

## Condensation Polymers Derived from *N,N'*-Dialkyl- and *N,N'*-Diarylylenediamines

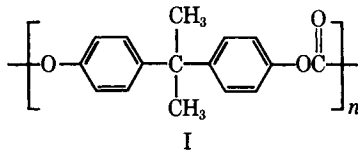
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### Synopsis

A series of polyurethanes and poly(carbonate-urethanes) was prepared from diphenols and *N,N'*-dialkyl- and *N,N'*-diarylylenediamines. These polymers are rigid, non-crystallizable, high-softening thermoplastics. In several cases, their properties were at least equivalent to those of the known bisphenol polycarbonates. As expected, the poly(carbonate-urethanes) exhibit properties intermediate between those of the respective homopolymers. A structure-properties correlation is presented.

### INTRODUCTION

Polycarbonates derived from various bisphenols have been the object of intensive research.<sup>1,2</sup> These polymers have exhibited several very attractive properties, such as toughness, high softening temperature, thermal stability, etc. The representative of this class which has achieved considerable commercial importance is the polycarbonate of 2,2-bis(*p*-hydroxyphenyl)propane (bisphenol-A) (I). This polycarbonate

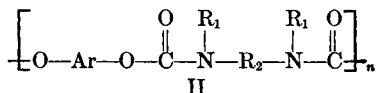


is marketed by the General Electric Co. under the name Lexan.

Other polymers derived from bisphenols were also studied intensively. Conix,<sup>3</sup> for example, prepared several polyesters from bisphenols and aromatic dicarboxylic acids. These polymers are tough resins with high softening temperatures.

Nitrogen-containing polymers formally analogous to the bisphenol polyesters and polycarbonates have been less thoroughly investigated. Polyamides derived from aromatic dibasic acids and primary aromatic diamines have been studied by both American<sup>4,5</sup> and Russian<sup>6</sup> workers. Since their properties are doubtless strongly influenced by hydrogen bonding, however, these polymers are not so closely related to their oxygen analogs as are the corresponding polymers derived from secondary aromatic diamines. Some

of the latter have been reported<sup>5,6</sup> but have not been closely characterized. Almost nothing has been published regarding the polyurethanes (II), although some related polyurethanes<sup>7</sup> and



R<sub>1</sub> = alkyl or aryl

R<sub>2</sub> = arylene

poly(carbonate-urethanes)<sup>8</sup> were recently reported. The present paper describes the preparation and properties of two series of polymers: a group of polyurethanes of the general structure II, and a group of poly(carbonate-urethanes), i.e., copolymers of structures I and II.

## EXPERIMENTAL

### Materials

4,4'-Methylenebis(*N*-methylaniline) was prepared by the method of Fedotova et al.,<sup>9</sup> m.p. 54.5–56.2°C.; 4,4'-methylenebis(*N*-ethylaniline) was prepared similarly, b.p. 195°C./0.25 mm.,  $n_D^{25}$  1.6063. *N,N'*-Diphenylhexamethylenediamine was prepared by the method of Billman and Caswell,<sup>10</sup> m.p. 75–76°C. *N,N'*-Diphenyl-*p*-phenylenediamine was obtained by recrystallization of commercially available material (benzene-petroleum ether), m.p. 146–147°C. 4,4''-Methylenebis(diphenylamine), m.p. 121–122°C. (reported<sup>11</sup> m.p. 122–123°C.) and 4,4''-isopropylidenebis(diphenylamine), m.p. 98.5–99.5°C. (reported<sup>12</sup> m.p. 99–100°C.) were prepared from the corresponding diphenols via the Chapman rearrangement.<sup>13</sup>

The dichloroformates were prepared from the diphenols and phosgene. Melting points of the products were as follows: from bisphenol-A, 94–95°C. (reported<sup>14</sup> m.p. 96–98°C.); from tetrachlorobisphenol-A, 164–166°C. (reported<sup>14</sup> m.p. 163–165°C.); from 4,4'-sulfonyldiphenol, 139–141°C. (reported<sup>15</sup> m.p. 143–144°C.).

The isophthaloyl chloride used was recrystallized from petroleum ether, m.p. 44–45°C.

### Preparation of Polyurethanes

Three methods were used for preparation of the polyurethanes: (A) an inverse interfacial polycondensation technique,<sup>16</sup> (B) direct interfacial reaction,<sup>17</sup> and (C) an anhydrous catalytic solution process.<sup>18</sup> Representative examples of each are given.

