

## Condensation Polymers by an Anhydrous Catalytic Solution Process

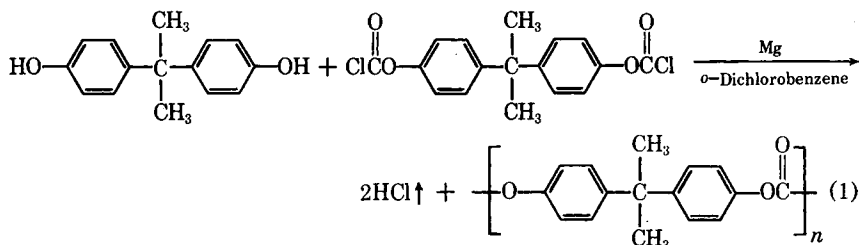
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### Synopsis

The preparation of high polymers by the anhydrous, magnesium-catalyzed reaction of an acid chloride with a compound possessing active hydrogen atoms, previously demonstrated in the specific case of bisphenol-A polycarbonate, has been shown to be applicable in a variety of systems. Polyesters, polyurethanes, poly(carbonate-urethanes), polyureas, and polyamides of high molecular weight were obtained in fair to excellent yields. This method is, therefore, a simple route to conventional types of polymers. In addition, it makes possible the preparation of polyurethanes derived from very weakly basic amines, such as *N,N'*-diarylarylenediamines. The latter cannot be incorporated into condensation polymers by any of the other presently known techniques.

### INTRODUCTION

In an earlier paper<sup>1</sup> it was shown that the magnesium-catalyzed reaction of bisphenol-A with the dichloroformate of bisphenol-A yields high molecular weight polycarbonate.



It was expected that similar techniques would prove useful in analogous systems involving the interaction of active halogen and hydrogen. The application of this magnesium-catalyzed solution process to the synthesis of polyesters, polyurethanes, and other condensation polymers is the subject of this paper.

### PRIOR ART

Polyesters derived from aliphatic glycols are readily obtainable by reaction of the latter with diacid chlorides;<sup>2,3</sup> no catalysts are necessary in

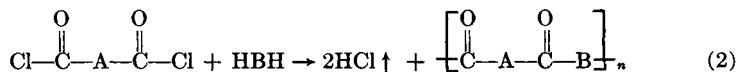
these syntheses, since high polymers result from simple heating of the reactants. The analogous reaction of a diphenol with a diacid chloride is sluggish and requires the application of high temperatures ( $>200^{\circ}\text{C}.$ ) in order to yield polymers of moderately high molecular weight.<sup>4-7</sup>

A few apparent exceptions to this rule have been noted. For example, Yamaguchi et al.<sup>8</sup> prepared a high molecular weight polyester by heating adipoyl chloride and hydroquinone in nitrobenzene solution at  $148^{\circ}\text{C}.$  Also, Volynkin and Braginskii<sup>9</sup> prepared a polyester by heating succinyl chloride with bisphenol-A in toluene, but neither the time of heating nor the molecular weight of the polymer was reported.

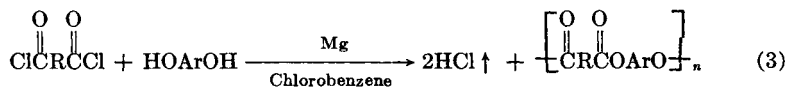
Several publications refer to the use of catalysts in the high temperature reaction of a diphenol with a diacid chloride. Tertiary bases have been reported<sup>10,11</sup> to be good catalysts. On the other hand, Korshak et al.<sup>12</sup> found magnesium metal and magnesium chloride completely ineffective in the subject reaction. However, high temperatures ( $>200^{\circ}\text{C}.$ ) were used by the Russian workers, and evidence from the present research indicates that high temperatures should be avoided with these catalysts to minimize degradation of the polymers.

