

## Diphenolic Acid Ester Polycarbonates

ROBERT P. FISCHER, G. ROBERT HARTRANFT,  
and JOHN S. HECKLES, *Research and Development Center, Armstrong  
Cork Company, Lancaster, Pennsylvania*

### Synopsis

Polycarbonates of methyl, ethyl, *n*-propyl, *n*-butyl, and *n*-hexyl 4,4-bis(4-hydroxyphenyl)pentanoate and copolycarbonates with bisphenol-A of 0.5-0.9 intrinsic viscosity in dioxane were prepared by a homogeneous  $\text{CH}_2\text{Cl}_2$ -pyridine method and the physical properties determined. Increasing the number of carbon atoms in the DPA ester alcohol group from 1 to 6 decreased the initial softening temperature of the polycarbonates from 126 to 58°C.; this change also increased the solubility of the polycarbonates in aromatic solvents and in three ketone solvents.  $\text{O}_2$  transmission rates were not affected by increasing the ester chain length.  $\text{CO}_2$  transmission rates increased as DPA ester alcohol chain length increased. Methyl DPA polycarbonate had the highest tensile strength and per cent elongation and the lowest  $\text{O}_2$  and  $\text{CO}_2$  transmission rates.

### INTRODUCTION

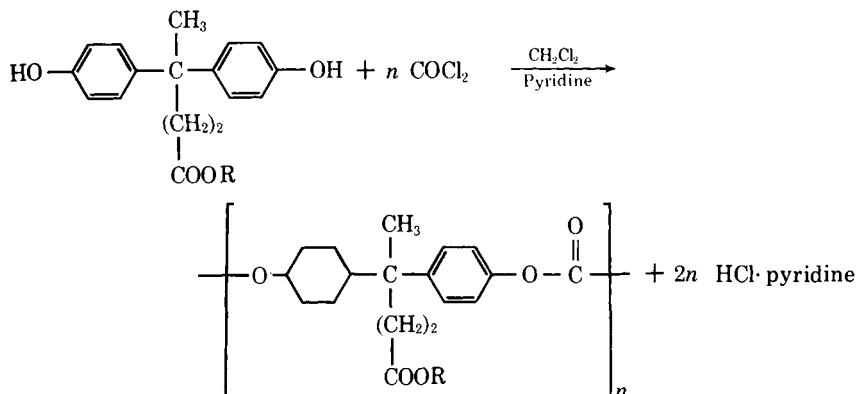
It was the purpose of this study to prepare polycarbonates from esters of 4,4-bis(4-hydroxyphenyl)pentanoic acid, known commonly as diphenolic acid (DPA). Use of this bisphenol with its pentanoic acid ester group should affect physical properties of the polycarbonate as well as provide the possibility of post reactions on the finished polymer.

The carboxy alkyl group was expected to increase compatibility with added plasticizers, increase polycarbonate solubility for casting or coating applications and act as an internal plasticizer. It was also expected to reduce solvent or plasticizer crazing and lower polycarbonate softening temperature. Copolycarbonates with other bisphenols can moderate the effect of the carboxy alkyl group.

The earliest polycarbonates were those prepared by reacting phosgene with hydroquinone and resorcinol. Fox<sup>1</sup> and Goldberg<sup>2</sup> of General Electric reported in 1957 methods of preparation and properties of bisphenol-A polycarbonates. At the same time Schnell<sup>3</sup> of Bayer in Germany reported preparation of the same bisphenol-A polycarbonates and polycarbonates based on other bisphenols. Large scale development of polycarbonates by General Electric and Mobay in the United States and by Bayer in Germany are based on bisphenol-A (BPA).

The DPA ester polycarbonates of this study were prepared by the direct reaction of phosgene with the DPA ester in a methylene chloride-pyridine solution. Pyridine acted as both the solvent and the HCl acceptor.

BPA polycarbonates can be made by this method by transesterification with diphenyl carbonate or interfacially by using aqueous NaOH and an organic solvent phase. Diphenolic acid behaved trifunctionally when phosgenated in  $\text{CH}_2\text{Cl}_2$ -pyridine solution, producing insoluble gel-type polymer. When the interfacial method was used, DPA ester hydrolyzed to the acid reacting trifunctionally, producing a large amount of polymer insoluble in  $\text{CH}_2\text{Cl}_2$ .



## EXPERIMENTAL

### Preparation of DPA Esters

Methyl ester was prepared by refluxing diphenolic acid with excess methanol and *p*-toluenesulfonic acid. Ester was precipitated by addition of water and recrystallized from methanol-water, m.p. 133–134°C.

