

## Elastomers Based on Polycyclic Bisphenol Polycarbonates\*

K. P. PERRY, W. J. JACKSON, JR., and J. R. CALDWELL,  
*Research Laboratories, Tennessee Eastman Company, Division of Eastman  
Kodak Company, Kingsport, Tennessee*

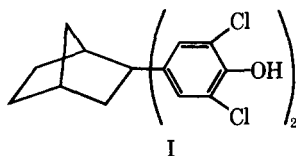
### Synopsis

Polycarbonate elastomers were prepared by the addition of phosgene to a pyridine solution of poly(tetramethylene ether) glycol and bisphenols containing norbornane-type groups. These elastomers do not contain the classical "tie-down" points—cross-links, hydrogen bonding, or crystallinity—which, heretofore, have been considered necessary for good elastomer properties. This work introduces a new concept in elastomer chemistry: bulky, three-dimensional groups are effective tie-down points. Most of the elastomers were prepared with 4,4'-(2-norbornylidene)bis(2,6-dichlorophenol). For comparison, several elastomers with bisphenol-A were also prepared. A statistically designed experiment was carried out to determine the effect of composition variables on the properties of these elastomers. The properties were determined on films cast from methylene chloride and, in many cases, on wet-spun fibers. These elastomers have elongations of 400–600% and instantaneous elastic recoveries up to 100%.

### INTRODUCTION

The preparation of polycarbonates was described by Schnell<sup>1</sup> and discussed in detail by Christopher and Fox.<sup>2</sup> These polymers were prepared from phosgene and a bisphenol, typically 4,4'-isopropylidenediphenol (bisphenol-A), which is the basis of a commercial polycarbonate.

New types of polycarbonates with exceptionally high glass transition temperatures were prepared by Jackson and Caldwell from bisphenols containing polycyclic rings.<sup>3</sup> One of these polymers, obtained from 4,4'-(2-norbornylidene)bis(2,6-dichlorophenol) (I), had a glass transition temperature of 290°C. This high



value was attributed to the bulky effect of the three-dimensional structure of the norbornane ring attached to two dichlorophenyl groups. This bis-

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

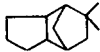
phenol was the basis for most of our work on polycarbonate elastomers. Other polycarbonate elastomers, described previously by Merrill,<sup>4</sup> contained block copolymers based on bisphenol-A polycarbonate. Goldberg<sup>5</sup> discussed polycarbonate block elastomers containing bisphenol-A copolycarbonates and carbonate-carboxylate tetrapolymers.

Elastomers can be considered to consist of two types of segments: a soft segment and a hard segment. For example, in the spandex elastomers<sup>6</sup> (segmented polyurethanes) the soft segment may be a polyester or polyether of low molecular weight (500-4000) with hydroxy endgroups. The hard segment may be considered as a low molecular weight polyurethane or polyurea which links the soft segments together. To produce an elastomer with a useful temperature range, the hard segment must be high-melting to counteract the very low-melting soft segment. The hard segment creates the tie-down points within the elastomer matrix. Tie-down points have been considered to be one of the basic molecular requirements for an elastomer, and they, in effect, restrain the gross mobility of the elastomer chains. These tie-down points may be in the form of crosslinks, hydrogen bonding, or crystallinity. In rubber, vulcanization is necessary to give a network of crosslinks. In the spandex elastomers, crosslinks can form by the reaction of excess isocyanate with urethane or urea groups to give allophanate and biuret formation between chains. Hydrogen bonding in the spandex elastomers between the carbonyl and NH groups also occurs, and this gives tie-down points. Instead of crosslinks other elastomers contain crystalline units in the hard segment which act as tie-down points. These are exemplified by the block polycarbonate elastomers of Merrill and Goldberg.