**Preparation of the Polyurethane from 4,4'-Methylenebis(*N*-methylaniline) and Bisphenol-A (Method A).** A solution of 11.32 g. (0.05 mole) of 4,4'-methylenebis(*N*-methylaniline) and 8.8 g. (0.09 mole) of 37.3% hydrochloric acid in 450 ml. of water was cooled to below 3°C. To this were added, in quick succession, solutions of 2.10 g. of Tergitol Anionic 7 (a sodium alkyl sulfate detergent) in 15 ml. of water and of 17.66 g. (0.05

mole) of bisphenol-A dichloroformate in 220 ml. of methylene chloride. To this rapidly stirred mixture was added dropwise a solution of 8.18 g. (0.2 mole) of 97.8% sodium hydroxide in 65 ml. of water; addition required 17 min., the temperature being maintained at  $-1.5$  to  $+1^{\circ}\text{C}$ . The mixture was held at  $0-1^{\circ}\text{C}$ . for an additional 24 min. and then allowed to warm up to room temperature.

The strongly alkaline aqueous phase was decanted, and the viscous organic layer was washed successively with water, an aqueous solution containing about 4.4% hydrochloric acid and 12% acetic acid, and five portions of water. The polymer was then precipitated by addition of the methylene chloride solution to 1 liter of ethanol in a Waring Blendor. The yield was 83%, and the reduced viscosity in methylene chloride was 0.68. (All reduced viscosities (RV) were measured at  $25^{\circ}\text{C}$ . at a concentration of 0.2 g./100 ml. solvent.) The polymer contained 5.10% nitrogen (theoretical 5.53%), and its infrared spectrum included a strong band at  $5.82\ \mu$ , characteristic of urethanes.

**Preparation of the Poly(carbonate-urethane) from Bisphenol-A and 15 Mole-% of 4,4'-Methylenebis(*N*-methylaniline) (Method B).\*** In a Waring Blendor was placed a mixture composed of 1.697 g. (0.0075 mole) of 4,4'-methylenebis(*N*-methylaniline), 3.99 g. (0.0175 mole) of bisphenol-A, 2.4 g. (0.06 mole) of sodium hydroxide, 0.5 g. of Duponol ME, 0.20 ml. of triethylamine, and 80 ml. of distilled water. A solution of 8.83 g. (0.025 mole) of bisphenol-A dichloroformate in 100 ml. of benzene was added to this mixture. Stirring was started and continued for 50 min. After 35 min., an additional 0.01 ml. of triethylamine was added to the reaction medium.

The crude reaction mixture was coagulated in 1500 ml. of isopropanol. The polymer was filtered and washed with 1 liter of distilled water on the filter. It was redissolved in 300 ml. of methylene chloride, washed, and recovered essentially as described in the preceding example.

The yield of the polymer was 90%; reduced viscosity in methylene chloride was 0.55. The polymer contained 1.76% nitrogen (theoretical 1.66%); its infrared spectrum exhibited two carbonyl absorption bands at  $\sim 5.65\ \mu$  (the carbonate) and at  $\sim 5.85\ \mu$  (the urethane).

**Preparation of the Polyurethane from *N,N'*-Diphenylhexamethylenediamine and Bisphenol-A (Method C).** A mixture of 3.53 g. (0.01 mole) of bisphenol-A dichloroformate, 2.68 g. (0.01 mole) of *N,N'*-diphenylhexamethylenediamine, 0.06 g. (25 mole-%) of 20 mesh magnesium powder, and 60 ml. of dry *s*-tetrachloroethane was heated under reflux in a stream of dry nitrogen for 7 hr. Hydrogen chloride evolution was rapid during the first 2 hr., then slowed and became practically insignificant after 5 hr. The reaction solution was very viscous at the end of the experiment. It was diluted with 50 ml. of fresh solvent and filtered through a Celite bed prepared in *s*-tetrachloroethane. The filtrate was coagulated in 1 liter of isopropanol.

\* The mole percentage of the diamine was defined as the ratio (times 100) of the number of moles of the diamine to the total number of moles of the bisphenol, bisphenol dichloroformate, and diamine.

A white polymer, reduced viscosity in *s*-tetrachloroethane 1.64, was obtained in a yield of 80%. The infrared spectrum of this polymer included a band at 5.8  $\mu$ , characteristic of urethanes.