Ethyl ester was prepared by refluxing diphenolic acid, ethanol, dichloroethane, and HCl catalyst. Excess alcohol was removed by water washing; the ester was crystallized from dichloroethane by cooling and recrystallized from methanol-water, m.p. 128.7–129.3°C.

*n*-Propyl ester was prepared by refluxing *n*-propyl alcohol, diphenolic acid, benzene, and HCl catalyst. Solution of ester was water washed to remove excess alcohol, then dissolved in toluene. Excess benzene and *n*-propyl alcohol were removed by distillation, and *n*-propyl DPA ester was crystallized from the toluene by cooling, m.p. 100–101°C.

Diphenolic acid, *n*-butyl and *n*-hexyl esters of diphenolic acid were obtained from the S. C. Johnson Co., Racine, Wisconsin and were used as received.

### Preparation of Polycarbonates

The DPA ester polycarbonates as well as the copolycarbonates containing bisphenol A were prepared by the methylene chloride-pyridine solution method. The molecular weights of the polycarbonates and copolycarbonates prepared by this method were approximately 30,000–50,000. The

preparation of the polycarbonate from methyl diphenolate follows and is representative of all the polycarbonate preparations.

Methyl diphenolate (114 g., 0.380 mole), 70 ml. (0.87 mole) of pyridine (distilled reagent grade) and 700 ml. of methylene chloride (refrigeration grade) were added to a 1-liter, three-necked Morton-type flask. The temperature of the solution was adjusted to 25°C. With vigorous stirring, phosgene was bubbled into the solution at the rate of 1 g./min. The temperature increased and was maintained at 35°C. by means of an ice bath. After about 80% of the theoretical amount of phosgene had been added, pyridine hydrochloride began to precipitate from the solution. When about 95% of the theoretical amount of phosgene had been added, the rate of addition was slowed to about 0.1 g./min. Phosgene was admitted at this rate until a definite increase in viscosity was noted. At this point, the flow of phosgene was stopped. The reaction mixture was added to 500 ml. of 10% aqueous hydrochloric acid with stirring for 10–15 min. The layers were allowed to separate (addition of 300–400 ml. of methanol to the mixture hastened the separation of layers). The methylene chloride layer was drawn off and the washing repeated with 10% hydrochloric acid and finally with water. The polycarbonate was precipitated from the methylene chloride solution by the addition of methanol in a high-speed blender. The precipitated polymer was filtered, washed with fresh methanol, air-dried, and finally dried in a vacuum oven at 80°C. for at least 16 hr. The yield was 118 g. (95% of theory).

#### Intrinsic Viscosity and Molecular Weight Determination

A straight line relationship between  $\log [\eta]$  and  $\log \bar{M}_w$  was found for methyl diphenolate polycarbonate for the range  $\bar{M}_w$  40,000–250,000.  $\bar{M}_w$  for five unfractionated methyl diphenolate polycarbonates were calculated from osmotic pressure  $\bar{M}_n$  by using the  $\bar{M}_w/\bar{M}_n$  values for the same five polycarbonates determined by gel permeation chromatography. A straight line relationship was not obtained between  $\log [\eta]$  and  $\log \bar{M}_n$  calculated from osmotic pressure because the  $\bar{M}_w/\bar{M}_n$  values for the five polycarbonates ranged from 1.8 to 3.7. The correlation between intrinsic viscosity and weight-average molecular weight for unfractionated methyl diphenolate polycarbonates in dioxane at 30°C. was found to be  $[\eta] = 1.16 \times 10^{-4} \bar{M}_w^{0.78}$ .

### DISCUSSION

#### DPA Ester Polycarbonates

Cast films, 3 mil in thickness, of the five polycarbonates were used for determining physical properties. Results are given in Table I.

Tensile strength decreases as the length of the alcohol part of the DPA ester increases from methyl to hexyl. Values for per cent elongation, folding endurance, and softening temperature also decreased with increasing length of the alcohol moiety from methyl to hexyl.

