Synthesis of Aromatic Polycarbonates by an Anhydrous Catalytic Solution Process.   I.   The Phosgene–Phenol Interaction

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Synopsis

A two-step, catalytic, anhydrous solution process was developed for the preparation of the polycarbonate of 2,2-bis(*p*-hydroxyphenyl)propane (bisphenol-A). It involves the preparation of the dichloroformate of bisphenol-A followed by its condensation with bisphenol-A in the presence of magnesium metal. Attempts were also made to develop a one-step, catalytic solution process. The reaction of bisphenol-A with phosgene, in the presence of aluminum chloride, a very powerful catalyst, led to polymers with reduced viscosities as high as 0.35. Higher viscosities were not obtained due to the lack of a suitable, nonreactive solvent.

INTRODUCTION

Aromatic polycarbonates have been intensively investigated in recent years.[1,2] They have shown a variety of unusual and interesting properties. The commercial importance of one member of this class, the polycarbonate (I) derived from 2,2-bis(*p*-hydroxyphenyl)propane, is well known.*
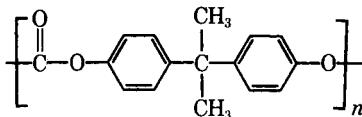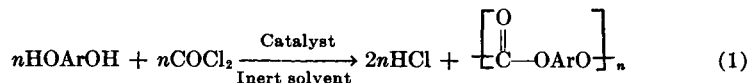

I

Several processes for the preparation of aromatic polycarbonates are known. Among these, three appear to be the most important:[1-3] (*1*) the direct phosgenation of the bisphenol in an interfacial system; (*2*) the ester-exchange reaction between the bisphenol and a diaryl carbonate, and (*3*) the direct phosgenation of the bisphenol in an inert solvent in the presence of a stoichiometric amount of tertiary organic base.

All of these processes produce high molecular weight polycarbonates in good yields. However, each of them involves certain practical problems,
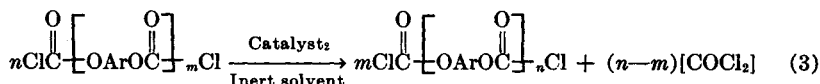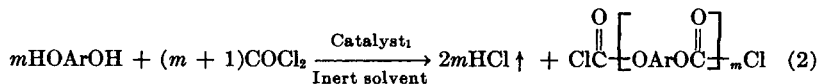
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* This polymer, also known generically as bisphenol-A polycarbonate is being marketed by Farbenfabriken Bayer A.-G. under the name Makrolon in Europe; by Mobay Chemical Co. under the name Merlon in the U.S.A. It has also been commercialized by the General Electric Co. under the name Lexan.

some of which might be avoided in an anhydrous, catalytic solution process. This paper describes research carried out to develop such a process.

One can visualize two variations for the catalytic reaction of bisphenols with phosgene to yield polycarbonates. The more direct is the reaction of equimolar amounts of the bisphenol and phosgene to yield high molecular weight polymer according to eq. (1).

$$n\text{HOArOH} + n\text{COCl}_2 \xrightarrow[\text{Inert solvent}]{\text{Catalyst}} 2n\text{HCl} + \left[\begin{matrix}\text{O}\\\parallel\\\text{C}\end{matrix}-\text{OArO}\right]_n \qquad (1)$$

Such a process possesses the inherent technical problem of maintaining the stoichiometric balance between the bisphenol and phosgene that is required to achieve high molecular weight polymer. The alternate route would lead initially to a chloroformate-terminated low molecular-weight polycarbonate, followed by molecular weight build-up via the chloroformate endgroups [eqs. (2) and (3)].

$$m\text{HOArOH} + (m+1)\text{COCl}_2 \xrightarrow[\text{Inert solvent}]{\text{Catalyst}_1} 2m\text{HCl}\uparrow + \text{ClC}\begin{matrix}\text{O}\\\parallel\end{matrix}\left[\text{OArOC}\begin{matrix}\text{O}\\\parallel\end{matrix}\right]_m\text{Cl} \quad (2)$$

$$n\text{ClC}\begin{matrix}\text{O}\\\parallel\end{matrix}\left[\text{OArOC}\begin{matrix}\text{O}\\\parallel\end{matrix}\right]_m\text{Cl} \xrightarrow[\text{Inert solvent}]{\text{Catalyst}_2} m\text{ClC}\begin{matrix}\text{O}\\\parallel\end{matrix}\left[\text{OArOC}\begin{matrix}\text{O}\\\parallel\end{matrix}\right]_n\text{Cl} + (n-m)[\text{COCl}_2] \quad (3)$$
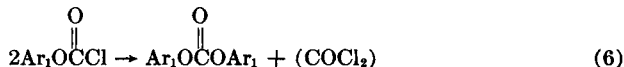
where $n \gg m$.