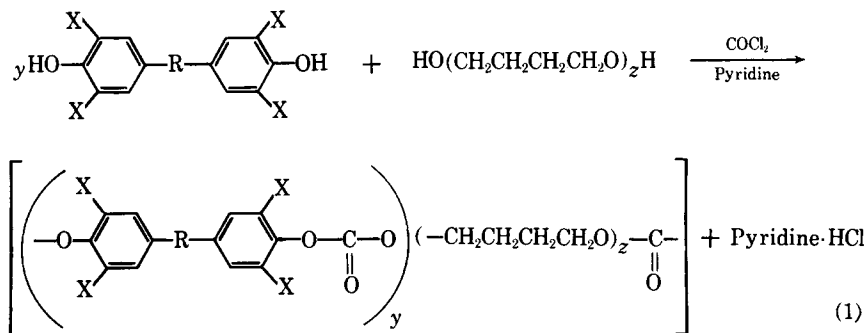
We prepared a series of polycarbonate elastomers which are not crosslinked, which contain no hydrogen bonding, and which, as shown by x-ray diffraction patterns, are not crystalline. These elastomers contain bulky, three-dimensional polycyclic groups (I) which contribute to the properties of the elastomer by acting as tie-down points since they hinder the motion of chain segments.

For the soft segment of the elastomer, poly(tetramethylene ether) glycol

TABLE I

Elastomer no.	R	X
1		Cl
2		H
3		H
4	$(\text{CH}_3)_2-\text{C} \begin{array}{l} \diagup \\ \diagdown \end{array}$	H

(PTMG) was used. This was copolymerized with bisphenol. Several other hydroxy-terminated soft segments were used, such as polyesters, polyformals, and polycarbonates, but only in a few compositions. The elastomers were prepared by treating the bisphenol and PTMG with phosgene in a solution of methylene chloride and pyridine [eq. (1)]. Most of the elastomers (Table I) were variations of 1, but to obtain comparative properties, elastomers 2, 3, and 4 were also prepared. Elastomer 4 was prepared with bisphenol-A.



Usually the bisphenol and PTMG were dissolved in the reaction solvent before the addition of phosgene. This allowed the possibility of the reaction of diol with diol, bisphenol with bisphenol, and diol with bisphenol through the carbonate link. Since the molar amount of bisphenol (81–91%) was much greater than the molar amount of diol (9–19%), segmentation of the bisphenol necessarily occurred. To avoid the possibility of linking two diol units together with phosgene, the bischloroformate of the diol can be used. This assures reaction with at least one bisphenol before the addition of phosgene to react with the remaining phenolic groups.

## EXPERIMENTAL

### Materials

The polycyclic bisphenols were prepared by the procedure of Jackson and Caldwell.<sup>3</sup> Bisphenol-A was commercial material which had been recrystallized from aqueous acetic acid.

The pyridine used was Baker and Adamson reagent grade (Allied Chemical Corporation).

The methylene chloride used was refrigeration grade.

Phosgene was used as a 10% solution in distilled 1,2-dichloroethane. This stock solution was prepared in a well-ventilated hood by bubbling phosgene into a known amount of solvent in a container with a Dry Ice trap attached to the receiver. This solution was then diluted with more solvent to obtain 10 g. of phosgene per 100 ml. of 1,2-dichloroethane.

### Apparatus

In a well ventilated hood, a three-necked flask was fitted with a stirrer, thermometer, and glass dropping funnel. The stirrer control box was wired with a milliammeter which indicated the amount of torque on the stirrer. This gave a relative measure of the viscosity of the elastomer.

### Polymerization Procedure

To a 500-ml. flask fitted as described previously were added 16.8 g. (0.004 mole) of PTMG of molecular weight 4200, 9.1 g. (0.0218 mole) of 4,4'-(2-norbornylidene)bis(2,6-dichlorophenol), 105 ml. of methylene chloride, and 25 ml. of pyridine. The 10% phosgene stock solution was added to the rapidly stirred reaction mixture from a graduated dropping funnel. The temperature was maintained at 20–30°C. by means of a water bath. Thickening of the elastomer solution was indicated by the milliammeter attached to the stirrer control box. Slow addition of the phosgene solution was continued until the meter showed that there was no further build-up; usually the mixture had wrapped around the stirrer. The volume of phosgene solution used was 29 ml. (10–30 molar excess of phosgene was usually required; the presence of carbon dioxide and possibly some chlorine accounts for the indefinite amount of phosgene used). Water was added and the elastomer was diluted with methylene chloride. The solution was stirred with dilute hydrochloric acid and then washed with a large quantity of water to remove pyridine hydrochloride. After the aqueous layer was separated, 1.0 g. of antioxidant (an alkylated phenol) was added to the solution. The elastomer was precipitated in 50:50 acetone-methanol solution and dried overnight in a vacuum oven at 60°C. (Antioxidants were necessary to keep the polyether segment from degrading while the elastomer was heated.) The inherent viscosity of the elastomers in chloroform was about 3.

