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Interfacial Synthesis Part I: Phase-Transfer Catalyzed Synthesis of Polyhydroxy Ether

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ABSTRACT

A convenient, rapid and efficient method for the synthesis of linear, moderate molecular weight polyhydroxy ethers has been developed. Based on the principle of "phase-transfer catalysis" the method involves the reaction of quaternized bis-phenate ion-pair with epichlorohydrin in aqueous alkali-dioxane system, at the reflux temperature of ≈ 86°C, using a quaternary ammonium salt as an effective reagent for the transportation of the bis-phenate-A ion to the organic phase in a highly reactive form. In contrast to several other processes where phase-transfer catalysts are involved, the present procedure appears to be truly catalytic with respect to quaternary ammonium salt. The successful use of polyethylene glycols (MW 300-14,000) as phase-transfer catalysts is also of great importance due to their low toxicity and relatively low cost. The role of phase-transfer catalysts in biphasic systems for preparative macromolecular systhesis has also been briefly outlined.

INTRODUCTION

The term "phase-transfer catalysis" (PTC) was coined by Starks [1] to describe reactions which are accelerated by small quantities of quaternary ammonium or phosphonium cations (Q^+) which are usually visualized as assisting in the transfer of one reactant across an interface [1,2]. Subsequently, macrocyclic crown ethers, cryptates, etc. (C) were used extensively for the same purpose [3-6]. Due to the extreme usefulness of PTC reactions in preparative organic chemistry, synthetic exploitation of PTC to effect reactions in biphasic systems has been recently surveyed [7-9].

A typical phase-transfer reaction is the cyanide displacement on 1-halooctane [1,4,10] (Fig. 1):
Here, the organic soluble Q^+ (or C) transports the anion from the aqueous phase to the organic phase. Moreover, linear or cyclic ethers serve the same purpose [4,10]. Starks and Owens [2] collected evidence that such processes occur in the organic phase and do not involve micelles. Arguments against micellar catalysis rested on the following factors: the observed linearity of reaction rate as a function of transfer agent concentrations in the organic phase, the consideration of the catalytic efficiency as a function of transfer agent aggregation in the organic phase, the effectiveness of the poor surfactants like tetradodecyl ammonium salts as catalysts and the ability of these salts to

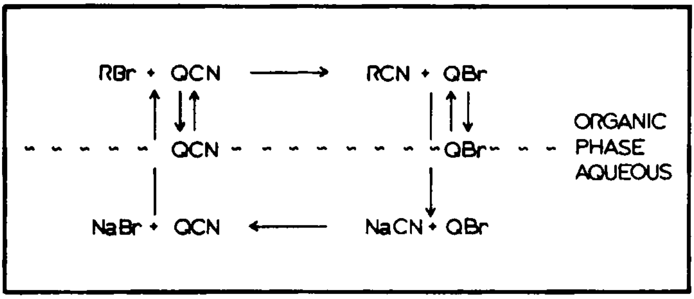


FIG. 1. Generalized Phase - Transfer Reaction Scheme.

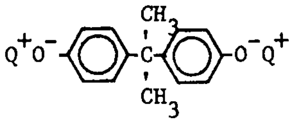
participate in the displacement reacitons at high rates even in non-polar media.

Phase transfer catalysis (PTC) could in principle offer several advantages over solution conducted nucleophilic displacement step-growth polymerizations. These would include the substitution of inexpensive solvents for anhydrous aprotic solvents such as DMSO, DMAC, etc., lower reaction temperature, and shorter reaction times. This process is, of course, strikingly analogous to what macromolecular chemists have called "Interfacial Polymerization" for some time [11-13].

Indeed, Morgan utilized tetraethylammoniumchloride effectively as an accelerator for the synthesis of poly(arylester) homopolymers [14] under typical interfacial conditions [12,13].

The utilization of quaternary ammonium or phosphonium salts (or any suitable PTC) for the polymer synthesis from bifunctional phenols can be viewed by considering the PTC cycle (Fig. 2) shown here.

Thus, it is logical to correlate the migrational mobility of the newly formed ion-pairs to and across the phase boundary with enhanced rate in these biphasic polymerization systems.