### Testing Procedures

All polymer samples were prepared by casting thin film (0.001–0.003 in.) from chloroform. Complete removal of solvent required drying the film in a vacuum oven at 60–80°C. for 24 hr.

**Room Temperature Tensile Properties.** Individual test specimens  $\frac{1}{8}$  in. wide were shear cut from the cast film. The stress-strain behavior was determined on an Instron tensile tester on a 2-in. gauge length sample at a strain rate of 10%/min. The room temperature tensile properties were calculated by eqs. (1)–(3).

$$\text{Tensile modulus (psi)} = \frac{\text{Load at 1\% strain (lb.)}}{\text{Cross sectional area (sq. in.)}} \times 100 \quad (1)$$

$$\text{Tensile strength (psi)} = \frac{\text{Breaking load (lbs.)}}{\text{Cross-sectional area (sq. in.)}} \quad (2)$$

$$\text{Elongation at break (\%)} = \frac{\text{Breaking length} - \text{Original length}}{\text{Original length}} \times 100 \quad (3)$$

**Pendulum Impact.** Similar thin film specimens were used to measure impact properties. The impact characteristics of the films were determined on a modified Baldwin impact tester. A  $\frac{1}{4}$ -in. diameter rod was used as the impacting head of the pendulum. A 1 by  $\frac{1}{8}$ -in. film sample was mounted transverse to the path of the pendulum and located at the bottom of the swing. The  $\frac{1}{4}$ -in. rod struck the  $\frac{1}{8}$ -in. face of the sample half way between the ends. The energy to break the sample was determined by the difference between the initial height and the recovery height of the pendulum after it had broken the sample.

$$\text{Pendulum impact} \left( \frac{\text{ft.-lb.}}{\text{in.}^3} \right) = \frac{\text{Pendulum energy loss}}{\text{Volume of sample}} \quad (4)$$

**Glass Transition Temperature.** The glass transition temperature was determined on the thin film samples by measuring the recovery characteristics as a function of temperature.<sup>19</sup> A film specimen was strained 1% at the rate of 10%/min. and then allowed to return at the same rate. The recovery or resilience was calculated from the ratio of the recovered length to original length. This test was repeated at elevated temperatures. A programmed rate of heating of 1.5–2°C./min. was used, measurements being repeated at intervals of 3–5°C. The glass transition temperature  $T_g$ , is defined as the minimum in a plot of resilience versus temperature. For amorphous polymers, the minimum resilience is 10–30%.

**Permeability.** The gas transmission rates were measured in a Dow gas permeability cell according to ASTM D1434-63.

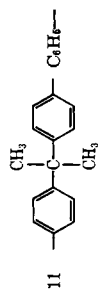
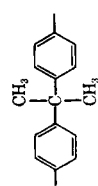
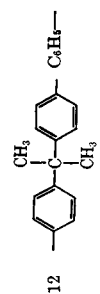
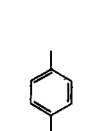
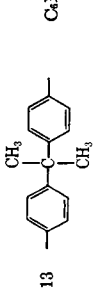

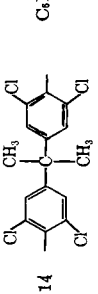

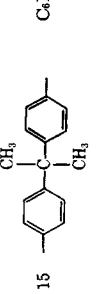

TABLE I  
 Polyurethanes  $\left[ \text{O}-\text{Ar}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{N}-\text{R}_2-\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}_1-\text{O} \right]_n$ , and Their Properties

Polymer no.	Ar	R <sub>1</sub>	R <sub>2</sub>	RV	Method of preparation	T <sub>g</sub> , °C.	Properties <sup>a</sup>			
							Tensile strength, psi	Tensile modulus, psi	Elongation at break, %	Pendulum impact, ft.-lb./in. <sup>2</sup>
1		CH <sub>3</sub> -		0.68 <sup>b</sup>	A	155	10,600	330,000	100	130
2		CH <sub>3</sub> -		0.53 <sup>b</sup>	C	210	10,000	331,000	4	—
3		CH <sub>3</sub> -		2.68 <sup>b</sup>	C	170	7,410	228,000	5	—
	(3:1) 	CH <sub>3</sub> -		0.60 <sup>b</sup>	C	170	10,250	353,000	4	—