It can readily be seen that three different reactions are involved in these processes. They are: (1) the reaction of a phenol with phosgene to yield a chloroformate and hydrogen chloride:

$$\text{Ar}_1\text{OH} + \text{COCl}_2 \rightarrow \text{Ar}_1\text{O}\overset{\text{O}}{\overset{\parallel}{\text{C}}}\text{Cl} + \text{HCl} \qquad (4)$$
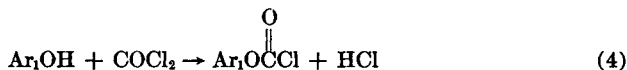
(2) the closely related reaction of a phenol with a chloroformate to yield a carbonate:

$$\text{Ar}_1\text{OH} + \text{Ar}_1\text{O}\overset{\text{O}}{\overset{\parallel}{\text{C}}}\text{Cl} \rightarrow \text{Ar}_1\text{O}\overset{\text{O}}{\overset{\parallel}{\text{C}}}\text{OAr}_1 + \text{HCl} \qquad (5)$$

and (3) the reaction of chloroformates to yield carbonates and the elements of phosgene:

$$2\text{Ar}_1\text{O}\overset{\text{O}}{\overset{\parallel}{\text{C}}}\text{Cl} \rightarrow \text{Ar}_1\text{O}\overset{\text{O}}{\overset{\parallel}{\text{C}}}\text{OAr}_1 + (\text{COCl}_2) \qquad (6)$$

Reactions (5) and (6) should be promoted by the same general classes of catalysts, whereas (7) might be predicted to require a different one. Catalysts, effective in promoting reactions (5) and (6) are the subject of this paper.

PRIOR ART

Aromatic hydroxyls are normally quite unreactive toward phosgene. Chloroformates and carbonates are not formed in significant yields in the absence of bases.[4] However, exceptions can be found in the literature. For example, Petersen[5] has reported the reaction of mixed xylenols with phosgene at 160–170°C., in the absence of catalysts, to give dixylyl carbonates in a 94% yield. Kempf[6] obtained diphenyl carbonate and phenyl chloroformate by heating phenol and phosgene in a sealed tube at 140–150°C.
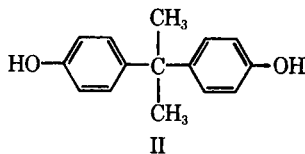
Catalysts for the reaction of phenol and phosgene have been described in the literature. Richter[7] has reported that aluminum chloride catalyzes the condensation of phenol and phosgene to give diphenyl carbonate. A patent[8] has claimed the preparation of diaryl carbonates by the reaction of phenol and phosgene in the presence of an amphoteric metal phenate between 150 and 250°C. The metals used were aluminum, titanium, iron, zinc, and tin. Lee[9] described the preparation of diaryl carbonates by the reaction of phenols and phosgene in the presence of tetramethylammonium halides.

The analogous reaction of phenols with carboxylic acid chlorides is also sluggish when catalysts are absent. Hill[10] reported that aluminum chloride and other metal halides are extremely efficient catalysts for the esterification of acidic alcohols, including 2,4,6-trichlorophenol, by acid chlorides. Magnesium has also been reported[11] to be an efficient catalyst for the esterification of phenols by acid chlorides.

A similar situation is encountered in the polymer field. While it is easy to prepare polyesters from aliphatic glycols and diacid chlorides by simple heating of the reactants,[12,13] much higher temperatures and longer reaction times are required for the preparation of phenolic polyesters[14,15] by an analogous thermal reaction. Finally Wagner[16] reported the use of catalytic amounts of organic bases (pyridine) and inert solvents (chlorobenzene) for the condensation of diacid chlorides with bisphenols to give polyesters.

EXPERIMENTAL

All work was carried out with 2,2-bis(p-hydroxyphenyl)propane (II), known generically as bisphenol-A.

