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Mechanism of Catalyst Action in Interfacial Polycondensation of Chlorobisphenol and Isophthaloyl Chloride

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ABSTRACT

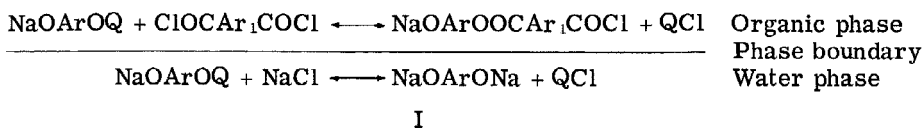
The mechanism of action of quaternary ammonium salt catalysts in the synthesis of aromatic polyesters was investigated. The possibility of formation of compounds of these salts and bisphenols and their extraction in the form of an ion pair into the organic phase was investigated. The structure of the compounds obtained was determined.

INTRODUCTION

This paper is a continuation of work on the synthesis and application of aromatic polyesters (polyarylates) obtained by the method of interfacial polycondensation [1-4]. Together with a paper dealing with the kinetics of this reaction [5], this is an attempt to explain the mechanism of the reaction.

The catalytic action of quaternary ammonium salts is well known and described for the synthesis of many polymers obtained in the inter-phase process. Investigations carried out by Morgan [6, 7], Eareckson [8], Kolesnikov and Fortunatov [9], Smirnova [10], and Schnell [11, 12] have dealt with polymers such as polyamides, polyesters, and polycarbonates. The reaction mechanism proposed by Morgan for the interfacial polycondensation of bisphenols and diacid chlorides seems especially interesting. It was formed by analogy to the mechanism developed by Starks [13] for the reaction of cyanides with alkyl chlorides. One of the intermediate steps in the mechanism is the formation of an ion pair QA (where Q designates the quaternary ammonium salt cation and A is the anion being transported across the phase boundary) which is extracted into the organic phase. A more precise description of this type of extraction may be found in a paper by Brandström [14].

The situation existing for polyarylates can be visualized as shown in I, where Ar and Ar₁ are aryl radicals and Q⁺ represents a quaternary ammonium salt cation.



EXPERIMENTAL

Materials

2,2-Bis(4-hydroxyphenyl)-1,1-dichloroethane (CBP II) was obtained as described in the literature [15]. Isophthaloyl chloride was obtained from Fluka AG and purified by vacuum distillation. Triethylamine was purified by distillation over zinc dust, bp 89-90°C. Tetra-n-butylammonium hydroxide (TBA) was obtained from BDH Chemicals Ltd.

Triethylbenzylammonium chloride (TEBA) was obtained from 12.6 g of benzyl chloride and 10 g of triethylamine. The crystals formed after 24 hr were filtered off, washed with a small amount of benzene, and dried at room temperature in a vacuum desiccator.

Synthesis of Tetraalkylammonium Chlorobisphenolates

The synthesis was carried out with a 0.17 N water solution of triethylbenzylammonium hydroxide and 40% aqueous solution of tetra-n-butylammonium hydroxide. The products were crystallized twice from

acetone. The reaction conditions are presented in Table 1. The obtained crystals were identified by using elementary analysis, infrared spectra, and NMR. The IR spectra were obtained on a UR-60 instrument (Carl Zeiss, Jena) by the KBr method. The NMR spectra were obtained by the field sweeping technique in deuterium acetone. The IR and NMR spectra of tetra-*n*-butylammonium and triethylbenzylammonium chlorobisphenolates are presented in Figs. 1-4. Table 2 presents the results of elementary analysis.

Extraction of Ion Pairs

Several extractions were carried out to test the possibility of transport of the bisphenolate anion from the aqueous phase to the organic phase. The composition of the aqueous phase and extraction conditions are presented in Table 3. The crystals obtained from the organic phase in trial 5 were crystallized from acetone and then identified. Figures 5 and 6 and Table 2 present the results of the analysis. The organic phase was tested each time for the presence of an ion pair by using IR spectroscopy.

The organic phase obtained in trial 7 was used in polymer synthesis. The organic phase after extraction was placed in a three-necked flask. A 5.85 g portion of isophthaloyl chloride dissolved in 60 ml of methylene chloride was dropped into the flask over 10 min, while the contents of the flask were vigorously stirred. The reaction was carried on for 2 hr at 18°C. The polymer thus obtained was separated by the method described in the patent literature [1]. The spectrum of this polymer is presented in Fig. 7.