ANAL. Calcd.: Cl, 11.3%. Found: Cl, 11.1%.

The bischloroformate of PTMG was prepared by the action of phosgene on the glycol in an inert solvent. The polymerization was carried out as before except that the bisphenol and PTMG bischloroformate were allowed to react before the introduction of phosgene.

### Film and Fiber Preparation

Films of the elastomers were cast from methylene chloride and dried overnight at 60°C. *in vacuo*. Elastomer properties were evaluated on film strips which were  $\frac{1}{8}$  in. wide, 3–4 mils thick, and 3 in. long. Fibers were wet-spun from methylene chloride into ethyl alcohol.

### RESULTS AND DISCUSSION

Polycarbonate elastomer film properties are listed in Table II. These were used to determine the compositions which would give the best prop-

TABLE II  
Properties of Films From Polycarbonate Elastomers

Expt. no.	Elastomer no.	Composition of elastomer		Film [η]	Elongation at break, %	Tenacity, g./den.	Second cycle loop <sup>a</sup>						Elastic recovery from 400% extension, %	Permanent set, %		
		Wt.-%	Mol. wt.				30% Power, 30% ex-tension, 10 <sup>3</sup> g./den.		100% Power, 100% re-tension, 10 <sup>3</sup> g./den.		Power, 30% turn, 10 <sup>3</sup> g./den.	Power, 100% re-tension, 10 <sup>3</sup> g./den.		Elastic recovery from 400% extension, %	After 1 min.	After 60 min.
							PTMG		g./den.	den.						
1	1	55	2500 <sup>b</sup>	1.5	380	0.65	30	41	0	10	10	98.0 <sup>c</sup>	65	25		
2	1	55	4000 <sup>b</sup>	2.6	400	0.62	40	51	0	7	7	98.5	145	100		
3	1	55	4100	2.8	430	0.60	38	49	0	9	9	88.0	105	50		
4	1	60	2700 <sup>b</sup>	1.5	380	0.32	18	28	1	18	18	99.6 <sup>c</sup>	70	20		
5	1	60	4200	2.9	440	0.53	20	30	0	14	14	97.5	40	15		
6	1	63	3700	2.5	430	0.54	21	32	0	14	14	99.0	45	17.5		
7	1	65	2500 <sup>b</sup>	2.5	420	0.27	11	23	3	12	12	99.7	46	16		
8	1	65 <sup>d</sup>	3200	2.4	500	0.21	12	22	2	13	13	99.8	30	12		
9	1	65	4200	3.5	430	0.50	20	33	6	22	22	99.8	32	12		
10	1	65	5500	2.4	470	0.56	20	30	0	14	14	98.2	40	20		
11	1	65	6600	2.4	470	0.56	21	30	1	15	15	97.9	40	20		
12	1	67	4200	3.1	410	0.27	14	24	4	16	16	99.7	30	10		
13	1	69	2500 <sup>b</sup>	3.4	500	0.17	9	15	4.5	11	11	99.7	95	50		
14	1	70	4100	2.6	480	0.40	18	29	1	15	15	98.8	50	25		
15	2	65	4200	3.9	470	0.32	13	23	6	17	17	99.8	30	15		
16	3	65	4200	3.0	420	0.25	11	20	5	16	16	99.9	50	33		
17	4	65	4200	2.9	430	0.26	12	22	6	17	17	98.7	30	20		

<sup>a</sup> Properties measured at 300% extension.

<sup>b</sup> No modifier in PTMG; all others contained 6-8 mole-%.

<sup>c</sup> Recovery at maximum elongation.