A similar situation is encountered with the closely related aromatic polyesters of phosphonic acids. Although these polyesters can be prepared by a noncatalyzed condensation of the acid chloride with the dihydroxy compound,<sup>13</sup> magnesium, magnesium chloride, and several other compounds were claimed to be effective catalysts.<sup>14</sup>

The encouraging results obtained in earlier work<sup>1</sup> with the magnesium-catalyzed synthesis of aromatic polycarbonates prompted a study of the applicability of this catalysis to other polymer-forming reactions of the general type:



Contrary to the indications of Korshak et al.,<sup>12</sup> polyesters of high molecular weight were obtained under relatively mild conditions by the reaction:



The preparation of polyurethanes and polymers of several other classes according to eq. (2) was also successful.

## EXPERIMENTAL

The following two examples are representative.

### Preparation of the Polyester from Isophthaloyl Chloride and Bisphenol-A

**Materials.** Isophthaloyl chloride was recrystallized from petroleum ether, m.p.  $44-45^{\circ}\text{C}.$ ; bisphenol-A was recrystallized from toluene, m.p.

157–158°C.; chlorobenzene was distilled and dried over  $\text{MgSO}_4$ ; Mg powder, 20 mesh, from Matheson Coleman and Bell.

**Experiment.** A mixture of 2.03 g. (0.01 mole) of isophthaloyl chloride, 2.28 g. (0.01 mole) of bisphenol-A, 0.12 g. (0.005 mole) of Mg powder, and 25 ml. of chlorobenzene was heated under reflux, in a stream of dry nitrogen, for 8.5 hr. Rapid evolution of hydrogen chloride took place at the start of the heating period. The viscosity of the reaction mixture increased considerably during that time, and after 6 hr. polymer started to precipitate. Evolution of hydrogen chloride was complete at the end of the heating period.

The reaction mixture, which solidified on cooling, was dissolved with slight heating in 150 ml. of *s*-tetrachloroethane. The solution was filtered, and polymer was recovered from the filtrate by coagulation in approximately ten times its volume of isopropanol. A slightly yellow polyester was obtained. The yield was 97%, and the reduced viscosity (measured at 25°C. at a concentration of 0.2 g./100 ml. in *m*-cresol) was 0.65.

#### Preparation of a Polyurethane from Bisphenol-A Dichloroformate and 4,4'-Methylenebis(*N*-ethylaniline)

**Materials.** 4,4'-Methylenebis(*N*-ethylaniline) was prepared according to the method of Fedotova et al.,<sup>15</sup> b.p. 195°C./0.25 mm.,  $n_D^{25}$  1.6063; bisphenol-A dichloroformate was recrystallized from *n*-hexane, m.p. 94–95°C.; *s*-tetrachloroethane was distilled and dried over magnesium sulfate; magnesium powder, 20 mesh, was from Matheson Coleman and Bell.

**Experiment.** A mixture of 2.58 g. (0.0102 mole) of the diamine, 3.59 g. (0.0102 mole) of bisphenol-A dichloroformate, 0.06 g. (0.0025 mole) of magnesium powder, and 60 ml. of *s*-tetrachloroethane was heated under reflux, in a stream of dry nitrogen, for 3 hr. The evolution of hydrogen chloride was very rapid initially and appeared complete within 2.5 hr. The reaction mixture became very viscous and developed a green color. After cooling, it was diluted with 100 ml. of chloroform and filtered. The filtrate was coagulated in approximately ten times its volume of isopropanol. A practically colorless polyurethane was obtained in a yield of 98%. Its reduced viscosity (in chloroform) was 1.17. The infrared spectrum of this polymer (taken on a film) exhibited a strong absorption band at 5.8  $\mu$ , indicative of the urethane linkage.

Similar procedures were used for the preparation of all other polymers. In some instances the polymeric materials were isolated by evaporation of the solvent, instead of coagulation.

A slight modification, which proved advantageous in the preparation of certain polyurethanes derived from weakly basic amines, consisted of gradually adding a solution of the diamine to a boiling solution of the chloroformate containing the solid catalyst. Heating under reflux was continued until the evolution of hydrogen chloride ceased, and the reaction mixture was worked up as shown in the examples above.