(continued)

TABLE I (continued)

Polymer no.	Ar	R <sub>1</sub>	R <sub>2</sub>	RV	Method of preparation	T <sub>g</sub> , °C.	Properties <sup>a</sup>			
							Tensile strength, psi	Tensile modulus, psi	Elongation at break, %	Pendulum impact, ft.-lb./in. <sup>3</sup>
5	(1:3) 	CH <sub>3</sub> —		0.85 <sup>b</sup>	C	195	11,100	340,000	5	—
6		C <sub>2</sub> H <sub>5</sub> —		0.72 <sup>c</sup>	A	130	9,000	285,000	6	12-17
7		C <sub>2</sub> H <sub>5</sub> —		0.54 <sup>c</sup>	A	200	8,200	300,000	5-8	10-17
8		C <sub>2</sub> H <sub>5</sub> —		0.52 <sup>c</sup>	A	160	11,500	330,000	5	—
9	(1:1) 	CH <sub>3</sub> —		0.88 <sup>c</sup>	A	190	10,300	330,000	10-100	30-50
10		C <sub>2</sub> H <sub>5</sub> —		0.96 <sup>c</sup>	C	160	10,400	340,000	6	30-40

11			0.84 <sup>c</sup>	C	190	9,500	270,000	6-8	25
12			0.48 <sup>d</sup>	C	180	11,000	325,000	4	5-12
13			1.64 <sup>d</sup>	C	90	8,000	320,000	12-20	—
14			0.86 <sup>d</sup>	C	120-130	7,500	345,000	7-8	—
15			1.05 <sup>d</sup>	C	115	9,600	320,000	5-6	—

<sup>a</sup> Determined on films cast from chloroform.

<sup>b</sup> In methylene chloride.

<sup>c</sup> In chloroform.

<sup>d</sup> In *s*-tetrachloroethane.

## RESULTS

This work was directed primarily toward the synthesis and evaluation of polyurethanes. Results are summarized in Table I. All of the polymers were amorphous and noncrystallizable. Resistance to heat aging in the presence of air was measured on several of the polyurethanes. The pertinent data are given in Table II.

TABLE II  
Heat Aging of Several Polyurethanes in Air

Polymer no. <sup>a</sup>	Exposure to Air		Pendulum impact, ft.-lb./in. <sup>3</sup>		RV <sup>b</sup>	
	Time, hr.	Temp., °C.	Before aging	After aging	Before aging	After aging
1	335	175	130	5	1.22	Insoluble
10	335	175	40	13	1.06	1.00 <sup>c</sup>
11	{ 164 164	{ 180 200	25	23	0.84	0.91

<sup>a</sup> The polymer numbers correspond to those of Table I.

<sup>b</sup> These reduced viscosities were measured in chloroform.

<sup>c</sup> This reduced viscosity was measured after 209 hr.

An investigation was also made of the influence of urethane linkages on the properties of bisphenol-A polycarbonate. A series of poly(carbonate-urethanes) was prepared according to eq. (5) where  $x = y + z$ . (See p. 3345.)

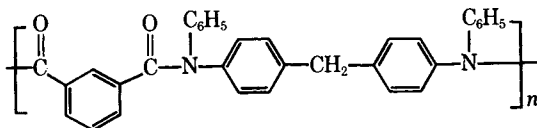
The molar percentage  $P$  of the diamine is defined as

$$P = [z/(x + y + z)] \times 100 \quad (6)$$

The percentage of urethane linkages in the copolymer is equal to  $2P$ . The poly(carbonate-urethanes) that were prepared are recorded in Table III. Included in this table are also typical properties of Lexan and of the corresponding urethane homopolymers.

As may be seen from Table III, good incorporation of the diamine into the polymers was obtained. All of the polymers were amorphous, apparently noncrystallizable materials. Gas transmission data were obtained for one polymer (No. 18) and are shown in Table IV along with the corresponding values obtained on Lexan.

The condensation of isophthaloyl chloride with 4,4''-methylenebis(diphenylamine) (method C) yielded the polyamide III.



III

The properties found on a film of this polymer cast from chloroform are listed in Table V.