RESULTS AND DISCUSSION

If Morgan's view that the catalysts acts as a transporter across the phase boundary is correct, then one may expect that: the ion pair formed by the exchange of the sodium cation for the tetraalkylammonium cation is stable, that extraction of this ion pair into the organic phase does occur, and that it is possible to conduct a synthesis of the polymer in homogeneous conditions, i. e., only in the organic solvent using a solution of the ion pair as a substrate.

Identification of the Obtained Compounds

Two compounds with a structure similar to that postulated in the mechanism were synthesized. These are tetra-*n*-butylammonium chlorobisphenolate (I), and triethylbenzylammonium chlorobisphenolate (II).

TABLE 1. Synthesis of Chlorobisphenolates

Compound	CBP II (g)	TBA (ml)	TEBAOH (ml)	Reaction temp (°C)	Mp (°C)
I Tetra-n-butylammonium chlorobisphenolate	2.2	17.5	-	65-70	152-154
II Triethylbenzylammonium chlorobisphenolate	1.5	-	60	50-55	142-144

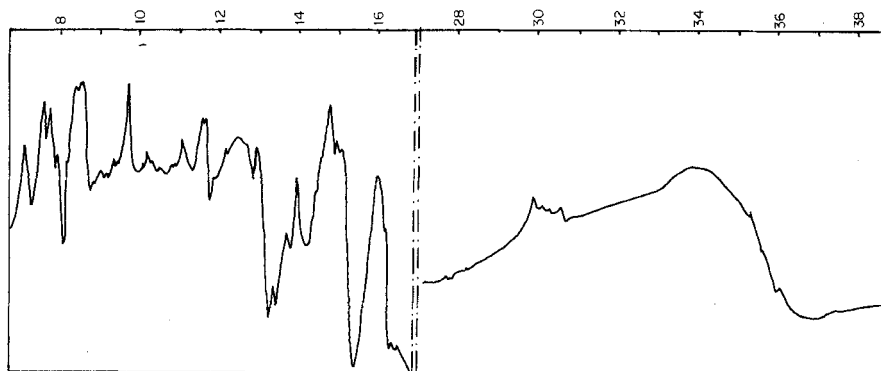


FIG. 1. IR spectrum of triethylbenzylammonium chlorobisphenolate.

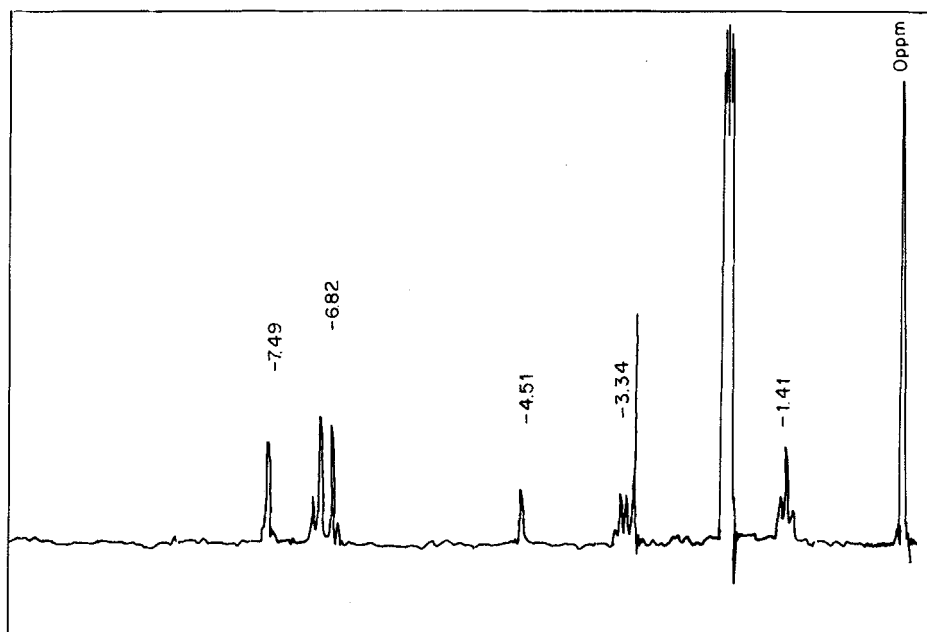


FIG. 2. NMR spectrum of triethylbenzylammonium chlorobisphenolate.