II

Because phosgene is a gas, its direct use in condensation polymerizations is hampered by stoichiometry control problems. Therefore, the reaction of bisphenol-A with its dichloroformate was used for catalyst screening experiments.

Catalyzed Condensations of Bisphenol-A Dichloroformate

Materials. Bisphenol-A dichloroformate was recrystallized from *n*-hexane, m.p. 93–94°C.; bisphenol-A was recrystallized from toluene, m.p. 157–158°C. Solvents were distilled and dried over $MgSO_4$. Reference to the purity or origin of catalysts is made in the corresponding tables.

Procedure. A mixture of bisphenol-A, bisphenol-A dichloroformate, solvent, and catalyst was heated under reflux in a stream of dry argon or nitrogen. The course of the reaction was followed by observing the evolution of hydrogen chloride. Polymers were isolated by filtration of the cooled solution through a bed of filter aid (Celite), followed by coagulation in isopropanol.

Reduced Viscosities. All reduced viscosities (RV) were measured in methylene chloride at 25°C. and at a concentration of 0.2 g./100 ml.

Catalyzed Condensations of Bisphenol-A with Phosgene

Materials. Phosgene, 99+% purity, was from the Matheson Co.; bisphenol-A and solvents were as above.

Procedure A. A flask equipped with a gas inlet tube, a sealed stirrer, a thermometer, and a water-cooled reflux condenser surmounted by a condenser containing Dry Ice and acetone was charged with bisphenol-A, solvent, and catalyst. The reaction mixture was heated to the desired temperature, and addition of phosgene gas was started from a cylinder on a balance. The rate of phosgene addition was adjusted to permit slow refluxing of phosgene from the Dry Ice condenser. Hydrogen chloride gas which was evolved was absorbed in running water. When phosgene addition was complete, sparging with dry nitrogen was started and continued until no further hydrogen chloride could be detected. The solution was cooled, filtered (if necessary), and the polymer isolated by coagulation in isopropanol.

Procedure B. A solution of phosgene in the reaction solvent was prepared. The phosgene content was determined by reaction with an excess of methanolic potassium hydroxide followed by back-titration with nitric acid.*

The apparatus consisted of a five-necked flask equipped with a sealed stirrer, a thermometer, a gas-dispersion tube, a reflux condenser cooled by alcohol at about −15°C. and surmounted by a Dry Ice condenser, and a T-tube arranged to permit addition of both the phosgene solution and dry nitrogen. In the flask were placed the bisphenol-A, the catalyst, and the solvent. A slow stream of dry nitrogen was started through the gas-dispersion tube and continued throughout the experiment. The phosgene solution was then added in one portion, and stirring and heating were started. Evolution of hydrogen chloride began at about 60°C., but it became more rapid as depletion of phosgene allowed the reflux temperature

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* We are indebted to Mr. R. A. Wilhelm, formerly of these laboratories, for the development of this analytical method.

to rise, reaching a maximum in the range of 110–130°C. Heating under reflux was continued for several hours after the end of detectable hydrogen chloride evolution in order to insure completion of the reaction. The polymers were isolated as in procedure A.

Endgroup Analysis. The hydroxyl content of the product was determined by infrared analysis of the reaction mixture prior to coagulation.* An aliquot was used for determination of total solids and after removal of the solvent, of hydrolyzable (and sometimes total) chlorine.

Method B gave the more reproducible results and was used in most of the experiments. However, both methods were practically useful only with catalyst which gave relatively high reaction rates, i.e., complete reaction within about 9 hr. at temperatures below about 130°C. In prolonged runs in open systems only low polymers were obtained, presumably because of losses of phosgene. On the other hand, attempts to use higher initial reaction temperatures by operating under pressure resulted in the hydrogen chloride-catalyzed degradation[17] of bisphenol-A. Best results were obtained when hydrogen chloride was rapidly expelled by both boiling and sparging with inert gas.

RESULTS

System: Bisphenol-A and Bisphenol-A Dichloroformate

A catalyst was considered good if it afforded polymer with a reduced viscosity of 0.45 or above after a reasonable reaction time (12 hr. or less). The best catalyst studied was magnesium powder (Table I). The most satisfactory reaction solvent was o-dichlorobenzene; in chlorobenzene the reaction was quite slow, and the relatively low molecular weight obtained in 1,2,4-trichlorobenzene suggests some decomposition of the polymer. While the tabulated experiments all employed 100 mole-% of magnesium (based on either reactant), other runs indicated equivalent results with 5 or 1000 mole-% of this catalyst. This demonstrated the catalytic nature of the reaction.