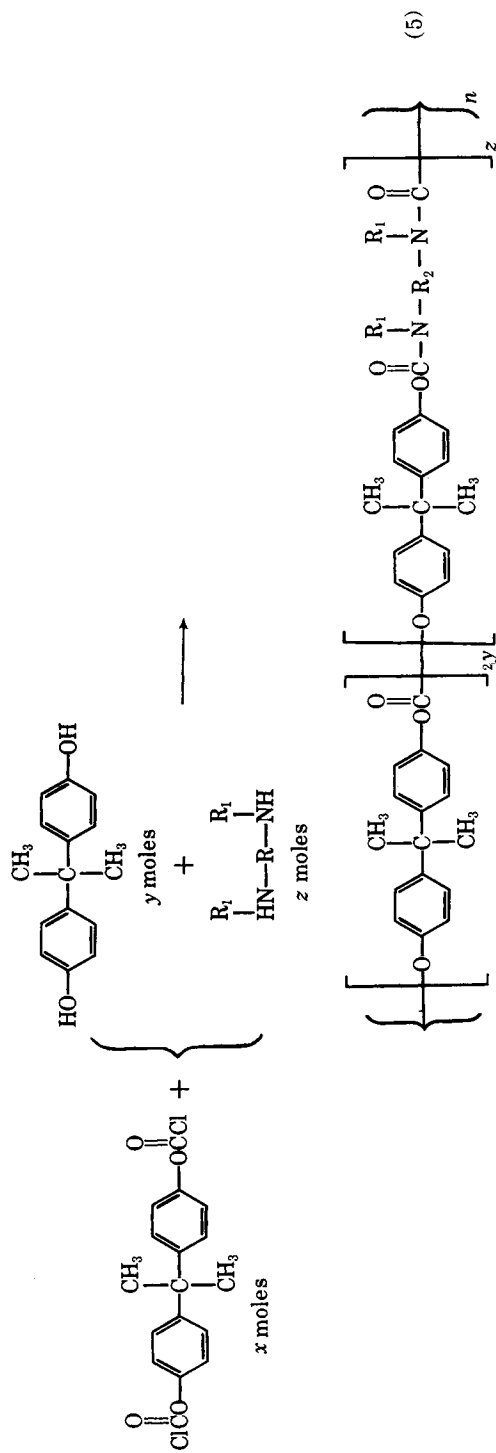
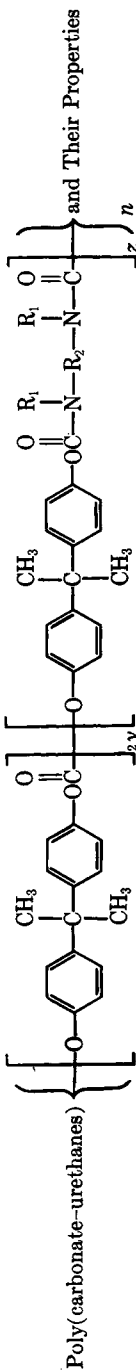


TABLE III

Poly- mer no.	R <sub>1</sub>	R <sub>2</sub>	P, %	RV	Method of prepara- tion	N, % <sup>a</sup>		T <sub>g</sub> , °C.	Tensile strength, psi	Elongation at break, %	Pendulum impact, ft.-lb./in. <sup>3</sup>
						Calc'd.	Found				
16	—	—	0	—	—	—	—	8,000– 10,000	300,000	50–100	100–500
17	CH <sub>3</sub> —		5	1.8°	B	0.53	0.73	—	8,270	276,000	60
18	CH <sub>3</sub> —		15	0.55°	B	1.66	1.76	155	10,420	326,000	6
18	CH <sub>3</sub> —		30	0.93°	B	3.31	3.50	145	11,400	340,000	50
20	CH <sub>3</sub> —		40	0.95°	B	4.42	4.50	—	10,950	322,000	7
21	CH <sub>3</sub> —		50	0.68°	A	5.53	5.10	155	10,600	380,000	100