<sup>d</sup> Contained 2 mole-% Niax Triol (1000 mol. wt. polyoxypropylenetriol) which gives slight crosslinking.

TABLE III  
Results of Designed Experiments on Polycarbonate Elastomer Films<sup>a</sup>

Property	Desired response	Level of variables to give the desired response <sup>b</sup>		
		PTMG wt.-% (range of 55-65%)	PTMG mol. wt. (range of 2500-4000)	Elastomer viscosity (range of 1.5-2.5)
Elastic recovery, % return	Maximum	High	Low	—
Permanent set at 30°C., % <sup>c</sup>	Minimum	High	High <sup>d</sup>	High
Elongation, %	Maximum	High	High <sup>e</sup>	—
% Set at start of second cycle <sup>f</sup>	Minimum	High	—	High
Tenacity	Maximum	Low	High	Low
Extension power, second cycle, 100%	Maximum	Low	High	—
Return power, second cycle, 100%	Maximum	High	—	High

<sup>a</sup> Results from two designed experiments. A dash indicates no significant effect.

<sup>b</sup> The significance of other variables, such as the PTMG molecular weight distribution, was not certain in these experiments. It was determined that 4-8% modifier in PTMG improved the elastomer's permanent set.

<sup>c</sup> Measured in the same way as permanent set except that the sample was cooled to 0°C. and released, then gradually warmed.

<sup>d</sup> Low molecular weight PTMG was indicated when a low weight per cent of PTMG was used.

<sup>e</sup> This is a trend and the significance of it is not certain.

<sup>f</sup> Measured 1 min. after the completion of first cycle.

erties. A few of these compositions represent elastomers from two designed experiments. For comparison, data on elastomers 2, 3, and 4 are also included. Table III contains conclusions from the two designed experiments. For these experiments, 26 elastomers were prepared, and properties were determined on films made from these elastomers. This table indicates the desired level of the variables in the elastomer (weight per cent

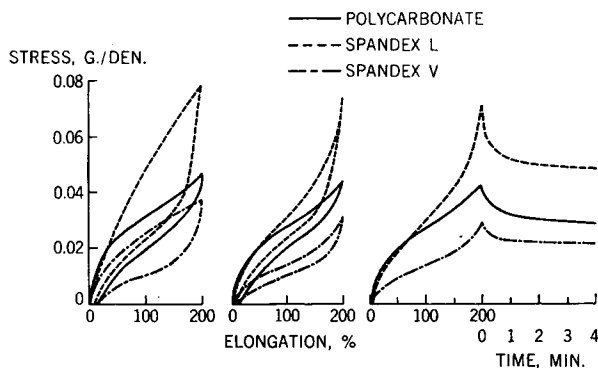


Fig. 1. Stress vs. strain and stress decay with time at 200% extension.