Other catalysts studied included magnesium chloride, the double salt $MgCl_2 \cdot (CH_3)_4NCl$, manganese metal, aluminum chloride, aluminum isopropoxide, tin (IV) chloride, and zirconium (IV) chloride. Representative results obtained with these catalysts are given in Table II. With molybdenum (V) chloride, not listed in the table, extensive decomposition took place. It is clear that none of these substances was as effective as magnesium powder.

System: Bisphenol-A and Phosgene

The catalyst employed most frequently was aluminum chloride. The results are shown in Table III and in Figure 1.

* This method was developed by Mr. W. R. Utynok, formerly of these laboratories.

TABLE I

Reaction:　Bisphenol-A　+　Bisphenol-A　Dichloroformate, Catalyzed by Magnesium Powder[a,b,c]

Solvent and volume, ml.	Reaction temperature, °C.	Reaction time, hr.	Coagulated polymer		
			Color	RV	Yield, %
Chlorobenzene, 12.5	133	18	White	0.43	85
Chlorobenzene, 12.5	133	31	White	0.46	90
o-Dichlorobenzene, 12.5	180	7	White	0.50	94.4
o-Dichlorobenzene, 12.5	180	10	Slightly yellow	0.55	91.7
o-Dichlorobenzene, 25	180	10	White	0.61	97.2
1,2,4-Trichlorobenzene, 12.5	213	2.66	Yellow	0.46	90

[a] Reactants:　bisphenol-A　(0.0071　mole)　+　bisphenol-A　dichloroformate　(0.0071 mole) + magnesium powder (0.0071 mole) + solvent.

[b] Magnesium powder, 20 mesh, Matheson Coleman and Bell.

[c] No reaction was observed in the absence of catalyst [o-dichlorobenzene, reflux (~180°C.) 24 hr.].
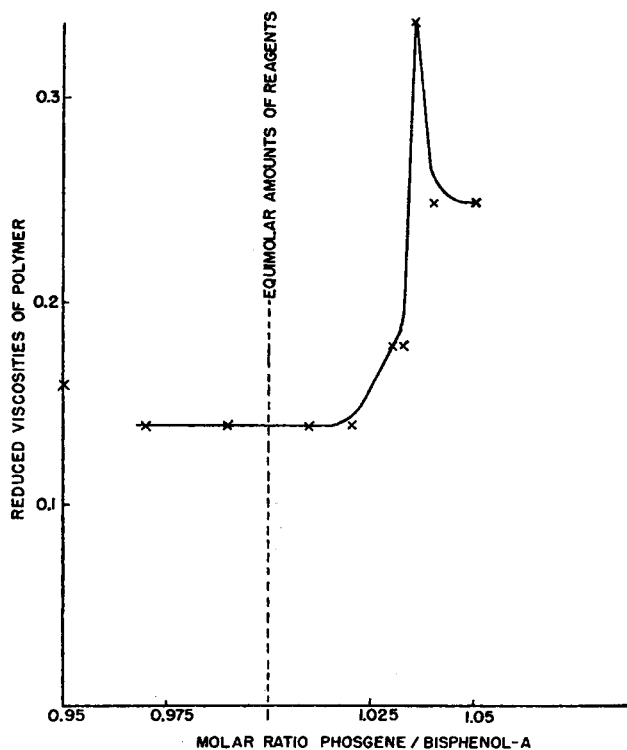

Fig. 1. Reduced viscosities of polymer obtained by phosgenation of bisphenol-A catalyzed by aluminum chloride (solvent:　chlorobenzene) vs. molar ratio phosgene/ bisphenol-A.