TABLE I  
Physical Properties of Diphenolic Acid Ester Polycarbonates

	Tensile strength, psi	Elongation, %	Elmendorf tear strength, g./mil	Folding endurance, double folds	$[\eta]$	Softening temp., °C.
MeDPA	9590	43	10	1800	0.49	126
EtDPA	9650	13	7	1580	0.54	103
<i>n</i> -PrDPA	8210	32	10	650	0.70	96
<i>n</i> -BuDPA	7590	7	7	1130	0.69	92
<i>n</i> -HeDPA	5790	11	12	1010	0.45	57
BPA	9230	46	7	2800	0.45	211

There is an alternating effect in the first four DPA ester polycarbonates. The polycarbonates of DPA esters of alcohols with odd numbers of carbon atoms have higher per cent elongations and tear strengths than the even number (ethyl and butyl) DPA ester polycarbonates. The alternating effect also occurs in the melting points of the DPA esters but not in the softening points of the different polycarbonates.

DPA ester polycarbonates were more soluble in organic solvents than BPA polycarbonates. Figure 1 illustrates the effect of the DPA ester alcohol chain length on the solubility of DPA ester polycarbonates in benzene, toluene, xylene and Hi-Flash naphtha (American Mineral Spirits Co.). BPA polycarbonate was insoluble in xylene and toluene and was less than 2% soluble in benzene. MeDPA polycarbonate was more than 5% soluble in benzene but was soluble in toluene to the extent of only 0.89%. EtDPA polycarbonate was more than 5% soluble in toluene but only 0.48% soluble in xylene. *n*-PrDPA and *n*-BuDPA polycarbonates were both more than 5% soluble in xylene. In the case of Hi-Flash naphtha the *n*-HeDPA ester polycarbonate was required for at least 5% solubility.

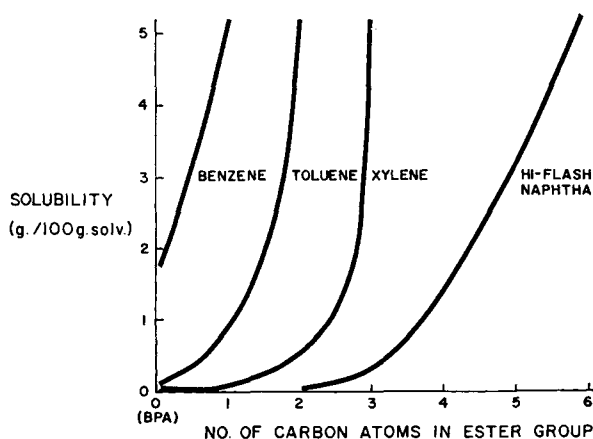


Fig. 1. Solubility of DPA ester polycarbonates in aromatic hydrocarbons.

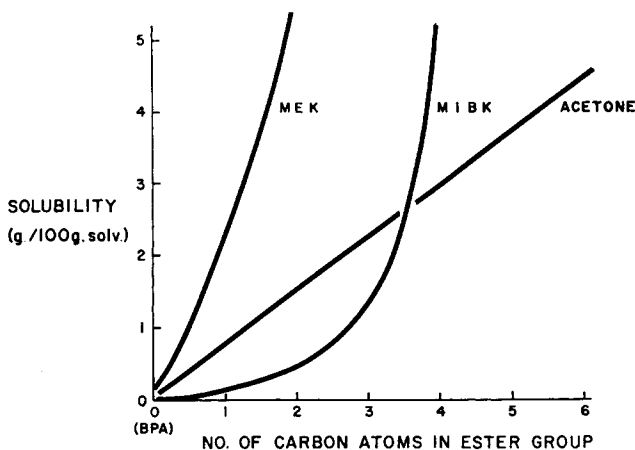


Fig. 2. Solubility of DPA ester polycarbonates in ketones.

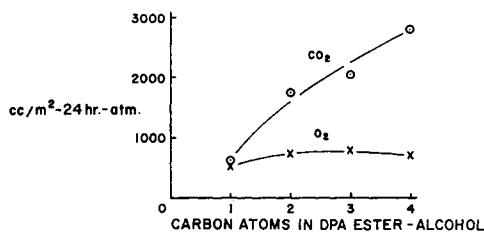


Fig. 3. O<sub>2</sub> and CO<sub>2</sub> transmission rates for 3 mil DPA ester polycarbonate films.

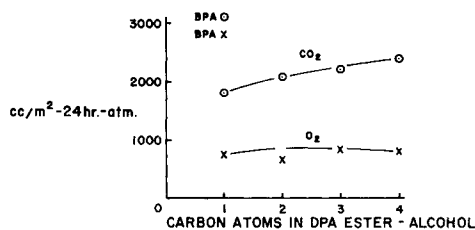


Fig. 4. O<sub>2</sub> and CO<sub>2</sub> transmission rates for 3 mil 1:1 bisphenol A-DPA ester copolymer films.