Properties<sup>b</sup>

22	C <sub>2</sub> H <sub>5</sub> —		10	1.24 <sup>d</sup>	B	1.09	1.22	145	8,700	270,000	14	56-82
23	C <sub>3</sub> H <sub>5</sub> —		20	1.20 <sup>d</sup>	B	2.16	2.32	140	8,100	255,000	41-74	42-66
24	C <sub>3</sub> H <sub>5</sub> —		30	1.20 <sup>d</sup>	B	3.21	3.44	135	9,100	250,000	75-104	60-84
25	C <sub>2</sub> H <sub>5</sub> —		50	0.72 <sup>d</sup>	A	—	—	130	9,000	285,000	6	12-17
26	C <sub>8</sub> H <sub>5</sub> —		10	0.52 <sup>d</sup>	C	—	—	160	7,800	290,000	10-14	35-60
27	C <sub>8</sub> H <sub>5</sub> —		25	0.80 <sup>d</sup>	C	2.46	2.44	160	7,600	300,000	17-37	33
28	C <sub>8</sub> H <sub>5</sub> —		50	0.96 <sup>d</sup>	C	4.44	4.52	160	10,400	340,000	6	30-40
29 <sup>e</sup>	CH <sub>3</sub> —		20	0.90 <sup>d</sup>	B	—	—	170	9,000	300,000	17-32	35-60

<sup>a</sup> Nitrogen analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

<sup>b</sup> Determined on films cast from chloroform.

<sup>c</sup> In methylene chloride.

<sup>d</sup> In chloroform.

<sup>e</sup> In this experiment, 1 mole of bisphenol-A dichloroformate was treated with 0.6 mole of bis(*p*-hydroxyphenyl) sulfone and 0.4 mole of 4,4'-methylenebis(*N*-methylamine); the formula of the copolymer, obtained in an 85% yield, was presumably

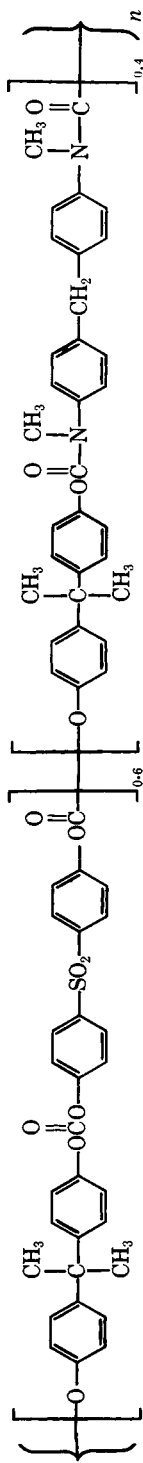


TABLE IV. Gas Transmission Data of a Poly(carbonate-urethane) and of Lexan

Polymer	Permeability at 25°C., cm. <sup>3</sup> (STP) mil/100 in. <sup>2</sup> /24 hr.-atm.			
	H <sub>2</sub>	CO <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>
No. 18, Table III	1220	610	—	30
Lexan	1720	1000	185	36

TABLE V. Properties of III

RV (in chloroform)	0.53
$T_g$ , °C.	150
Tensile strength, psi	5,600
Tensile modulus, psi	295,000
Elongation at break, %	4-8

## DISCUSSION

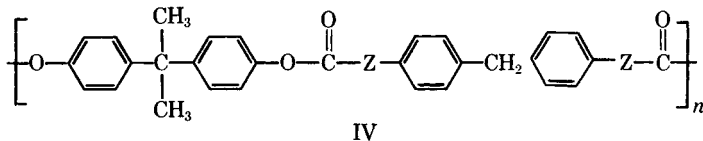
### Mechanical Properties

It should be possible to explain the mechanical properties of a given polymer in terms of its transition temperatures. Since the new polymers prepared in this study all proved to be amorphous and apparently noncrystallizable, no consideration of crystalline melting points is involved. In all cases, the major glass transitions are well above room temperature; as would be expected from this, tensile strengths and tensile moduli are quite high. Much greater variability was observed in those properties reflecting the toughness of these polymers, i.e., their elongations and impact strengths. Toughness in stiff, amorphous thermoplastics is attributed<sup>20</sup> to secondary transitions below room temperature. Brittleness and low ductility, on the other hand, may be either inherent to a given polymer or the result of flaws in the test samples. Unfortunately, limitations in the amounts of available material prevented measurements of low temperature transitions in the present study.

### Structure-Property Correlations

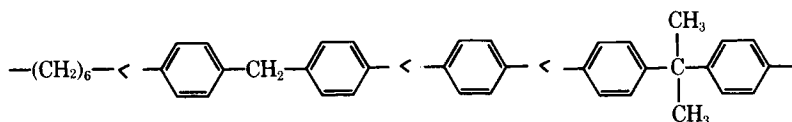
Relationships between structure and glass transition temperature for a number of similar polymers can be found in Table I. Polymers 1-5 illustrate the effect of replacing residues of bisphenol-A by those of tetrachlorobisphenol-A. The latter, with its relatively bulky *ortho* substituents, decreases the rotational freedom of the chains and thereby raises the glass transition temperature. Values of  $T_g$  for the copolymers lie between those of the homopolymers. The same effect is illustrated by polymers 6-8, 13-15, and 22-25 (Table III).