Both the lyophilic nature of the quaternary ammonium or phosphonium cations (or any PTC), the extractibility of the phenate ion by them and the polarity of the organic phase seems to have a significant influence on the catalytic effect. Moreover, the availability of the transported reagent in a highly reactive form will be more advantageous. Furthermore, a continuous cycle is allowed by the fact that the quaternary salt migrates back and forth across the interface, thus providing a certain neces-

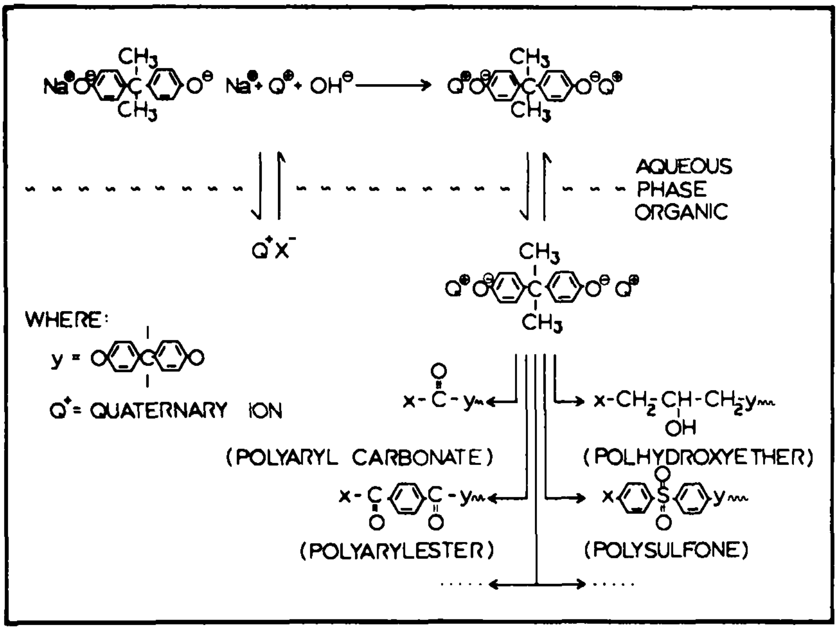


FIG. 2. Biphasic Reaction Scheme of Polymer Synthesis From Bifunctional Phenols.

sary concentration in each phase. Under these conditions the basic and essential requirements which are fulfilled are:
a) the PTC should be able to transport one reactant from its phase to the other reactant's phase; b) the transported reactant should be available in a highly reactive form; and c) the PTC should be recycled.

Thus, despite the apparent similarity of these PTC reactions and prior interfacial polymer syntheses, there may be significant mechanistic difference between them, and there may also be ample opportunities for new synthetic applications in preparative polymer chemistry. Mechanistically, in the former case, the locus of the polymerization may be considered to be more in the organic phase than at the interface.

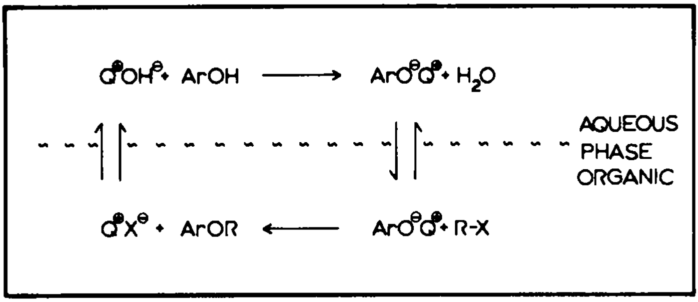
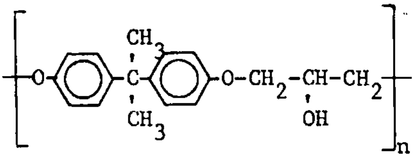


FIG. 3. Model Reaction Scheme For Hindered Phenols in Biphasic Medium.

Intriguing uses of PTC model ether syntheses have been given by Freedman et al [15] and McKillop et al [16]. In both cases the phenol is added as a solution in concentrated sodium hydroxide along with the quaternary ammonium salt and mixed with a methylene chloride solution of an alkylating agent. The phenol is converted into the corresponding quaternary ammonium phenoxide in the aqueous phase, which due to discrete solubility in the organic phase will migrate into the methylene chloride solution. The migration is followed by rapid alkylation and the formation of the phenol ether. Even highly hindered phenols gave high yields.

These model experiments [1,2,14-18] suggest a possible route for the preparation of high molecular weight polyhydroxyether or, even, poly(arylene ether sulfones) and their block copolymers under mild reaction conditions in the presence of a good PTC. The polymerization might proceed even without utilizing a dipolar aprotic solvent.