For aromatic solvents the longer the DPA ester alcohol group the greater the solubility.

Length of the DPA ester alcohol also affected solubility in acetone, MEK, and MIBK (Fig. 2). Bisphenol A polycarbonate was practically insoluble in the three ketones, while the solubility of the DPA ester polycarbonates increased with the number of C atoms in the ester portion of the molecule.

Oxygen and CO<sub>2</sub> transmission rates of 3 mil cast films of DPA ester polycarbonates were determined by ASTM method 1434-58. The effect of alcohol chain length and molecular weight were determined. With a single exception the O<sub>2</sub> and CO<sub>2</sub> transmission rates of an 0.5 and an 0.9 intrinsic

viscosity series of DPA ester polycarbonates were similar. The effect of alcohol chain length on transmission rates is given in Figure 3. The O<sub>2</sub> and CO<sub>2</sub> transmission rates of 1-1 bisphenol-A-DPA ester (Me, Et, Pr, and Bu) copolycarbonates are given in Figure 4.

Oxygen transmission rates were not affected by DPA ester alcohol chain length or by forming copolycarbonates with bisphenol-A. CO<sub>2</sub> transmission rates increased as the DPA ester alcohol increased from methyl to butyl (MeDPA 710 cc., *n*-BuDPA 2815 cc.). In the 1:1 BPA-DPA ester copolycarbonate series, CO<sub>2</sub> transmission increased from 1800 cc. for the 1:1 MeDPA-BPA copolycarbonate to 2380 cc. for the 1:1 *n*-BuDPA-BPA copolycarbonate. The MeDPA ester polycarbonate had the lowest O<sub>2</sub> and CO<sub>2</sub> transmission rates of all the films tested.

Impact strength of MeDPA polycarbonate was 2.7 ft.-lb./in. notch, which is much less than the 18 ft.-lb. measured for bisphenol A polycarbonate. Water vapor transmission of MeDPA polycarbonate was 1.9 perms/2 mil film, approximately the same as the value (2.1 perms) measured for bisphenol A polycarbonate.

### DPA Ester-BPA Copolycarbonates

Copolycarbonates of MeDPA, EtDPA, *n*-PrDPA, and *n*-BuDPA ester with 33, 50, and 67 mole-% BPA, with 0.46-0.70 intrinsic viscosity in dioxane, were prepared. Physical properties are summarized in Table II. Copolycarbonates of *n*-PrDPA and *n*-BuDPA ester with 33, 50, and 67 mole-% BPA had higher tensile strengths than the *n*-PrDPA and *n*-BuDPA

TABLE II  
Physical Properties of Diphenolic Acid Ester-Bisphenol A Copolycarbonates

	BPA, mole-%	Tensile strength, psi	Elonga- tion, %	Elmendorf tear strength, g./mil	Folding endurance, double folds	[ $\eta$ ]
MDPA	0	9590	43	10	1800	0.49
	33	8370	29	9	2260	0.52
	50	8700	22	11	2300	0.48
	67	9130	48	13	2400	0.46
EDPA	0	9650	13	7	1580	0.54
	33	9525	10	9	1380	0.56
	50	9660	23	11	3300	0.54
	67	8760	13	9	2240	0.53
<i>n</i> -PrDPA	0	8210	32	10	650	0.70
	33	9300	59	9	1290	0.61
	50	9600	21	8	2360	0.54
	67	9350	25	9	1120	0.51
<i>n</i> -BuDPA	0	7590	7	7	1130	0.69
	33	9240	35	10	1510	0.53
	50	8620	40	9	1510	0.49
	67	9170	67	9	2400	0.54
BPA	100	9230	46	7	2800	0.45

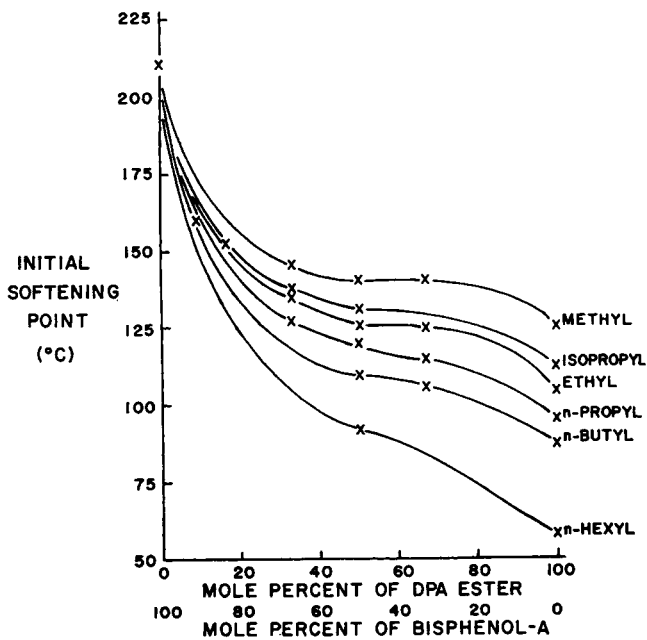


Fig. 5. Softening temperature of 1:1 bisphenol A-DPA ester copolycarbonates.