TABLE IV  
 Properties of Fibers from Polycarbonate Elastomers<sup>a</sup>

Expt. Elastomer No.	Composition of elastomer		Yarn [η]	Denier	Elongation at break, %	Tenacity, g./den.	Second cycle loop <sup>b</sup>						Elastic recovery from 400% extension, %	Permanent set, %		Shrinkage in boiling water, %	Flow pt. at 0.02 g./den. °C.	
	PTMG <sup>c</sup>	Wt.-%					Mol. wt.	30% Power, extension, 10 <sup>3</sup> g./den.	100% Power, extension, 10 <sup>3</sup> g./den.	30% Power, return, 10 <sup>3</sup> g./den.	100% Power, return, 10 <sup>3</sup> g./den.	10% Power, return, 10 <sup>3</sup> g./den.		10% Power, return, 10 <sup>3</sup> g./den.	After 1 min.			After 60 min.
1	60	4200	2.7	441	480	0.87	18	27	0	10	98.5	54.5	22.0	1.5	194			
2	62	3200	2.8	212	440	0.65	16	28	2	16	100	28.0	4.0	29.0 <sup>d</sup>	132			
3	62.5	4200	2.3	494	585	0.33	9	16	1	8	100	43.5	15.0	7.0	141			
4	65	4200	2.3	420	470	0.35	16	25	3	16	98.2	48.0	23.0	0	—			
5	65	4200	2.3	590	510	0.63	—	—	2 <sup>f</sup>	14 <sup>f</sup>	98.9	50.0	23.0	—	138			
6	65	4200	3.0	421	500	0.60	14	24	3	15	99.4	34.5	12.5	4.5	165			
7	65	4200	3.5	352	425	0.46	13	23	2	13	99.7	34.0	13.5	6.0	166			
8	65	4200 <sup>g</sup>	2.6	357	470	0.51	11	21	4	15	99.6	39.0	16.0	3.0	158			
9	67.5	4200	3.2	417	610	0.37	9	16	2	10	100	46.0	20.5	12.0	158			
10	70	4200	2.9	431	610	0.23	9	18	4	13	97.7	49.5	29.5	5.0	124			
11	55	4200	3.1	162	354	0.79	18 <sup>h</sup>	36	0	16	98.4 <sup>i</sup>	81.0	56.0	—	220			
12	60	4200	2.5	289	366	0.67	9 <sup>h</sup>	26	0	12	97.7 <sup>i</sup>	80.0	64.0	—	204			
13	65	4200	2.9	497	388	0.55	7 <sup>h</sup>	18	0	12	94.7 <sup>i</sup>	76.5	65.5	—	172			
Commercial spandex L	—	—	—	622	495	0.91	7	21	0	11	99.3	26	17.0	3.0	202			
Commercial spandex V	—	—	—	685	680	0.38	4	9	0	5	99.8	15.5	7.0	4.0	172			
Rubber	—	—	—	500	600	0.34	5	11	3	8	99.6	3.5	1.5	4.0	218			

<sup>a</sup> Fibers wet-spun from methylene chloride into ethyl alcohol.

<sup>b</sup> Properties measured at 400% extension.

<sup>c</sup> Contained 6 mole-% modifier in PTMG.

<sup>d</sup> Shrinkage due to high draft ratio during spinning process.

<sup>e</sup> Dry-spun, same elastomer as in experiment no. 5.

<sup>f</sup> Estimated from first cycle.

<sup>g</sup> The bischloroformate of PTMG was used.

<sup>h</sup> Power measured at 200% extension.

<sup>i</sup> Recovery at maximum elongation.

of PTMG, molecular weight of PTMG, inherent viscosity), within the range measured, to give good elastomer properties. Most of the conclusions stated later are based on results of the designed experiments. Table IV is a list of properties on fibers and includes many in the composition range of the polymers studied in the designed experiments. Since elastomer properties in the second cycle of the test are considered to be more representative of elastomers than the properties in the first cycle, these are given in Tables II and IV. Figures 1 and 2 show stress-strain curves for a polycarbonate elastomer fiber (Table IV, experiment 6), which contains bisphenol I and 65 wt.-% PTMG, and curves of two spandex

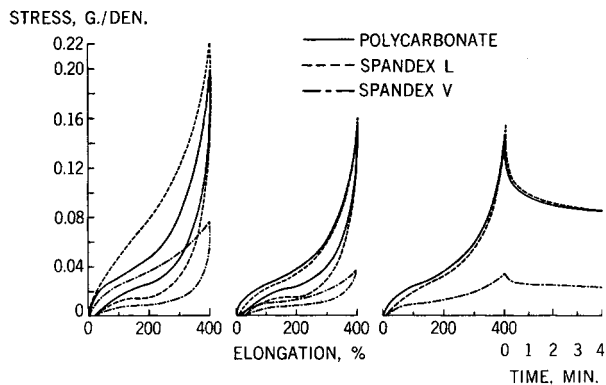


Fig. 2. Stress vs. strain and stress decay with time at 400% extension.

elastomer fibers. The top half of the curves represents the power of the elastomer on the extension cycle, and the bottom half represents the power on the return cycle. The fibers were held in the extended state during the third cycle. The decrease in power with time was recorded to give the stress decay of the fiber. Note that the properties of the polycarbonate elastomer compare favorably with those of the spandex elastomers.