It should be noted that the choice of solvent is a critical factor. The solvent must be inert under reaction conditions and should dissolve, or at least swell, the polymer formed. This is illustrated by a comparison of chlorobenzene and *s*-tetrachloroethane as solvents for the reaction of bisphenol-A dichloroformate with piperazine. In chlorobenzene, a poor solvent for the polyurethane, the product was obtained in a yield of only 27% and had a low molecular weight (reduced viscosity 0.11). In *s*-tetrachloroethane, a good solvent, the yield was 80%, and the reduced viscosity 0.54.

Some reactions were accompanied by the formation of variable amounts of gelled insoluble material. The cause of gel formation is unknown and probably involves a combination of factors. However, it is preferable to use an oil bath to minimize localized overheating on the walls of the reaction flask.

## RESULTS AND DISCUSSION

### Preparation of Polyesters

High molecular weight polyesters were easily prepared by the reaction of diacid chlorides with diphenols in equimolar amounts in the presence of magnesium powder. Chlorobenzene was the solvent of choice. The results are shown in Table I.

All the polyesters listed in Table I were previously known and prepared by classical methods.<sup>16-21</sup>

The effect of temperature on the reaction was briefly studied. When experiment 1 of Table I was repeated at a higher temperature (180°C.), only low polymer (reduced viscosity 0.12) was obtained. This result, presumably attributable to thermal and/or catalyzed degradation of the polymer, provides a reasonable explanation for the negative results of Korshak et al.<sup>12</sup>

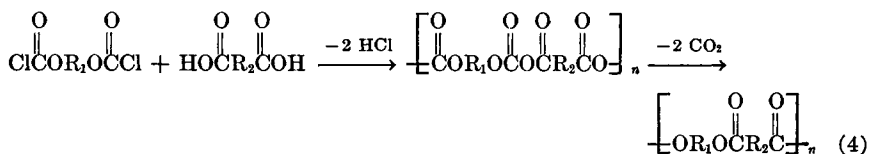
The reaction appears to be subject to steric hindrance. When a solution of 4,4'-dihydroxy-3,3',5,5'-tetrakis(*tert*-butyl)biphenyl and isophthaloyl chloride in chlorobenzene was heated under reflux in the presence of magnesium under the general conditions shown in Table I, practically no evolution of hydrogen chloride was observed. The greater part of the starting material was recovered unchanged.

Since the effectiveness of magnesium in catalyzing the reaction of phenols with chloroformates had been well established,<sup>1</sup> no serious efforts were made to compare rates of catalyzed and noncatalyzed reactions in the polyester series. However, a comparison of a typical magnesium-catalyzed experiment (Table I, run 1) with reported<sup>4</sup> noncatalytic experiments (Table I, runs 1A and 1B) shows that the difference in rates is substantial.

An alternate procedure was also developed for the preparation of polyesters. It consisted in reacting a dichloroformate with a dicarboxylic acid in an inert solvent, in the presence of magnesium. (Similar reactions in pyridine as reaction medium have been reported.)<sup>22</sup> The magnesium-

catalyzed reaction of bisphenol-A dichloroformate with isophthalic acid in *s*-tetrachloroethane gave the polyester, reduced viscosity (in *s*-tetrachloroethane) 0.36, in 96% yield. The structure of the product was established by comparison of its infrared spectrum with that of an authentic sample of poly(bisphenol-A isophthalate).

The reactions probably proceed via mixed carbonic-carboxylic anhydrides, as shown in eq. (4).



Extensive studies of these mixed anhydrides in recent years<sup>23-25</sup> have shown that they may, under some conditions, decompose in an alternate way, i.e., with formation of carboxylic anhydrides and carbonate esters. No evidence for products of this type was obtained in our experiments, however.

The use of a disulfonyl chloride in the magnesium-catalyzed reaction with diphenols was unsuccessful. No reaction was observed when 4,4'-biphenyldisulfonyl chloride was heated with bisphenol-A in the presence of magnesium in *s*-tetrachloroethane, *o*-dichlorobenzene, or 1,2,4-trichlorobenzene.