TABLE II

Reaction: Bisphenol-A + Bisphenol-A Dichloroformate(1:1) in the Presence of Miscellaneous Catalysts

Bisphenol A, moles	Solvent and volume, ml.	Catalyst and concn., mole-%	Reaction temperature, °C.	Reaction time, hr.	Coagulated polymer		
					Color	Yield, (%)	RV
0.0071	o-Dichlorobenzene, 12.5	$MgCl_2$, 15[a]	180	24	White	96	0.38
0.0071	o-Dichlorobenzene, 12.5	$MgCl_2$, 100[b]	180	10	White	94	0.40
0.0071	o-Dichlorobenzene, 12.5	$MgCl_2 \cdot (CH_3)_2NCl$, 15[c]	180	44	White	97	0.44
0.0071	1,2,4-Trichlorobenzene, 12.5	Manganese(100)[d]	213	17	Slightly yellow	84	0.44
0.0071	Chlorobenzene, 12.5	Aluminum iso-propoxide, 2[e]	133	24	White	92	0.24
0.01	Chlorobenzene, 75	$AlCl_3$, 5[e]	133	6	White	97	0.23
0.0071	Chlorobenzene, 12.5	$SnCl_4$, 10[e]	133	22.5	White	90	0.28
0.01	Chlorobenzene, 30	$ZrCl_4$, 5[e]	133	9.5	Slightly pink	90.5	0.25

[a] Anhydrous magnesium chloride, containing about 20% magnesium oxide, was prepared by fusion of $MgCl_2 \cdot 6H_2O$.

[b] Anhydrous magnesium chloride, containing about 5% magnesium oxide, obtained from Dow Chemical Company.

[c] Prepared by a published procedure[18] for the preparation of $MgCl_2 \cdot NH_4Cl$. Analysis: calcd. Cl, 52%; found: Cl, 50.7%.

[d] Fisher Scientific Company, certified reagents.

[e] Anhydrous reagent grade.

TABLE III

Phosgenation of Bisphenol-A Catalyzed by Aluminum Chloride[a]

Bisphenol-A concn.	Mole ratio (phosgene/ bis- phenol-A)	AlCl₃, mole-%	Coagulated polymer		OH end- groups, %	Chlorine, %	
			Yield, %	RV		Hydrolyz- able	Total
0.266 mole/488 ml.	0.95	1.9	82	0.16	1.1	—	—
0.257 mole/490 ml.	0.975	2.0	90	0.14	0.92	—	—
0.263 mole/490 ml.	0.99	1.9	90	0.14	0.84	0.15	0.27
0.264 mole/494 ml.	1.00	1.9	89	0.18	0.70	0.57	0.64
0.289 mole/494 ml.	1.01	1.7	87	0.14	0.40	—	—
0.270 mole/494 ml.	1.02	1.8	85	0.14	0.40	—	—
0.229 mole/490 ml.	1.03	2.0	86	0.18	0.56	0.14	0.54
0.225 mole/490 ml.	1.0325	2.0	93	0.18	0.48	—	—
0.310 mole/494 ml.	1.035	1.6	99.5	0.34	0.04	0.26	0.87
0.244 mole/490 ml.	1.04	1.95	91	0.25	0.35	—	—
0.258 mole/490 ml.	1.05	1.95	93	0.25	0.09	—	—
0.250 mole/490 ml.[b]	1.05	2.0	90	0.25	0.08	0.34	0.84

[a] The catalyst was anhydrous aluminum chloride, reagent grade. Phosgenations were conducted in chlorobenzene solution according to procedure B.

[b] This run was made to ascertain the reproducibility of the results.

The data show that hydroxyl- and chloroformate-terminated polycarbonates of relatively low molecular weight were easily prepared. Hence, the first step of the projected synthesis of the polymer was in principle accomplished.
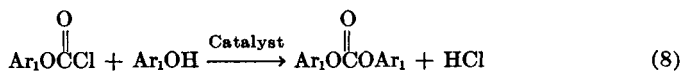
It is of interest to note the occurrence of a maximum in the molecular weight of polymer as a function of the molar phosgene/bisphenol-A ratio. The significance of this maximum will be discussed below.

Other catalysts were found less effective. Tetramethylammonium chloride (procedure A) afforded a low polymer (RV = 0.1). Similarly, low polymers were obtained with magnesium powder, magnesium chloride, and mixtures of magnesium chloride with quaternary ammonium salts (procedures A and B).