### Physical Properties of Polycarbonate Elastomers

Since there is no crosslinking, hydrogen bonding, or crystallinity in the polycarbonate hard segment, the restraint of gross chain mobility is attributed to the bulky, three-dimensional norbornane ring attached to two dichlorophenyl groups. This bulk makes movement of the hard segment difficult when the elastomer is stretched and therefore behaves as a tie-down point. The three-dimensional norbornane ring also causes chain stiffness by restricting the freedom of movement of the phenyl rings attached to it.

All elastomers listed in the tables contain PTMG soft segments, but other segments, such as hydroxy-terminated polyesters, polyformals, and polycarbonates were used in a few limited experiments. Since inherent viscosities were not as high when these segments were used, the properties



of elastomers made from them did not compare favorably with those of the elastomers containing PTMG.

Several attempts were made to improve the properties of some of the elastomers by orientation and heat setting. Slight improvement was noted in the overnight permanent set, but usually tenacity and elongation were reduced. The lack of crystallinity in the polycarbonate elastomer hard segment decreases the value of heat setting.

### **Solubility**

The polycarbonate elastomers were soluble in a host of solvents, such as methylene chloride, 1,2-dichloroethane, chloroform, tetrachloroethane, dioxane, benzene, toluene, cyclohexanone, and dimethylformamide. They were swollen in acetone, ethyl acetate, and tetrachloroethylene and were insoluble in hexane, naphtha, cyclohexane, and aliphatic alcohols.

### **Inherent Viscosity and Molecular Weight**

The inherent viscosity was measured in reagent grade chloroform at 25°C. An inherent viscosity of about three gave the best range of properties; most properties were improved or remained the same up to this viscosity except for tenacity, which decreased as inherent viscosity increased.

The number-average molecular weight of several elastomers was measured by the ebullioscopic method. Inherent viscosities of 2.0 and 3.3 gave molecular weights of about 80,000 and 150,000, respectively.

### **Glass Transition Temperature**

The glass transition temperatures of several elastomers containing 65 wt.-% PTMG were determined by differential thermal analysis and found to be -66°C. to -70°C. This range is in the area of the glass transition temperature of rubber and is slightly higher than that of spandex-type elastomers.

### **Elongation at Break**

Elongation was measured by placing two marks 3 cm. apart on the film or fiber and stretching it along a meter stick until it broke. The distance between the marks when the sample broke was recorded as the elongation at break. The main influence on the elongation was the weight per cent of PTMG used; the elongation increased as the amount of PTMG was increased. Elongations were usually in the 400-600% range.

### **Tenacity**

Tensile properties were measured on an Instron tensile tester for film and fiber samples. For example, a fiber was clamped into the tester at a 2-in. gage length. The testing machine was set to extend the fiber to 400%

elongation at a rate of 1000%/min. and then to return it to its original position, and thus plot the stress versus strain (Fig. 1). There was a 1-min. rest period between cycles. On the third cycle, tenacity was measured when the fiber was stretched to its breaking point. Stress decay was measured when the fiber was extended to 400% and the machine stopped with the recorder chart moving.

Tenacity is a measure of the tensile strength of a fiber or film. To convert tenacity (g./den.) into tensile strength (lb./in.<sup>2</sup>), the following can be used:

$$\text{Tensile strength (lb./in.}^2\text{)} = 12,800 \times \text{specific gravity} \times \text{tenacity (g./den.)}$$

For example, one of our polycarbonate elastomers with a specific gravity of 1.13 and tenacity of 0.6 g./den. had a tensile strength of 8670 lb./in.<sup>2</sup>.

The tenacity of the polycarbonate elastomers generally increased as the weight per cent of PTMG decreased. Tenacity also increased as the inherent viscosity decreased from 3.5 to 1.5. Tenacity usually improved when the molecular weight of PTMG was increased from 2500 to 4000. The elastomers usually had a tenacity in the range of 0.2–0.9 g./den.