### Preparation of Polyurethanes

The successful preparation of polyesters prompted a study of the applicability of the magnesium-catalyzed solution process to systems in which the hydroxyl functions were replaced by amino groups. Primary diamines were only briefly investigated, since their polymers precipitated from the chlorinated hydrocarbon solvents at relatively low molecular weights and could be prepared more satisfactorily by standard methods. Secondary diamines, on the other hand, gave excellent results.

The preparation of the polyurethanes derived from bisphenols and various piperazines, some of which have been described by Wittbecker,<sup>26</sup> was successfully accomplished by the method of eq. (5). Results are shown in Table II.

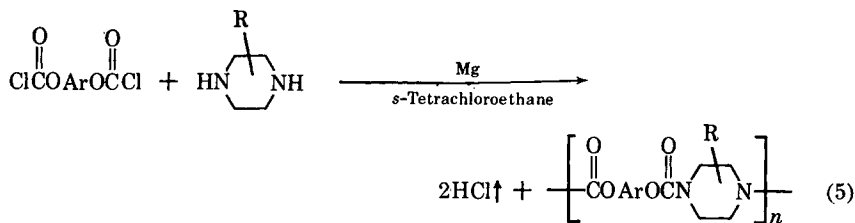
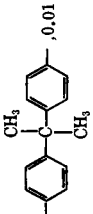

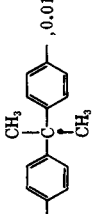

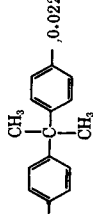

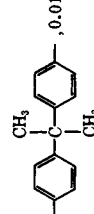
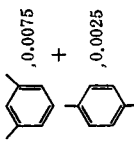
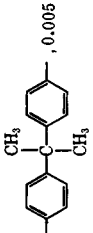
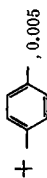

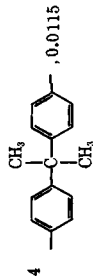
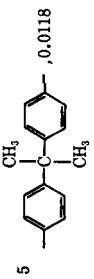
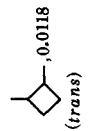
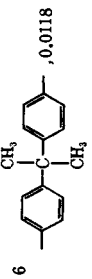
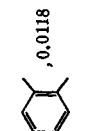


TABLE I  
Preparation of Polyesters by the Magnesium-Catalyzed Reaction of Diphenols (HOArOH) with Diacid Chlorides (Cl-C(=O)-R-C(=O)-Cl)

Run no.	Ar and amt., moles	R and amt., moles	Magnesium, mole-% <sup>a</sup>	Solvent and volume, ml.	Reaction time, hr.	Reaction temp., °C.	Polymer	
							Yield, %	RV
1	 ,0.01	 ,0.01	50	Chlorobenzene, 25	8.5	133	97	0.65 <sup>b</sup>
1A	 ,0.01	 ,0.01	None	Dinil, 25 <sup>c</sup>	8.5	150	d	d
1B	 ,0.022	 ,0.022	None	Dinil, 100 <sup>c</sup>	6 10	220 220	81 83	0.40 <sup>e</sup> 0.48 <sup>e</sup>
2	 ,0.01	 ,0.0075 + ,0.0025	50	Chlorobenzene, 25	8	133	98	0.59 <sup>f</sup>
3	 ,0.005 +  ,0.005	 ,0.01	50	Chlorobenzene, 25	20	133	70 <sup>g</sup>	0.62 <sup>h</sup>

4		,0.0115	$-(CH_2)_2-$ ,0.0115	20	Chlorobenzene, 20	17	133	85	0.41 <sup>i</sup>
5		,0.0118	 ( <i>trans</i> )	21	Chlorobenzene, 20	16	133	90	0.50 <sup>i</sup>
6		,0.0118		21	Toluene, 25	24	110	90	0.21 <sup>f</sup>

<sup>a</sup> Based on either reactant.