polycarbonates. Tear strengths of the copolycarbonates were more like those of the DPA ester polycarbonates, even when 67 mole-% of the copolycarbonate was BPA. Folding endurance of the 3-mil films of the copolycarbonates was higher than that of the DPA ester polycarbonate and more like that of the BPA polycarbonate.

The softening temperatures of the DPA ester polycarbonates and copolycarbonates with BPA are given in Figure 5. As the length of the DPA ester alcohol increased from methyl to hexyl, the initial softening temperature decreased from 125 to 58°C. BPA polycarbonate started to soften at 210°C. Copolycarbonates of BPA with the five DPA esters had softening temperatures which were intermediate between those of the respective polycarbonates. By the use of copolycarbonates it is possible to select a polymer with a softening temperature between 60 and 210°C. The softening temperatures are initial temperatures at which the polycarbonate starts to deform and flow under a slight pressure. For temperature of complete melting of a polymer another 75–100°C. should be added to these values.

The authors wish to acknowledge the assistance of Mrs. Shirley M. Swayne who determined polycarbonate intrinsic viscosities and solubilities and prepared film samples.

### References

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3. Schnell, H., *Angew. Chem.*, **68**, 633 (1956); *Ind. Eng. Chem.*, **51**, 157 (1959).

### Résumé

On a préparé des polycarbonates de pentanoate de méthyl, éthyl, *n*-propyl, *n*-butyl et *n*-hexyl- 4,4-bis-4-hydroxyphényle et des copolycarbonates avec le bisphénol-A de viscosité intrinsèque de 0.5–0.9 en solution dans le dioxane au moyen d'une méthode homogène dans le chlorure de méthylène et la pyridine et les propriétés physiques en ont été déterminées. En accroissant le nombre d'atomes de carbone dans le groupe DPA ester-alcool de 1 à 6, on diminue la température de ramollissement initiale du polycarbonate de 126 à 58°C; cette variation accroît également la solubilité des polycarbonates dans les solvants aromatiques et dans trois solvants cétoniques. Les vitesses de transmission d'oxygène ne sont pas affectées par cet accroissement de longueur de chaîne de l'ester. La vitesse de transmission du CO<sub>2</sub> croît avec un accroissement de la longueur de chaîne du DPA ester-alcool. Le polycarbonate de méthyl-DPA présente une force à la tension et un pourcentage d'élongation les plus élevés et des vitesses d'élongation et de transmission d'O<sub>2</sub> et de CO<sub>2</sub> les plus basses.

### Zusammenfassung

Polycarbonate aus Methyl-, Äthyl-, *n*-Propyl-, *n*-Hexyl-, 4,4-bis(4-Hydroxyphenyl)-pentanoat- und Copolycarbonate mit Bisphenol-A mit einer Viskositätszahl von 0,5–0,9 in Dioxan wurden im homogenen CH<sub>2</sub>Cl<sub>2</sub>-Pyridinsystem dargestellt und die physikalischen Eigenschaften bestimmt. Eine Erhöhung der Anzahl der Kohlenstoffatome in der DPA-Ester-Alkoholgruppe von 1 auf 6 setzte die Anfangserweichungstemperatur der Polycarbonate von 126° auf 58° herab; diese Änderung erhöhte auch die Löslichkeit der Polycarbonate in aromatischen Lösungsmitteln und in drei Ketonlösungsmitteln. O<sub>2</sub>-Durchtrittsgeschwindigkeiten wurden durch Erhöhung der Esterkettenlänge nicht beeinflusst. CO<sub>2</sub>-Durchtrittsgeschwindigkeiten nahmen mit steigender DPA-Ester-Alkoholkettenlänge zu. Methyl-DPA-Polycarbonate besaßen die höchste Zugfestigkeit und prozentuelle Elongation sowie die niedrigste O<sub>2</sub>- und CO<sub>2</sub>-Durchtrittsgeschwindigkeit.

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