The effect of chain substituents on the glass transition temperature is illustrated by the sequence of polymers (IV). The value of  $T_g$  for the parent polycarbonate ( $Z = -O-$ ) is 145-150°C.<sup>21</sup>



Replacement of oxygen by the group  $-\text{NCH}_3$  decreases chain flexibility and raises  $T_g$  to  $155^\circ$  (polymer 1), and a slight further increase results from the replacement of the *N*-methyl group by *N*-phenyl (polymer 10). Rather surprisingly, however, the glass transition temperature of polymer 6 ( $Z = -\text{NCH}_2\text{CH}_3$ ) was found to be only  $130^\circ\text{C}$ . This ethyl-methyl relationship holds also for polymers 2, 7 and 4, 8, although the difference in transition temperatures is smaller. Similar observations were reported by Korshak<sup>22</sup> and by Fedotova<sup>6</sup> on polyamides analogous to polymers 1 and 6. It is possible that in these cases the increase in chain stiffness resulting from the greater bulk of the *N*-ethyl group is more than compensated for by interference with interchain forces.

Effects of the group  $R_2$  on the glass transition temperature may be seen in the series of polymers 10-13, in which the order is



The relative position of polymers 10 and 12 is rather surprising, since the addition of benzyl groups,  $-\text{C}_6\text{H}_4\text{CH}_2-$ , to the repeat unit would ordinarily be expected to increase  $T_g$ , as was observed for the polyhydroxyethers of hydroquinone and bis(*p*-hydroxyphenyl)methane.<sup>23</sup>

### Thermal Stability

From the data of Table II, it is apparent that polymer 11 is very stable in air at  $180$ – $200^\circ\text{C}$ ., and polymer 10 is somewhat less stable. Polymer 1 became partially insoluble, probably because of crosslinking, and then gradually embrittled. The difference between polymers 10 and 11 is probably attributable to the benzylic hydrogens present in the former, since these are doubtless sites at which free radical reactions can occur.

The instability of polymer 1 may result from oxidative attack at the *N*-methyl group. This is uncertain since the sample used had been prepared interfacially (method A) and was probably contaminated with inorganic impurities, known<sup>24</sup> to be sources of instability in polycarbonates.

### CONCLUSIONS

A series of polyurethanes and poly(carbonate-urethanes) was prepared from diphenols and *N,N'*-dialkyl and *N,N'*-diarylarlylenediamines. Examinations of their properties showed that they are rigid, thermoplastic, noncrystallizable resins, possessing high softening temperatures. In several cases, their properties were at least equivalent to those of the known bisphenol polycarbonates. As expected, the poly(carbonate-urethanes) exhibit properties intermediate between those of the respective homopolymers.

## References

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## Résumé

Une série des polyuréthanes et poly(carbonate-uréthanes) a été préparée à partir des diphenols et *N,N'*-dialkyl- et *N,N'*-diarylarylènediamines. Ces polymères sont des thermoplastiques rigides, non cristallisables, possédant des hauts points de ramollissement. Dans plusieurs cas, leurs propriétés étaient au moins équivalentes à celles des polycarbonates des bisphénols connus. En accord avec les prévisions, les propriétés des poly(carbonate-uréthanes) se situent entre celles des homopolymères respectifs. Une corrélation structure-propriétés est présentée.

## Zusammenfassung

Eine Reihe von Polyurethanen und Poly(carbonat-urethanen) wurde aus Diphenolen und *N,N'*-Dialkyl- und *N,N'*-Diarylarylendiaminen hergestellt. Diese Polymeren sind harte, nicht kristallisierbare thermoplastische Massen mit hohem Erweichungspunkt. In verschiedenen Fällen waren ihre Eigenschaften denen der bekannten Bisphenol-polycarbonate mindestens gleichwertig. Wie erwartet besitzen die Poly(carbonat-urethane) Eigenschaften, die zwischen denen der entsprechenden Homopolymeren liegen. Die Beziehung zwischen Struktur und Eigenschaften wird diskutiert.

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