<sup>b</sup> In *m*-cresol.

<sup>c</sup> These results are due to Korshak et al.<sup>4</sup> The identity of "dinil" was not given by the authors.

<sup>d</sup> In text, ref. 4, the rate constant for this reaction in dinil at 150°C. is given as  $5.72 \times 10^{-3}$  l./mole-sec. From this, one can calculate that only about 41% of the acid chloride groups should have been consumed under the stated reaction conditions.

<sup>e</sup> In cresol; not otherwise qualified.<sup>4</sup>

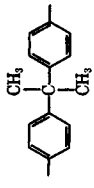

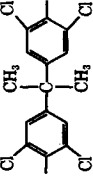

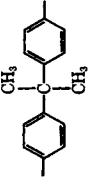

<sup>f</sup> In methylene chloride.

<sup>g</sup> Some insoluble gel also was formed.

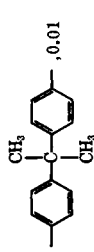
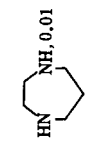
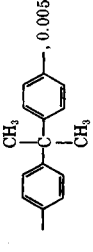
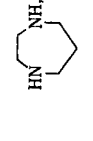
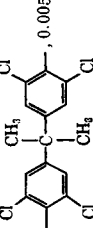

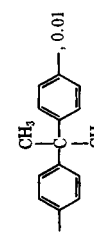
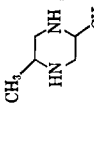
<sup>h</sup> In *s*-tetrachloroethane.

<sup>i</sup> In chloroform.

TABLE II  
Magnesium-Catalyzed Preparation of Polyurethanes from Bisphenol Dichloroformates (ClCOOArOCCl) and Piperazines<sup>a</sup>

Run no.	Ar and amt., moles	Diamine and amt., moles	Reaction time, hr.	Polymer	
				Yield, %	RV
1	 , 0.01	 , 0.01	20	80	0.54 <sup>b</sup>
2	 , 0.01	 , 0.01	24	90	0.51 <sup>b</sup>
3	 , 0.005	 , 0.01	24	80	0.41 <sup>b</sup>



4			18	83	0.29 <sup>b</sup>
5			18	80	0.33 <sup>b</sup>
6			24	70°	1.74 <sup>d</sup>
7			24	85	0.84 <sup>d</sup>

<sup>a</sup> The reactions were carried out in refluxing *s*-tetrachloroethane ( $\sim 146^\circ\text{C}$ ). The volume of solvent was 60 ml., except in run 1, where 30 ml. was used. The catalyst was magnesium powder (0.0025 mole).

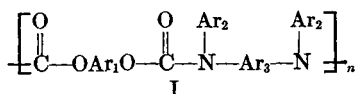
<sup>b</sup> In *m*-cresol.

<sup>c</sup> Some gel was also formed in this reaction.

<sup>d</sup> In chloroform.

When the reaction between piperazine and bisphenol-A dichloroformate (Table II, run 1) was repeated without magnesium, high polymer was obtained (reduced viscosity 0.50), but in only 48% yield. Hydrogen chloride was evolved very slowly. It is possible, therefore, that a major effect of the catalyst is to aid in the decomposition of amine hydrochlorides, but this point has not yet been investigated.

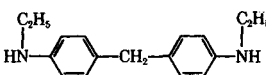
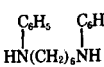
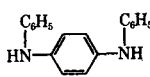
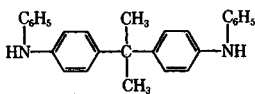
The catalytic method for polyurethane preparation was particularly useful in the case of weakly basic diamines. Four representative examples are shown in Table III. Polymers of high molecular weight were obtained not only with amines of the mixed alkyl-aryl type (runs 1 and 2), but also with the very weakly nucleophilic *N,N'*-diarylarylenediamines (runs 3 and 4). Since the latter fail to give polyurethanes by conventional methods, the anhydrous process permitted preparation of the previously unknown structures of type I:



The properties of several such polyurethanes have been studied and will be reported in a subsequent paper.<sup>27</sup>

The alternate preparation of a polyurethane from a diphenol and a dicarbonyl halide was demonstrated by the catalyzed reaction of bisphenol-A with 1,4-piperazinedicarbonyl chloride:

TABLE III  
Preparation of Polyurethanes from Weakly Basic Diamines<sup>a</sup>


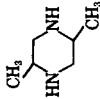
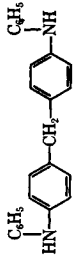
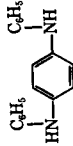
Run no.	Bis-phenol-A di-chloro-formate, moles	Diamine and amt., moles	Reaction time, hr.	Polymer		
				Yield, %	RV	
1	0.0102		0.0102	3	98	1.17 <sup>b</sup>
2	0.01		0.01	7	80	1.64 <sup>c</sup>
3	0.005		0.005	17	90	0.48 <sup>c</sup>
4	0.01		0.01	12	92	0.53 <sup>b</sup>

<sup>a</sup> The reactions were carried out in *s*-tetrachloroethane at the reflux temperature ( $\sim 146^\circ\text{C}$ ). The volume of solvent was 60 ml., except in run 3, in which 40 ml. was used. The catalyst was magnesium powder (25 mole-%, based on either reactant).

<sup>b</sup> In chloroform.

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

TABLE IV  
Preparation of Poly(carbonate-urethanes) by the Magnesium-Catalyzed Solution Process<sup>a</sup>

Run no.	Bisphenol-A, moles	Bisphenol-A dichloroformate, moles	Diamine and amt., moles	Reaction time, hr.	Yield, %	RV <sup>b</sup>	Polymer	
							N calc'd, %	N found, % <sup>c,d</sup>
1	0.005	0.0125		36	95	0.96	3.97	3.60
2	0.0075	0.0125	"	24	97	0.88	2.48	2.33
3	0.01	0.0125	"	36	91	1.05	1.17	1.10
4	0.0075	0.0125		34	93	0.59	2.42	2.35
5	0.01	0.0125	<i>trans</i> "	34	98	0.76	1.15	1.19
6	0.005	0.01		45	84	0.80	2.46	2.44
7	0.008	0.01	"	48	83	0.52	—	—
8	0.006	0.01		48	95	0.33	2.15	2.01
9	0.008	0.01	"	48	95	0.32	1.09	1.05

<sup>a</sup> Reactions were carried out in *s*-tetrachloroethane (60 ml.) at the reflux temperature ( $\sim 146^\circ\text{C}$ ). The catalyst was magnesium powder (25 mole-% based on the chloroformate).

<sup>b</sup> In chloroform.

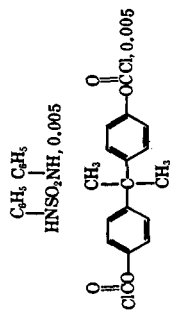
<sup>c</sup> Microanalyses by Galbraith Laboratories, Inc., Knoxville, Tenn.

<sup>d</sup> The infrared spectra of these polymers included characteristic carbonyl absorption bands at  $\sim 5.65 \mu$  (carbonate) and at  $\sim 5.85 \mu$  (urethane). The relative intensities of these bands were a function of the nitrogen content.

TABLE V  
Miscellaneous Applications of the Anhydrous Catalytic Solution Process<sup>a</sup>