This paper will describe our preliminary results on the PTC synthesis of polyhydroxyethers (PHE).



Moreover, it will contrast the solution and interfacial processes and the role of PTC in macromolecular synthesis.

EXPERIMENTAL

2,2-bis(p-hydroxyphenyl) propane (Bisphenol-A) purified polymerization grade from Union Carbide Corporation was used. Epichlorohydrin was obtained from Aldrich Chemical Company and was distilled before use. All PTC's were pure grade commercial materials and were used without further purifications. Spectrograde dioxane and tetrahydrofuran were used as received.

A typical synthesis of bisphenol A derived polyhydroxyether by interfacial PTC polycondensation is given below.

To a 200 ml. three-necked flask equipped with a stirrer, thermometer and condenser is added 4.2 gm. (0.105 mol) of NaOH in 30 ml. of water followed by 11.415 gm. (0.05 mol) of bisphenol-A, 4.625 gm. (0.05 mol) of epichlorohydrin in 15 ml. of dioxane and 0.228 (0.001 mol) of benzyltriethylammonium chloride. The mixture is rapidly stirred and heated to reflux which occurs at a temperature of about 86°C. Heating is continued for six hours. The mixture is cooled. The aqueous phase separated by decantation and the organic phase diluted with 75 ml. of dioxane, or vice-versa. The organic rich phase is poured into about 100 times its volume of acidified cold water yielding a relatively solvent-free polymer in the form of shreds. The polymer is dried overnight in a vacuum oven at 50°C. Intrinsic viscosity [η] of the polymer in THF at 25°C typically is 0.24 dl/gm. The yield is 8.9 gm (≈55.5%).

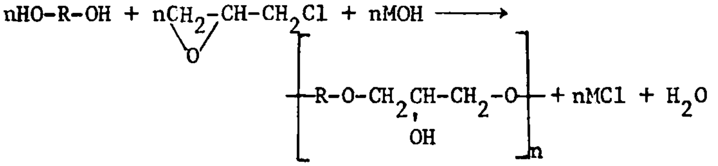
RESULTS AND DISCUSSIONS

Chemistry of Polyhydroxyether (PHE) Synthesis

Polyhydroxyethers (PHE) are the linear analogs of three-dimensional epoxy resin networks. They can be synthesized by the reaction of bifunctional phenols such as bisphenol-A with either (i) epichlorohydrin or, alternatively with (ii) its preformed monomeric diglycidyl ether using suitable basic catalysis [19, 20]. However, due to the complexity and commercial interest in these systems relatively little systematic details of the syntheses are available in the published literature.

These classes of polymer are different from the well known epoxy resins in two aspects: first, they are much higher in molecular weight, and, secondly, they do not contain any terminal epoxide functionality.

Theoretically, the equimolar amounts of bifunctional phenols, epihalohydrin and base should provide high molecular weight PHE as evident from the following equation (1).

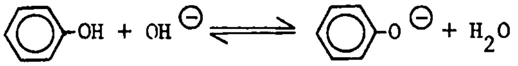


$$nHO\text{-}R\text{-}OH + nCH_2\text{-}CH\text{-}CH_2Cl + nMOH \longrightarrow \left[\text{-}R\text{-}O\text{-}CH_2\underset{OH}{CH}\text{-}CH_2\text{-}O\text{-} \right]_n + nMCl + H_2O \quad \ldots (1)$$

where R - any alkyl or, aryl unit

M - alkali metal

The reaction proceeds through the formation of both chlorohydrin (Eq. 3) and monoepoxy intermediates (Eq's. 6,8,9). The following reaction scheme provides an insight into the mechanistic aspects of PHE synthesis.