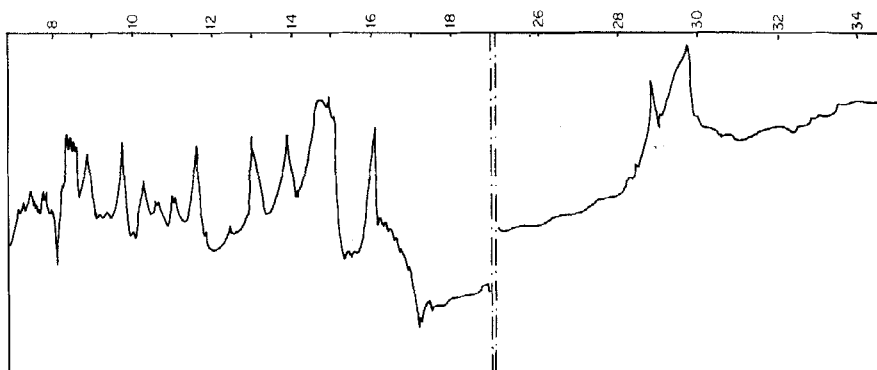


FIG. 3. IR spectrum of tetra-*n*-butylammonium chlorobisphenolate.

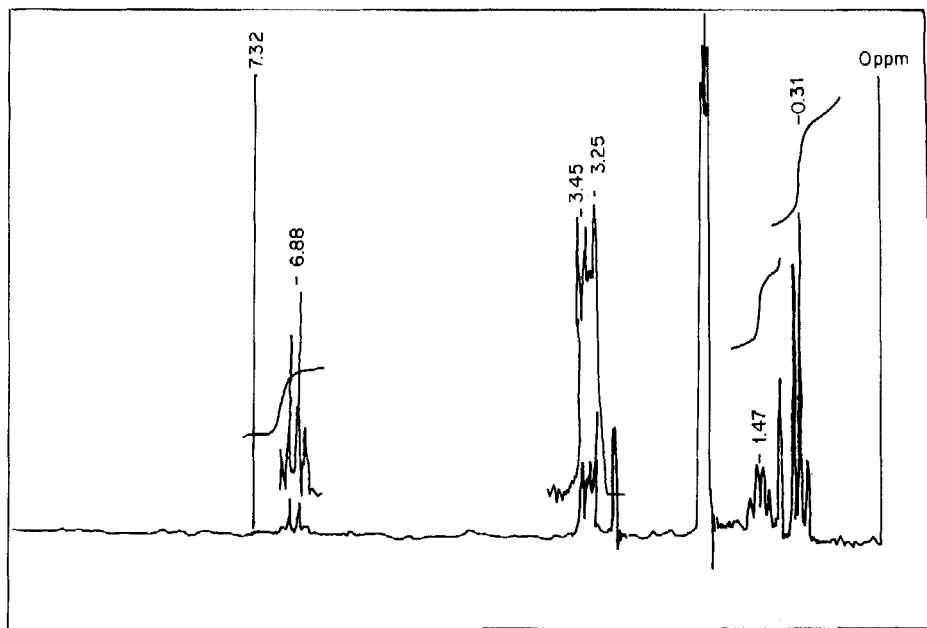


FIG. 4. NMR spectrum of tetra-*n*-butylammonium chlorobisphenolate.

MECHANISM OF CATALYST ACTION

TABLE 2. Elementary Analysis of Chlorobisphenolates

	Cl (%)	N (%)	H (%)	C (%)
I Tetra- <i>n</i> -butylammonium chlorobisphenolate	13.69	2.51	8.70	65.89
II Triethylbenzylammonium chlorobisphenolate	14.92	2.92	6.44	69.33
III Triethylbenzylammonium chloride	14.52	5.04	9.75	61.94

TABLE 3. Extraction of Chlorobisphenolates

Trial no.	CBP II (g)	NaOH (g)	TEBA (g)	TEBAOH (ml)	TBA (ml)	NaCl (g)	No. of extractions	Solvent	Volume of organic phase (ml)	Volume of aqueous phase (ml)	Temp (°C)	Time (sec)
1	5.62	2	0.23	-	-	-	1	CH ₂ Cl ₂	100	100	20	300
2	5.62	2	9.12	-	-	-	7	CH ₂ Cl ₂	100	100	20	300
3	5.62	2	9.12	-	-	-	15	CH ₂ Cl ₂	100	100	20	300
4	5.62	2	9.12	-	-	-	Cont. extract.	CH ₂ Cl ₂	600	1500	40	48 hr
5	5.62	2	9.12	-	-	16	5	CH ₂ Cl ₂	100	100	20	300
6	1.5	-	-	60	-	-	10	CH ₂ Cl ₂	60	60	20	300
7	4.5	-	-	-	30	-	2	CH ₂ Cl ₂	30	30	20	300