### Power

To stretch an elastomer, force must be applied to overcome the resistance of the elastomer to stretch. The elastomer also exerts a pull to return to its original length when the force that pulls it is released. Power may be defined as the stress required to extend or hold the elastomer at a certain extension or strain. Power (g./den.) was measured directly on the Instron tester. High return power in an elastomer is desired because it is a measure of the elastomer's holding ability, which can be especially important in foundation garments. The extension power increased, but return power decreased as the weight per cent of PTMG in the elastomer decreased. Extension power increased as the molecular weight of PTMG increased if the weight per cent of PTMG was held constant. This is contrary to accepted elastomer theory, but can probably be explained as follows: The hard segment becomes more effective as a tie-down point as its average length increases. Whenever the weight per cent or mole per cent of the soft segment was lowered, the elastomer became stiffer and less elastic.

### Elastic Recovery

Elastic recovery was measured by stretching a 10-cm. section of fiber to 50 cm. (400% extension) and releasing it immediately. If the sample recovered to 11 cm. in 1 min., the elastic recovery was 97.5%, which was calculated by dividing the amount recovered (39 cm.) by the original extension (40 cm.) and multiplying by 100.

The polycarbonate elastomers had excellent elastic recovery, but this was lowered if the weight per cent of PTMG was reduced below about 55%. The use of low molecular weight PTMG (2500) favored high elastic recovery, but recovery of 99–100% was common even when PTMG in the 4000 molecular weight range was used. Elastic recovery depends upon some type of tie-down point (crosslinking, hydrogen bonding, or crystallinity) in the hard segment. The norbornane ring attached to the dichlorophenyl groups gives enough bulk and rigidity to make it difficult to slip through the elastomer matrix, and it, in effect, behaves as a tie-down point. When bisphenol-A was used, elastic recovery was poorer in spite of crystallinity. It does not have the bulk of the norbornane ring.

### Permanent Set

Permanent set is defined as the percentage gain in length of the elastomer fiber or film when a given segment is momentarily stretched three times its length, relaxed to 1.5 times its length, and held in this state for 16 hr. The elastomer is released and the increase in length is noted after 1 min. and after 60 min. This gain in length is divided by the original length and multiplied by 100 to give the percentage permanent set. For example, a 20-cm. section of fiber is stretched to 80 cm. (300%) and then held 16 hr. at 50 cm. (150%). When the sample is released, the length is 24 cm. after 1 min. and 22 cm. after 60 min. This corresponds to 20% and 10% permanent set, respectively. A low permanent set is desirable, since this means that the sample will return almost completely to its original dimensions after prolonged stretching. The permanent set of the polycarbonate elastomers is somewhat high compared with the permanent set of the commercial spandex elastomers. Apparently, when the polycarbonate elastomer is held stretched for a long period of time, there may be some movement or slippage of short segments of the norbornane ring through the elastomer matrix. Once this movement has occurred, it appears to be just as difficult for these bulky segments to resume their original orientation when released. Hence, a higher permanent set is noted initially, but complete recovery is possible if sufficient time is allowed.

Permanent set was measured at 21°C. on the fibers and at 23°C. on the films. A high value was noted when the PTMG segment in the elastomer had crystallized. Permanent set was improved by using a modified PTMG, which crystallized only at appreciably lower temperatures or at higher elongations. The modification consisted of copolymerizing 6–8 mole-% of another monomer with tetrahydrofuran. This lowered the melting point of the PTMG, thereby improving the permanent set of the elastomer, especially at low temperatures. The modifier had more effect on high molecular weight PTMG since it melts at a higher temperature than does low molecular weight PTMG.

Low permanent set is favored when a high weight per cent of PTMG is used, when the molecular weight of the PTMG is high, and when the inherent viscosity of the elastomer is high,

### Shrinkage

Shrinkage was determined by placing a length of fiber in boiling water for 30 sec. and measuring the resulting decrease in length. Shrinkage, of course, must be held within reasonable limits, and up to 3 or 4% is considered acceptable. Shrinkage can be controlled to some extent by the rate of take-up of the fiber during the spinning. Heating the relaxed fiber and allowing it to contract usually reduces the shrinkage to zero.

### Flow Point

The flow point of the fiber is the temperature (centigrade) at which the fiber breaks after being held at that temperature for 5 sec. under a stress of 0.02 g./den. The relationship between flow point and use temperature of the fibers was not determined, but elastomers with flow points as low as 80 to 110°C. were often tacky and difficult to test. When the weight per cent of PTMG in the elastomer was increased, a corresponding decrease in the flow point was usually noted.