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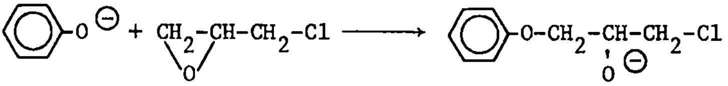

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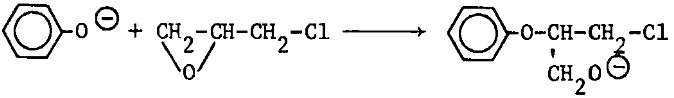

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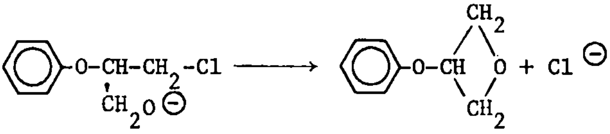

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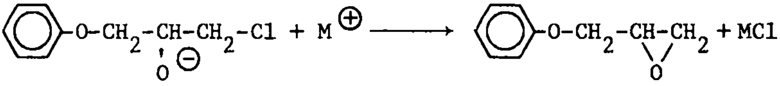

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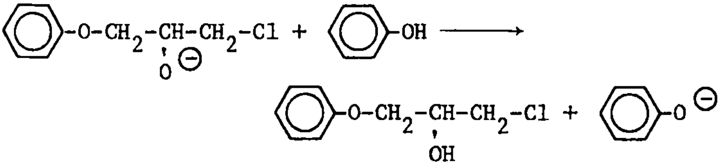

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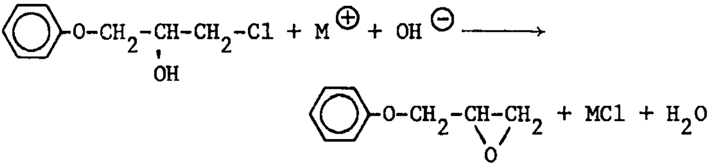

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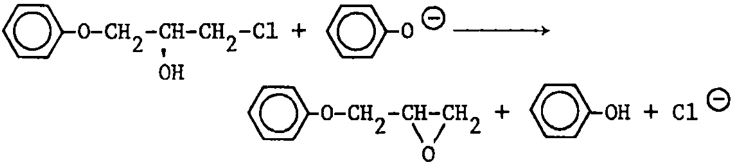

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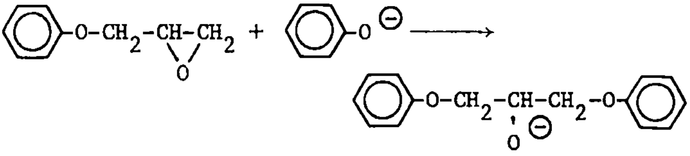

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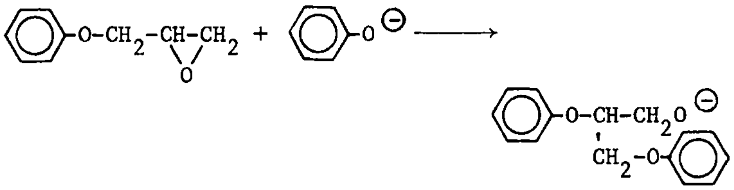

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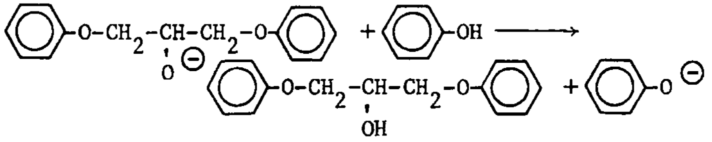
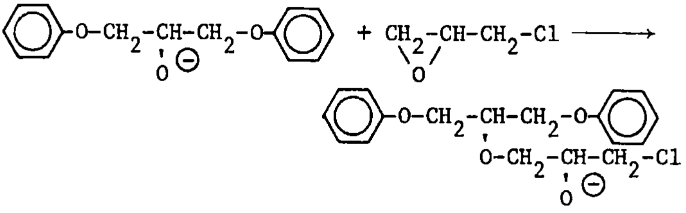


...(12)

The reactions [3,10] represent the "normal" addition of phenoxide anion to the least substituted carbon atom of the epoxide(oxirane) ring [21,22]. In contrast, the "abnormal" addition of the phenoxide anion to the most substituted carbon-atom of the oxirane ring[23-25] which may also occur will lead to the formation of either 1,3-chlorohydrin (Eq. 4) or 1,3-hydroxy ether (Eq. 11). The former will thus act as a chain-terminating step (Eq. 4), due to the relative inertness of 1,3-chlorohydrin to any further nuleophilic substitution. Moreover, subsequent ring closure of the same by dehydrohalogenation will result in the formation of a four-membered oxetane ring, which is also unreactive. However, it may be pointed out that unlike reaction (4) reaction (11) should not effect the polymer molecular weight.