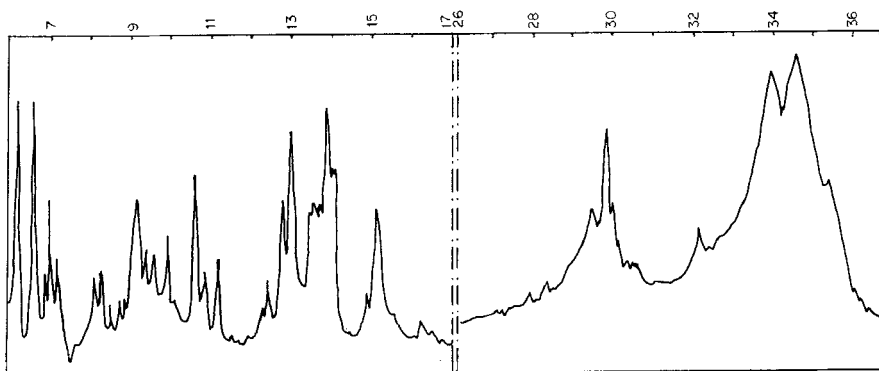


FIG. 5. IR spectrum of triethylbenzylammonium chloride.

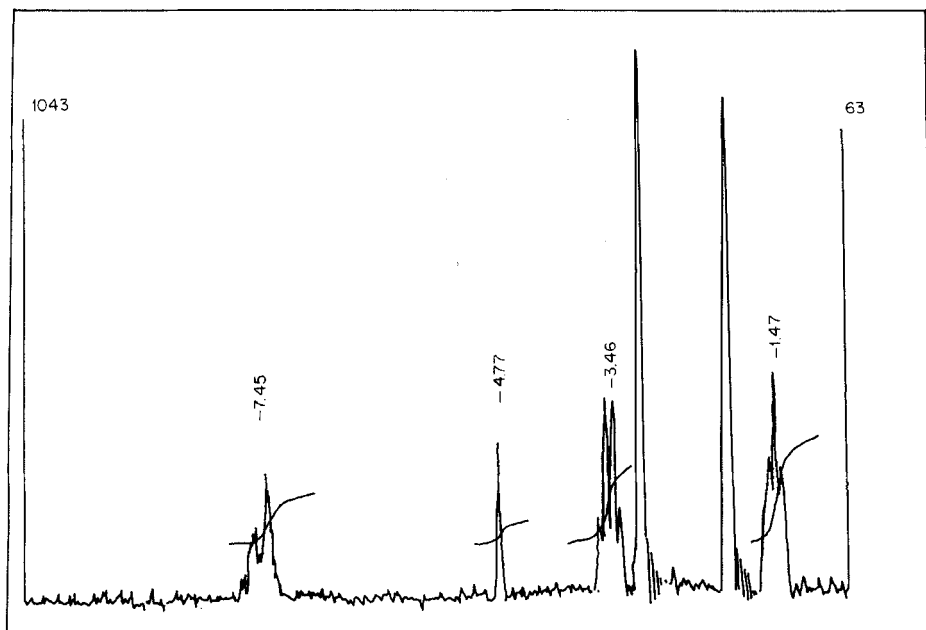


FIG. 6. NMR spectrum of triethylbenzylammonium chloride.

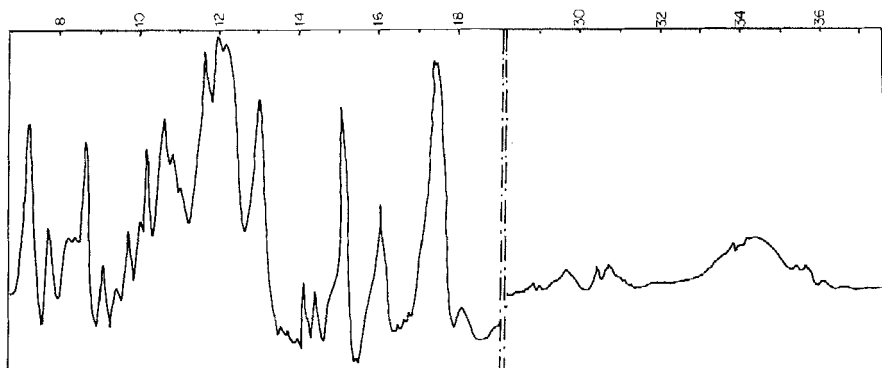
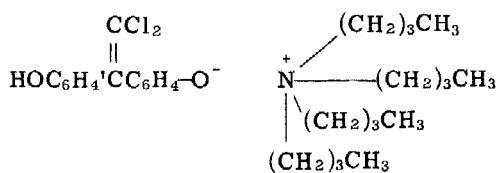
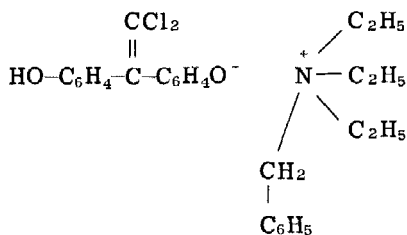