Run no.	Reactants and amts., moles	Solvent and volume, ml.	Reaction time, hr.	Reaction temp., °C.	Polymer	
					Yield, %	RV
1	<p>HN(CH<sub>2</sub>)<sub>5</sub>NH, 0.005  <math>\text{C}_6\text{H}_4(\text{Cl})-\text{N}(\text{C}_6\text{H}_5)\text{C}(=\text{O})\text{NH}_2</math>, 0.005</p>	Anisole, 40	48	155 (reflux)	70	0.28 <sup>b</sup>
2	<p><math>\text{C}_6\text{H}_5\text{NH}-\text{C}_6\text{H}_4-\text{CH}_2-\text{C}_6\text{H}_4-\text{NH}_2</math>, 0.01  <math>\text{ClCO}-\text{C}_6\text{H}_4-\text{COCl}</math>, 0.01</p>	<i>s</i> -Tetrachloroethane, 60	21	~146 (reflux)	34	0.53 <sup>c</sup>
3	<p><math>\text{HO}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-\text{OH}</math>, 0.007  <math>\text{CH}_2\text{NH}_2-\text{C}_6\text{H}_4-\text{CH}_2\text{NH}_2</math>, 0.003  <math>\text{ClCO}-\text{C}_6\text{H}_4-\text{COCl}</math>, 0.01</p>	<i>s</i> -Tetrachloroethane, 60	18	"	70	0.23 <sup>d,e</sup>

4



s-Tetrachloroethane, 40

21

"

55

0.08°

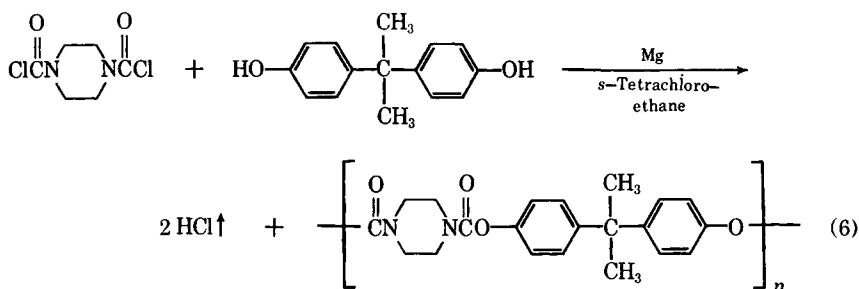
\* The catalyst was magnesium powder (25 mole-%, based on the acid chloride).

b In *m*-cresol.

c In chloroform.

d In *s*-tetrachloroethane.

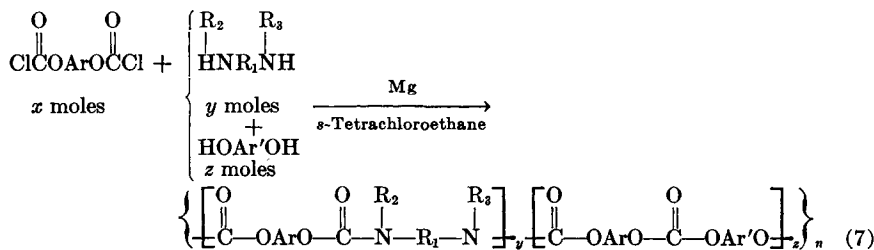
e Analysis (performed by Galbraith Laboratories, Inc., Knoxville, Tenn.): N calcd.: 2.54%; N found: 2.06%.



The reaction, which was sluggish, gave a 92% yield of a relatively low molecular weight polyurethane (reduced viscosity 0.30) after 48 hr. in refluxing *s*-tetrachloroethane. This result was not unexpected, since it is known<sup>28</sup> that carbamyl chlorides are less reactive toward nucleophiles than chloroformates.

### Poly(carbonate-urethanes)

Poly(carbonate-urethanes) have been studied in these and other laboratories.<sup>29-31</sup> A full account of their properties will be published shortly. One of the preparative methods by which they could be synthesized was the magnesium-catalyzed route [eq. (7)].



where  $x = y + z$ .

The results are listed in Table IV.

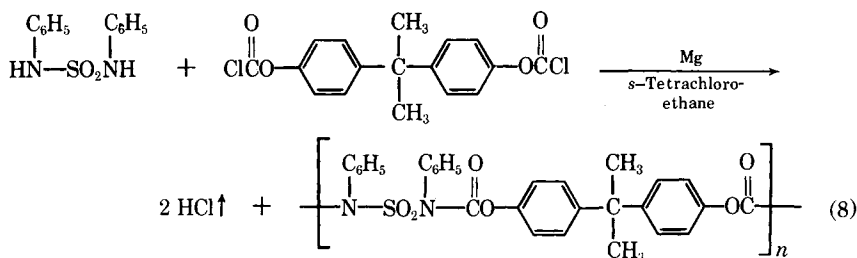
### Miscellaneous Applications

The application of the anhydrous catalytic solution process to other polymer systems was briefly explored. The experiments are listed in Table V.