Subsequent studies with model compounds [26] confirmed that there is a negligible amount of 1,3-chlorohydrin, formed. Formation of the intermediate monoglycidylether and the subsequent chain extension step are outlined in reactions (6-9) and (10) respectively.

One possible mode of branching which may occur in the presence of any unreacted epichlorohydrin is shown below.



...(13)

However, one should consider that for the base catalyzed reaction of diglycidylether of bisphenol-A and bisphenol-A, it has been shown that [27] as long as any phenolic groups is present, the epoxide will react with the phenolic functionality with the exclusion of any epoxide-(pendant secondary) alcohol reaction. This will certainly rule out any possibility of extensive branching, at least in the early stages of polymerization.

The alternative synthetic procedure is based on the reaction of diepoxides with equimolar quantities of dihydricphenols, in presence of a suitable base catalyst [28,29,30]. However, there is very little published literature describing the actual synthetic procedure. Nevertheless, several workers have studied the reaction of dihydricphenol with diepoxides [27,31,32] and pointed out that only a few selective catalysts can possibly lead to the formation of linear polyhydroxyether.

Table I summarizes the results of the synthesis of polyhydroxyether from bisphenol-A and epichlorohydrin (EPI) in presence of various phase-transfer catalysts. A comparison of several quaternary ammonium bromide salts bearing different alkyl groups indicates that as the length of the longest chain increases, the catalytic efficiency of the quaternary ion (Q^+) levels off. Even quaternary ammonium salts bearing lower alkyl groups such as $(C_2H_5)_4N^+$ act as an efficient catalyst. This is not surprising if one considers the fact that the polarity of dioxane allows it to be a good solvent for such small quaternary ions (Q^+) as $(C_2H_5)_4N^+$, $(C_3H_7)_4N^+$ etc. The polarity of this solvent is also

TABLE I. Interfacial Synthesis of Polyhydroxyether: with Various Phase-Transfer Catalyst

[Bisphenol-A] = [EPI] - 0.02 mole;
Solvent composition - H_2O (40)/dioxane (20);
Temperature = 86°C;
Time = 6 hrs.;
[C] - 0.02 mole per mole bisphenol-A;
[Base] - 3.00 mole per mole bisphenol-A.

CATALYST, C	BASE	$[n]^{THF}_{25°C}$	% Yield
$(C_2H_5)_4NBr$	NaOH	0.17	54.6
$[CH_3(CH_2)_3]_4NBr$	NaOH	0.17	49.2
$[CH_3(CH_2)_6]_4NBr$	NaOH	0.10	38.7
$[CH_3(CH_2)_3]_4PBr$	NaOH	0.12	47.5
DC-18-C-6	NaOH	0.14	38.7
$C_6H_5CH_2P(C_6H_5)_3(Cl)$	NaOH	0.12	47.5
$C_6H_5CH_2N(C_2H_5)_3(Cl)$	NaOH	0.25	47.5
$C_6H_5CH_2N(C_2H_5)_3(Cl)$	KOH*	0.34	70.0

*[C] - 2.55 mole per mole bisphenol-A

likely to affect the intrinsic reactivity of various Q^+ due to significant decreases in cation/anion interaction energy so that the exact choice of the catalyst structure may not be a very important factor in determining high reactivity [33]. In addition, the presence of concentrated alkali further influences the solubility so that even lower alkyl groups can often be used as the quaternary onium salt PTC's.

Contrary to literature reports, ammonium ions were found to be as effective as phosphonium ions bearing the same alkyl substituents. This may also relate to the fact that the polarity of the organic phase is of great importance in the present case.

Moreover, the presence of concentrated alkali can also considerably reduce the differences in the intrinsic reactivity of both tetraalkyl ammonium and phosphonium catalysts [7].

It may also be significant that the phosphonium cations have been reported to undergo a facile decomposition reaction around 50°C in the presence of hydroxide ion [34-37] and with strong sodium hydroxide (50% wt.) this decomposition occurs even at room temperature

$$R_4P^+OH^- \longrightarrow R_3PO + RH \qquad \ldots(19)$$

to give trialkyl phosphonium oxide which can not be recycled back to $R_4P^+X^-$. Clearly, the catalytic activity will be irreversibly lost under these conditions. Furthermore, this reaction is thought to be more rapid than the Hoffman elimination of the corresponding ammonium analog. In fact, the quaternary ammonium salts are stable in dilute sodium hydroxide (ca. 2-3M) around 80°C for 48 hrs. Thus, it is reasonable to assume that they will be fairly stable in the reaction conditions utilized for the present work. Thus, under strong alkaline conditions the quaternary ammonium salt should be the preferred catalyst over the corresponding phosphonium salt.