### CONCLUSIONS

Unfortunately, it is difficult to prepare an elastomer which has all the properties of an ideal elastomer. When the composition is changed to improve one property, another property usually suffers. It is apparent from the designed experiment results (Table III) that no one composition gives the best values for all properties.

As can be noted in Tables II and IV, elastomer 1 had better tenacity and power than elastomers 2, 3, and 4; it also had higher elongation, higher elastic recovery, and lower permanent set than elastomer 4 (bisphenol-A polycarbonate).

Since spandex elastomers have found wide consumer acceptance, their properties may be used as a guide, though they are probably far from ideal. Some of these properties, which can be considered to be representative, are given at the bottom of Table IV. The polycarbonate composition that compared most favorably with these commercial elastomers is represented by experiment 6. It contained 65 wt.-% of PTMG. It had an elongation of 500%, a tenacity of 0.6 g./den., and excellent elastic recovery (99.4% from 400% elongation). The stress-strain curves of this elastomer (Figs. 1 and 2) were measured at 200 and 400% extension for three cycles. On the second cycle, extension and return powers at 400% extension were superior to those of the spandex elastomers. The permanent set of the polycarbonate elastomer was somewhat high, especially after 1 min., but after 3 hr. it had decreased to 11%, and complete recovery was obtained in 13 days. For comparison, it took 3 days for the permanent set of spandex L to decrease to 11%. After 3 weeks it still had 8.5% set. The actual importance of the permanent set test is not certain, since wear tests have not been made on the polycarbonate elastomer.

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### Résumé

Des élastomères de polycarbonate ont été préparés par l'addition de phosgène à une solution pyridinique de poly(tétraméthylène-éther) glycol et de bisphenol contenant des groupements du type norbornane. Ces élastomères ne possèdent pas les points de liaison classiques—pontage, pont hydrogène, ou cristallinité—qui, jusqu'à présent, ont été considérés comme nécessaires pour avoir de bonnes propriétés élastomères. Ce travail introduit une nouvelle idée dans la chimie des élastomères: des groupements volumineux et tridimensionnels constituent des points de liaison efficaces. La plupart des élastomères ont été préparés avec le 4,4'-(2-norbornylidène)bis(2,6-dichlorophénol). A titre de comparaison plusieurs élastomères contenant du bisphénol-A, ont été également préparés. Une expérience statistique a été faite afin de déterminer l'influence des différentes compositions sur les propriétés de ces élastomères. Les propriétés ont été déterminées sur des films, préparés par conlage d'une solution dans le chlorure de méthylène, et dans plusieurs cas, sur des fibres à l'état humide. Ces élastomères possèdent des élongations de 400 à 600% et retournent instantanément à leur état initial à 100%.

### Zusammenfassung

Polykarbonatelastomere wurden durch Zusatz von Phosgen zu einer Pyridinlösung von Poly(tetramethylenäther)glycol und Bisphenolen mit Gruppen vom Norborantyp erhalten. Diese Elastomeren enthalten keine klassischen "Verknüpfung"-Punkte, Vernetzungen, Wasserstoffbindung oder Kristallinität, welche bisher als notwendig für gute Elastomereigenschaften gehalten wurden. Die vorliegende Arbeit führt ein neues Konzept in die Elastomerchemie ein: raumerfüllende, dreidimensionale Gruppen bilden wirksame Verknüpfungspunkte. Die meisten Elastomeren wurden mit 4,4'-(2-Norbornyliden)bis(2,6-dichlorphenol) dargestellt und zum Vergleich einige Elastomere mit Bisphenol-A. Ein statistisch ausgelegter Versuch wurde zur Bestimmung des Einflusses der Zusammensetzungsvariablen auf die Eigenschaften dieser Elastomeren ausgeführt. Die Eigenschaften wurden an Filmen aus Methylenchloridlösungen und in vielen Fällen an feucht gesponnenen Fasern bestimmt. Die Elastomeren weisen Elongationen von 400 bis 600% und eine momentane elastische Erholung bis zu 100% auf.

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