A polyurea was prepared by condensing the dicarbamyl chloride of *N,N'*-diphenyl-*p*-phenylenediamine with piperazine (Table V, run 1). Only a moderate molecular weight polymer was obtained, presumably because of its limited solubility.

A polyamide of high molecular weight was made by condensing 4,4'-methylenebis(diphenylamine) and isophthaloyl chloride (run 2, Table V). On the other hand, the use of a primary diamine (*m*-xylylenediamine, run 3, Table V) in conjunction with bisphenol-A and isophthaloyl chloride led to a poly(ester-amide) of only moderate molecular weight, probably because of solubility problems.

The last example (run 4) of Table V is of interest.



The attempt to prepare a polymer by the reaction shown in eq. (8) was prompted by the success encountered in the preparation of polyurethanes from weakly basic diamines. It was considered possible that amides or sulfonamides, despite their weak nucleophilicity, might be used successfully in this type of reaction leading to new classes of polymers. Run 4 (Table V) afforded a low polymer (RV = 0.08), thus showing that the reaction might be applicable in this field. It is clear, however, that much more work is needed in this area before definite conclusions can be drawn.

### CONCLUSION

The applicability of an anhydrous, magnesium-catalyzed solution process to the synthesis of several classes of polymers has been demonstrated. Polyesters, polyurethanes, poly(carbonate-urethanes), polyureas, and polyamides can be prepared by this method, often more conveniently than by previously published procedures. The reaction is of particular value with weakly basic diamines, which react only sluggishly under conditions of classical preparative polymer chemistry; it thus provides a route to the previously unknown condensation polymers derived from *N,N'*-diarylarlylenediamines.

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### Résumé

La préparation de hauts polymères par réaction d'un chlorure acide avec un composé à hydrogène actif en milieu anhydre en présence de magnésium comme catalyseur a été décrite précédemment dans le cas particulier du polycarbonate de bisphénol-A; elle peut être également appliquée à divers systèmes. Ainsi, on a obtenu avec de bons rendements, parfois même d'excellents rendements, des polyesters, polyuréthanes, poly(carbonate-uréthanes), des polyurées et des polyamides. Cette méthode est donc une voie d'accès facile à l'obtention de polymères conventionnels. En outre, elle rend possible la préparation de polyéthers dérivés d'amines très faiblement basiques, telles les *N-N'*-diarylarylènediamines. Ces dernières ne peuvent pas être incorporées dans un polycondensat par aucune autre technique actuellement connue. Les propriétés des ces nouveaux polymères seront décrites dans une publication ultérieure.

### Zusammenfassung

Die früher für den speziellen Fall des Bisphenol-A-polykarbonats angegebene Darstellung von Hochpolymeren durch die wasserfreie magnesiumkatalysierte Reaktion eines Säurechlorids mit einer Verbindung mit aktiven Wasserstoffatomen ist in einer Vielfalt von Systemen anwendbar. Polyester, Polyurethane, Poly(karbonat-urethane), Polyharnstoffe und Polyamide mit hohem Molekulargewicht wurden in guter bis ausgezeichnete Ausbeute erhalten. Diese Methode bildet daher einen einfachen Weg zu konventionellen Polymertypen. Ausserdem ermöglicht sie die Darstellung von Polyurethanen, welche sich von sehr schwach basischen Aminen, wie *N,N'*-Diarylarylendiaminen, ableiten. Letztere können durch kein anderes gegenwärtig bekanntes Verfahren in Kondensationspolymere eingebaut werden. Die Eigenschaften dieser neuen Polymeren werden in einer späteren Veröffentlichung beschrieben werden.

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