Surprisingly, benzyl triethyl ammonium ion was a very efficient catalyst compared to the several other PTC's which had been used, even considering a representative crown ether like dicyclohexyl-18-crown-6. In this context, it may be pointed out that for the synthesis of model phenolic ethers under typical PTC conditions, benzyl trialkyl ammonium ion was found to be very effective as PTC [34-37].

All these results strongly support the idea that the effectiveness of various PTC's must be related to the specific different system under investigation. The effectiveness will be governed for any individual system on the basis of several factors, some of which are given below:

- the polarity of the organic phase
- concentration of the inorganic salts in the aqueous phase
- the presence of solvating compounds for the particular anion
- reaction in presence of concentrated alkali
- solubility of the resulting macromolecule
- consideration of which step(s) are rate determining

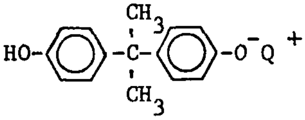
Here, one should also consider whether the rate determining step of the PTC cycle or sequence is in the organic phase reaction or in the phase-transfer step i.e., the PTC regeneration step. The latter will also be an important factor affecting the relative activities of catalysts having different structures.

Thus, one should be cautious about generalizations on the role of PTC in macromolecular synthesis, at least at the present level of understanding

We noted that a change from Na^+ to K^+ counterion for the bisphenate anion in the aqueous phase increased the polymer yield significantly and produced polymer having significantly higher intrinsic viscosity values. The result seems logical if we consider the probability of the presence of the anion as an ion-pair aggregate in relatively low-dielectric constant solvents like tetrahydrofuran or dioxane. In the case of small cations such as Na^+, these ion-pairs should be relatively "tight" (as compared to K^+ or Q_4N^+) and the electrostatic restraint will be considerably larger for the subsequent ether forming reaction. Thus, it should be desirable to utilize a loose ion-pair complex, where the positive charge will be spread over a large volume. This would decrease the electrostatic barrier to ether formation from $Li^+ > Na^+ > K^+ > Q_4N^+$.

A comparison of the cation radii shows only a moderate increase from tetramethyl to tetrabutyl ammonium cation $[(CH_3)_4N^+ < (C_2H_5)_4N^+ < (n\text{-}C_3H_7)_4N^+ < (n\text{-}C_4H_9)_4N^+ \approx 2.85 < 3.48 < 3.98 < 4.37Å]$ [38] and the calculated cation-anion interaction energies for the corresponding bromide salts $[Br^- = 1.95Å]$ [39] will be $3.1 < 2.8 < 2.5 < 2.4$ K Cal/mole respectively in dioxane ($\varepsilon = 2.2$). Thus, the relatively similar effectiveness of these quaternary ammonium salts as PTC is not at all surprising.

The base concentration seems to play an important role. Surprisingly, even less than a stoichiometric amount of base (< 2 mole of base per mole of bisphenol-A) yields a polymer of reasonable molecular weight. It is reasonable to presume that the presence of partially aqueous alkali soluble organic phase tends to increase the migration and the solubility of phenoxide



ion-pair and the reaction then proceeds through the formation of the monoepoxyintermediate. In fact, a base concentration in excess of 1 mole per mole of bisphenol-A is sufficient to yield a polymer (Table II).

Even the increased solubility of the phenoxide ion-pair in water, or better aqueous alkali - miscible solvent does not effectively enhance the rate of phenyl ether formation in the absence of any PTC (Table III). This is not surprising if one considers the fact that the rate of similar reactions in homogeneous systems (eg. dioxane) is higher by factor of 3×10^4 when the phenyl counter-ion is either quaternary ammonium or phosphonium than when it is an alkali metal (eg., $^{k}Bu_4N^+/^{k}K^+ = 3.3 \times 10^4$ for dioxane) [18]. A tenfold increase in the catalyst, $(C_2H_5)_4N^+Cl^-$, concentration from 1.79×10^{-3} moles to 1.79×10^{-2} moles does not affect the intrinsic viscosity of the resulting polymer.

