urethane linkage.

This approach to the preparation of novel polyurethanes was suggested and initiated by Dr. J. A. Parker. Many of the polymerizations and determinations were performed by J. J. Juliano and Carol S. Hawk. Their contributions are gratefully acknowledged.

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### Résumé

On a préparé des polyuréthanes thermoplastiques stables à la lumière par polycondensation interfaciale de diamines secondaires avec des bischloroformiates de polyesters diols dérivés des epsilon-caprolactones. Une relation linéaire a été obtenue au départ du diagramme logarithmique de la viscosité inhérente en fonction de  $M_n$ . L'effet de certaines variations de structure sur les propriétés des polyuréthanes est discuté. Ces variations comprennent le poids moléculaire du polyester diol, l'initiateur utilisé dans la préparation du polyester diol, l'introduction d'un substituant méthyle dans l'anneau caprolactone et la structure de la diamine. Les polyuréthanes préparées au départ d'un polyester diol de  $M_n$  de 2000 à 4000 sont des matériaux opaques et durs qui subissent une transition de fusion à 40–50°C, caractéristique du composant polyester. Des polyuréthanes qui sont flexibles et translucides à température de chambre sont obtenus soit en utilisant un polyester diol de bas poids moléculaire ou on copolyester diol contenant >25% de méthyl-epsilon-caprolactone. Les polyuréthanes décrites sont solubles dans la plupart des solvants ordinaires et peuvent être étirés à froid en produisant un matériau de force de tension élevée. Les études thermiques utilisant le DTA et TGA montrent une réaction exothermique qui débute au-dessus de 300°C. Une rapide diminution de poids commençant à 300–330°C et ralentissant vers 500°C, rend compte de 85–90% de l'échantillon total et est attribuée à la décomposition de la chaîne polyester.

### Zusammenfassung

Thermoplastische, lichtbeständige Polyurethane wurden durch Grenzflächenpolykondensation sekundärer Diamine mit Bischloroformiaten der von  $\epsilon$ -Caprolactonen abgeleiteten Polyesterdiolen dargestellt. Im logarithmischen Diagramm Viskositätszahl gegen  $M_n$  wurde eine geradlinige Beziehung erhalten. Der Einfluss gewisser Strukturänderungen auf die Eigenschaften der Polyurethane wird diskutiert. Variiert wurden das Molekulargewicht des Polyesterdiols, der bei der Darstellung des Polyesterdiols verwendete Initiator, die Einführung eines Methylsubstituenten in den Caprolactonring und die Struktur des Diamins. Aus Polyesterdiolen mit  $M_n$  von 2000–4000 dargestellte Polyurethane sind opake, steife Materialien mit einer für die Polyesterkomponente charakteristischen Schmelzumwandlung bei 40–50°C. Bei Raumtemperatur flexible und durchsichtige Polyurethane werden entweder mit einem niedermolekularen Polyesterdiol oder einem >25% Methyl- $\epsilon$ -caprolacton enthaltenden Copolyesterdiol erhalten. Die beschriebenen Polyurethane sind in einigen gebräuchlichen Lösungsmitteln löslich und können zur Bildung von Stoffen mit hoher Zugfestigkeit kalt gereckt werden. Thermische Versuche mit DTA und TGA zeigen eine oberhalb 300°C einsetzende exotherme Reaktion. Ein rascher, bei 300–330°C beginnender und bei 500°C abflachender Gewichtsverlust umfasste 85–90% der Gesamtprobe und wird auf die Zersetzung der Polyesterketten zurückgeführt.

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