DISCUSSION

General

In order to transform a phenolic hydroxyl group to a carbonate linkage via reaction with phosgene, the sequence of reactions shown in eqs. (7) and (8) is involved:

$$Ar_1OH + COCl_2 \xrightarrow{\text{Catalyst}} Ar_1O\overset{O}{\overset{\|}{C}}Cl + HCl \qquad (7)$$

$$Ar_1O\overset{O}{\overset{\|}{C}}Cl + Ar_1OH \xrightarrow{\text{Catalyst}} Ar_1O\overset{O}{\overset{\|}{C}}OAr_1 + HCl \qquad (8)$$

The overall reaction is:
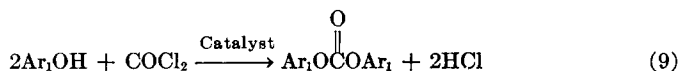
$$2Ar_1OH + COCl_2 \xrightarrow{\text{Catalyst}} Ar_1O\overset{\overset{\displaystyle O}{\|}}{C}OAr_1 + 2HCl \qquad (9)$$
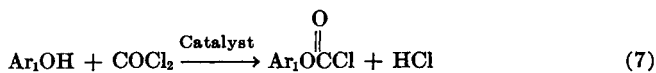
Both reactions (7) and (8) will presumably be promoted by the same type of catalyst. Phosgene is more reactive than a chloroformate. Therefore, depending on the experimental conditions, it might be possible to effect these reactions either stepwise or simultaneously. For instance, in the presence of a Lewis acid (aluminum chloride) the only product isolated was the carbonate. No chloroformate was obtained in reactions of phenol and phosgene carried out under the mildest conditions used (chlorobenzene at reflux, 133°C.). It was concluded that Lewis acids are highly effective in promoting the above-mentioned reactions.

Quaternary ammonium salts are much less powerful catalysts. In chlorobenzene, with a sufficient amount of phosgene, bisphenol dichloroformates are obtained in quantitative yields.[19] However, the use of more strenuous conditions can bring about the catalysis of both reactions. For example, diaryl carbonates are obtained from phenols and phosgene at ∼200°C. in the presence of these quaternary salts.[9]

Magnesium metal is an example of a catalyst with an intermediate activity. The reaction of phenol and phosgene in chlorobenzene solvent (133°C.) yields mainly carbonate, but some chloroformate[19] was also isolated. Furthermore, the present study has shown that in the presence of magnesium, the polycarbonate-forming reaction is slow in refluxing chlorobenzene; at higher temperature (o-dichlorobenzene, 180°C.), high molecular weight polymer resulted within a few hours (cf. Table I). Magnesium salts and manganese metal behave similarly. The use of manganese salts of carboxylic acid as intermediates in the preparation of phenolic esters has been described by Prasad et al.[20]

System: Bisphenol-A + Bisphenol-A Dichloroformate

As shown before, the best results were obtained with magnesium powder. High molecular weight polymers resulted reproducibly in these reactions. It was speculated that the magnesium cation might be the active catalytic species. Some support for this idea was furnished by the fact that examination of the magnesium at the end of the reaction showed that it was coated with a water-soluble chloride, presumably magnesium chloride. The idea was further supported by the fact that magnesium chloride was also found to give satisfactory catalysis.*

Much lower reaction rates were observed with the double salt $MgCl_2 \cdot$

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* The experiments with $MgCl_2$ did not yield polymers with molecular weights as high as those obtained with Mg metal. Presumably this was due to the presence of magnesium oxide (Table II, footnotes a and b) in the chloride used. Interaction of the oxide with the liberated hydrogen chloride would be expected to produce water. Separate experiments have shown that bisphenol-A polycarbonate undergoes serious degradation when heated under reflux with the above magnesium chloride and a trace of water.

(CH$_3$)$_4$NCl.   Manganese metal afforded a catalytic effect, but higher temperatures (~213°C.) were necessary to obtain high polymer.

The highest rates of reaction occurred with Lewis acids, i.e., aluminum chloride, aluminum isopropoxide, tin(IV) chloride, and zirconium (IV) chloride.   However, polymers with molecular weights in the useful range (RV $\geqslant$ 0.45) were not obtained; this behavior has been explained by the detection of a side reaction, as discussed in the following section.

System: Bisphenol-A + Phosgene

Polymers of the highest molecular weight were obtained by using a definite excess (ca. 3.5%) of phosgene (see Fig. 1).   Since the results were satisfactorily reproducible, it seems unlikely that they can be explained on the basis of poor control of phosgene addition.   Further, the hydroxyl content of the polymers (Table III) agreed with that expected from the nominal phosgene/bisphenol-A ratio.