TABLE II Interfacial Synthesis of Polyhydroxyether: Effect of Base Concentration

[Bisphenol-A] = [EPI] = 0.02 mole;
[$C_6H_5CH_2N(C_2H_5)_3(Cl)$ - 0.0004 mole;
Solvent - H_2O (40)/Dioxane (20);
Temperature - 86°C;
Time - 6 hrs.

[BASE] Per Mole Bisphenol-A	$[\eta]^{THF}_{25°C}$	% Yield
KOH		
2.55	0.34	70%
2.00	0.28	76%
1.70	0.30	82%
1.40	0.20	93%
0.85	Sticky Paste	---
NaOH		
2.1	0.24	55.5%
1.1	0.14	50.0%

TABLE III Interfacial Synthesis of Polyhydroxyether: Effect of Catalyst Concentration

[Bisphenol-A] - 0.050 mole; [EPI] - 0.050 mole;
[NaOH] - 0.1575 mole; H_2O/Dioxane - 120 ml./50 ml.;
Temperature - 86°C; Time - 6 hrs.

$[(C_2H_5)_4NCl]$	$[\eta]^{THF}_{25°C}$
CONTROL	----
0.00179 mole	0.15
0.0179 mole	0.15

Even a fraction mole percent of PTC effectively provides a certain concentration of the phenate ion-pair in the organic phase for rapid consumption. This will permit an efficient recycling of PTC for the continuous interfacial process, provided that sufficient base is present in the aqueous layer to regenerate the quaternary ammonium hydroxide from the halide which is formed in the course of reaction. The role of PTC here seems to be truly catalytic as theoretically envisaged for a typical PTC reaction.

Stoichiometric reactant balance seems to be necessary but the effect here is less pronounced than that usually observed in several other systems. (Table IV).

As long as the polymer remains soluble or at least well dispersed, solvent composition was not observed to affect the intrinsic viscosity, [η], of the resulting polymer (Table V).

Figure 4 shows the course of reaction in terms of the intrinsic viscosity of the polymer. These results indicate that the polymerization reaction is essentially complete in 6 hrs.

TABLE IV Interfacial Synthesis of Polyhydroxyether: Effect of Stoichiometry

$[C_6H_5CH_2N(C_2H_5)_3(Cl)]$ - 0.02 mole/mole Bisphenol-A;
[KOH] - 2.55 mole/mole Bisphenol-A; [Bisphenol-A] - 0.02 mole;
Solvent - H_2O (40)/Dioxane (20);
Temperature - 86°C; Time - 6 hrs.

Epichlorohydrin	$[\eta]^{THF}_{25°C}$	% Yield
100% (Theory)	0.34	70.0%
99% (Theory)	0.24	70.4%
101% (Theory)	0.22	68.66%

TABLE V Interfacial Synthesis of Polyhydroxyether: Effect of Solvent Composition

[Bisphenol-A] = [EPI] - 0.04 mole; [NaOH] - 0.084 mole; $[C_6H_5CH_2N(C_2H_5)_3(Cl)]$ - 0.0008 mole; temp - 85-87°C; Time - 6 hrs.

H_2O (ml.)	Dioxane (ml.)	$[n]^{THF}_{25°C}$	% Yield
60	60	0.24	70.0
80	80	0.24	70.4
80	60	0.24	72.0
80	40	0.25	72.3
40	40	0.25	71.8

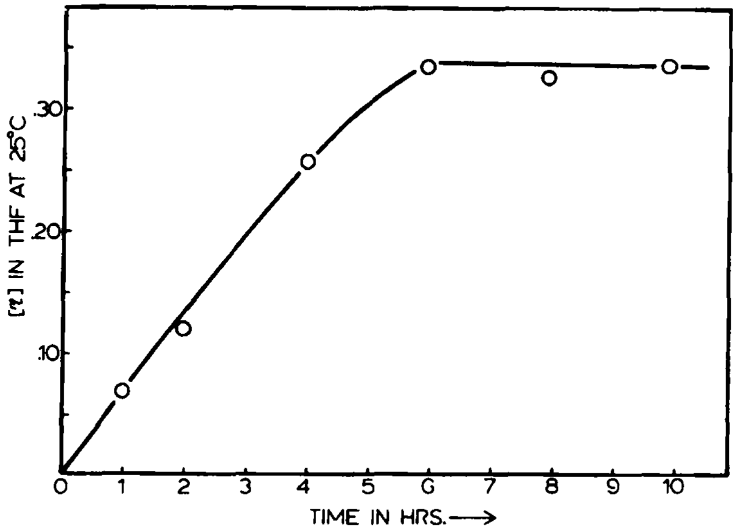


FIG. 4. Effect of Reaction Time on the Course of Interfacial Polymerization of Polyhydroxyether. [Bisphenol-A] = [EPI] - 0.02 mole, $[C_6H_5CH_2N(C_2H_5)_3(Cl)]$ - 0.0004 mole, H_2O (40)/Dioxane (20), Temperature - 86°C, [KOH] - 0.051 mole.