FIG. 7. IR spectrum of polyarylates.



II



III

The structure of both compounds was determined on the basis of their IR and NMR spectra. In the IR spectra of compounds I and II (Figs. 1 and 3) it is possible to find characteristic absorption peaks for chlorobisphenol atoms. Absorption at $840\text{--}850\text{ cm}^{-1}$ and $1495\text{--}1605\text{ cm}^{-1}$ corresponds to the aromatic ring. The band at 970 cm^{-1} may be assigned to the $=\text{C}\text{--}\text{Cl}$ bond [16]. Absorption in the range $1200\text{--}1250$ and 3400 cm^{-1} points to the presence of $\text{C}\text{--}\text{OH}$ bonds. Signals at $2900\text{--}3100\text{ cm}^{-1}$ correspond to aromatic and aliphatic

C-H bonds. In addition, a strong absorption band at $717\text{-}780\text{ cm}^{-1}$ indicative of a monosubstituted benzene ring appears in the IR spectrum of compound II. Additional information on the structure of both compounds can be found from the NMR spectra (Figs. 2 and 4). Identical triplets and quartets and similar values of δ indicate the presence of the CH_3CH_2 group. In the spectrum of compound I each signal of the quartet is additionally split into two components. The presence of multiplets in the range $\delta = 6.88\text{-}6.82$ ppm indicates a symmetrically substituted aromatic ring. In the spectrum of compound I there appear complicated multiplets at $\delta = 3.25$ ppm and 3.45 ppm, characteristic for the ABX type coupling appearing in the $\text{CH}_2\text{-CH-CH}_2\text{N}^+$ group. In the case of compound II there are signals corresponding to the isolated CH_2 group ($\delta = 4.77$ ppm) and the monosubstituted aromatic ring ($\delta = 7.45$ ppm). The absence of the signal from the hydroxyl proton in both spectra can be accounted for by the fact that deuterated solvents were used.

Transport of the Bisphenolate Anion

To test the possibility of bisphenolate dianion transport across the phase boundary, several trials of extraction were carried out. They were conducted in conditions quite different from those applied during polycondensation. The aqueous solutions were about 11 times as concentrated and the amount of TEBA used was stoichiometric. The organic phase (methylene chloride) did not contain isophthaloyl chloride. Trials 1-4 and 6 did not give the expected results. The IR spectra of the organic phases did not show any absorption in the investigated range. Addition of a large amount of sodium chloride to the aqueous phase (trial 5) produced crystals which were separated from the organic phase and analyzed (Table 2 and Figs. 5 and 6). On the basis of the obtained spectra it was determined, that the compound which had been extracted was triethylbenzylammonium chloride.

Substitution of the triethylbenzylammonium cation by the tetra-*n*-butylammonium cation (trial 7) resulted in the transport of the bisphenolate anion into the organic phase. The presence of the ion pair was determined on the basis of the IR spectrum of the solution, which turned out to be identical to the spectrum of the tetra-*n*-butylammonium chlorobisphenolate. The solution containing the extracted ion pair was used as a substrate and a polymer was obtained in homogeneous conditions. The spectrum of this polymer (Fig. 7) proved identical to the spectrum of the polymer obtained by the method of interfacial polycondensation.

CONCLUSIONS

These investigations prove that the exchange of the sodium cation for the tetraalkylammonium cation may take place, as the compounds obtained in such a manner are stable, were separated and identified.

When TEBA is used as a transporter (catalyst) across the phase boundary, transport of the bisphenolate anion into the organic phase does not occur.

Substitution of the TEBA cation by the more lipophilic tetra-*n*-butylammonium cation enabled extraction, and thus ensured concentration of bisphenolate anion in the organic phase was sufficient for the synthesis of a polymer.

The results of the investigations described in this paper are in agreement with the mechanism proposed by Morgan.

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