Further confirmation was obtained in experiments involving bisphenol-A dichloroformate, in which no serious problem of stoichiometry control was encountered.   As indicated above, only polymers of relatively low molecular weight were obtained with aluminum chloride catalyst (Table IV),

TABLE IV

Reaction of Bisphenol-A + Bisphenol-A Dichloroformate in Chlorobenzene, Catalyzed by Aluminum Chloride

Amounts of reagents				Reaction temp., °C.	Reaction time, hr.	Coagulated polymer	
Bisphenol-A, moles	Bisphenol-A dichloroformate, moles	AlCl$_3$, mole-%	Solvent, ml.			Yield, %	RV
0.02	0.02	5	150	Reflux (133)	6	99.4	0.27
0.01	0.01	5	75	133	6	97	0.23
0.01	0.01032	3.2	40	133	12	99.5	0.32
0.005	0.0052	2.25	25	133	6	90.5	0.09

in spite of high reaction rates.   The highest molecular weight was obtained by using a slight excess of the chloroformate.   The possibility was considered that a Lewis acid-catalyzed degradation of bisphenol-A was responsible for this failure.   Consequently, several polymers were saponified by methanolic ammonia and the phenols analyzed by paper chromatography.   No phenol other than bisphenol-A was detected.*

It is believed that these results are best explained by reactions of phosgene and the intermediate chloroformate groups with the solvent.   Aromatic chloroformates are known to give Friedel-Crafts condensations.[21]   Such reactions would account for both (1) the occurrence of the maximum in the

* This method was developed by Mr. A. E. Barnabeo from these laboratories.

molecular weight, and (*2*) the fact that this maximum is displaced toward the region of excess phosgene.

Analysis of the total solids from the polymerization reactions showed that their total chlorine content was appreciably higher than their content of hydrolyzable chlorine (cf. Table III). The two should have been equal if there had been no interaction with solvent.

Furthermore, phenyl *p*-chlorobenzoate was isolated from the reaction of phenyl chloroformate with chlorobenzene in the presence of an excess of aluminum chloride.

$$C_6H_5OCOCl + \underset{}{\bigotimes}\!\!-Cl \xrightarrow{AlCl_3} C_6H_5OCO-\underset{}{\bigotimes}\!\!-Cl \qquad (10)$$
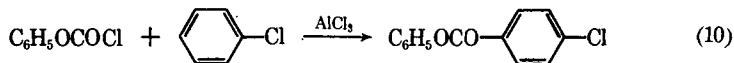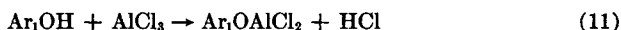
In an attempt to avoid this side reaction, a series of other solvents, including cyclohexanone, *o*-dichlorobenzene, mixtures of *o*-dichlorobenzene with *n*-hexane or *n*-heptane, and *s*-tetrachloroethane, was used.   However, none gave better results than chlorobenzene.

As stated before, a separate objective of the present work was the preparation of a low molecular weight, completely chloroformate-terminated polymer. These could be prepared very easily with aluminum chloride (chlorobenzene, 133°C.) by using large excesses of phosgene. No significant reaction with the solvent took place under these conditions; the prepolymers could be coupled to high molecular weight materials.[22]

Mechanism

Catalysis by Lewis acids may involve initial reaction with the phenol.

$$Ar_1OH + AlCl_3 \rightarrow Ar_1OAlCl_2 + HCl \qquad (11)$$

or with phosgene or a chloroformate

$$Ar_1O\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!-\!Cl + AlCl_3 \rightarrow \left[Ar_1O\!-\!\overset{\overset{\displaystyle O}{\|}}{C}{}^{(+)}AlCl_4{}^{(-)} \right] \qquad (12)$$

or

$$Ar_1O\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!-\!Cl + AlCl_3 \rightarrow \left[Ar_1OC\underset{Cl}{\overset{{}^{(+)}O-Al\overset{(-)}{Cl_3}}{<}} \right] \qquad (13)$$
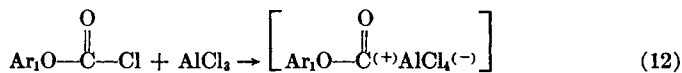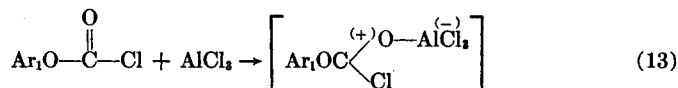
Formulation (13) is particularly attractive, since the pictured intermediate could coordinate with the phenol to form a second intermediate III:

$$
\begin{array}{c}
\overset{(-)}{OAlCl_3} \\
\diagup \\
Ar_1O\!-\!C \\
\ \ \ |\ \diagdown \\
\ \ \ |\ \ \ Cl \\
\ \ O^{(+)} \\
\diagup\ \diagdown \\
Ar_1\ \ \ \ H \\
III
\end{array}
$$

Collapse of III would form the carbonate and hydrogen chloride with regeneration of the catalyst. Similar intermediates were postulated by Hill[10] in his study of Lewis acid-catalyzed esterification of acidic alcohols and phenols by acid chlorides.

The mechanism of the magnesium catalysis is unknown. It should be pointed out that the magnesium-catalyzed reactions were purely heterogeneous: no trace of magnesium could be detected in the filtered reaction solutions. On the other hand, at the catalyst concentrations used, homogeneous systems were obtained with the Lewis acids. It is reasonable to assume that this difference contributes significantly to the observed difference in reaction rates.

CONCLUSIONS

The results of the present work, are summarized below. (*1*) A two-step, catalytic, anhydrous solution process was developed for the preparation of bisphenol-A polycarbonate:
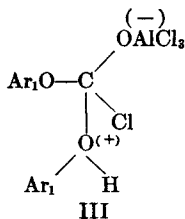
$$HO-C_6H_4-C(CH_3)_2-C_6H_4-OH + 2COCl_2 \xrightarrow[\text{Chlorobenzene, } 133^\circ \text{C.}]{(+)(-) \equiv N \, Cl}$$

$$2HCl\uparrow + ClCO-O-C_6H_4-C(CH_3)_2-C_6H_4-OCCl \qquad (14)$$

$$ClCO-O-C_6H_4-C(CH_3)_2-C_6H_4-OCCl \; + $$

$$HO-C_6H_4-C(CH_3)_2-C_6H_4-OH \xrightarrow[\text{o-Dichlorobenzene} \\ 180^\circ \text{C.}]{Mg}$$

$$2\,HCl\uparrow + \left[\begin{matrix} O \\ \| \\ C-O-C_6H_4-C(CH_3)_2-C_6H_4-O \end{matrix} \right]_n \qquad (15)$$

(*2*) The direct phosgenation of bisphenol-A in the presence of aluminum chloride afforded chloroformate-terminated prepolymers. The latter can be converted to high polymers by treatment with suitable catalysts.[22]

(3) Attempts to develop a one-step catalytic process for the synthesis of bisphenol-A polycarbonate failed, probably because of the lack of a suitable reaction solvent.

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Résumé

Un procédé catalytique, en deux étapes, utilisant un milieu anhydre, a été mis au point pour la préparation du polycarbonate du 2,2-bis(*p*-hydroxyphényl)propane (bisphénol-A). Il consiste en la préparation du dichloroformiate de ce bisphénol, suivi de sa condensation avec le bisphénol-A en présence du magnésium métallique. Des essais ont également été faits en vue du développement d'un procédé catalytique en une étape. La réaction entre le bisphénol-A et le phosgène en présence d'un catalyseur très énergique comme le chlorure d'aluminium a permis l'obtention de polymères possédant une viscosité réduite de 0.35. Des viscosités plus élevées n'ont pas été obtenues par suite de l'absence d'un solvant non-réactif convenable.

Zusammenfassung

Ein zweistufiges katalytisches Verfahren wurde zur Herstellung des Polycarbonats aus 2,2-Bis(*p*-hydroxyphenyl)propan (Bisphenol-A) in wasserfreier Lösung entwickelt. Es besteht in der Herstellung des Dichloroformates von Bisphenol-A und seiner darauffolgenden Kondensation mit Bisphenol-A in Gegenwart von metallischem Magnesium. Weiters wurden Versuche zur Entwicklung eines einstufigen katalytischen Lösungsverfahrens ausgeführt. Die Reaktion von Bisphenol-A mit Phosgen in Gegenwart von Aluminiumchlorid, einem sehr wirksamen Katalysator, ergab Polymere mit Viskositätszahlen bis zu 0.35. Höhere Viskositätszahlen konnten mangels eines brauchbaren inerten Lösungsmittels nicht erreicht werden.