However, much more investigation of the parameters influencing molecular weight is required.

Polyethylene glycol (MW 300-14,000) was found to be an effective PTC for polyhydroxyether synthesis in the biphasic system. (Table VI). The successful use of linear polyethers are particularly of great interest due to their low toxicity and relatively low cost. Essentially, there is only one other report on the successful use of PEG as PTC in interfacial polymer synthesis [40]. The molecular weight of PEG has no significant effect both on the percentage yield and the intrinsic viscosity of the polyhydroxyether. It seems that in the presence of partially aqueous-alkali soluble organic phase, the intrinsic reactivity of these PTC's is similar for all practical purposes.

Unimodel distribution of the Gel-Permeation Chromatography curve of PTC interfacially prepared PHE is in line with our other unpublished interfacial work (Figure 5).

TABLE VI Interfacial Synthesis of Polyhydroxyether: Polyethyleneglycol (PEG) as Phase Transfer Catalyst

[Bisphenol-A] = [EPI] - 0.02 mole;
[KOH] - 0.051 mole;
H_2O (40) - Dioxane (20);
Temperature - 86°C;
Time - 6 hrs.

PEG (2.25 gm.)	$[\eta]^{THF}_{25°C}$	% Yield
MW - 300	0.22	61
MW - 1,000	0.175	64
MW - 1,540	0.23	56
MW - 4,000	0.19	64
MW - 14,000	0.22	64

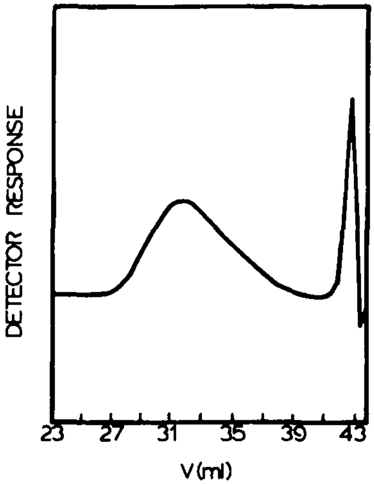


FIG. 5. G.P.C. Curve of an Interfacially Prepared Polyhydroxyether

It will be appropriate here to comment on our related work on quaternary ammonium hydroxide catalyzed synthesis of PHE in an homogeneous medium (dioxane) from bisphenol-A and diglycidyl-ether of bisphenol-A and the commercially available Phenoxy Resin (Union Carbide) of medium molecular weight (Table VII). PHE of comparable intrinsic viscosity can be prepared by PTC synthesis in a biphasic system within a shorter time and at a compara-

TABLE VII Synthesis of Polyhydroxyether: Interfacial and Solution Dioxane Methods

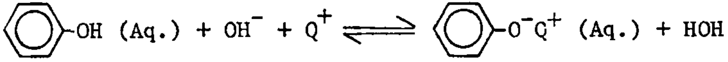
Catalyst	Phase	Temp.	Time	$[\eta]^{THF}_{25^\circ C}$
$C_6H_5CH_2N(C_2H_5)_3OH$	Single	≈ 100°C	72 hrs.	0.42
$C_6H_5CH_2N(C_2H_5)_3(Cl)$	Biphasic	≈ 86°C	6 hrs.	0.34
NaOH*	--------	-------	-------	0.43

* Phenoxy Resin (U.C.C.)

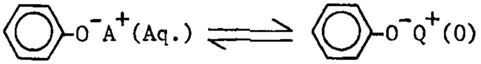
tively lower reaction temperature, which certainly should reduce the possiblity of branched polymer formation. Furthermore, in-depth studies pertaining this system may provide us also a convenient method for PTC synthesis of linear high-molecular weight polyhydroxyether.

Mechanistic Aspects

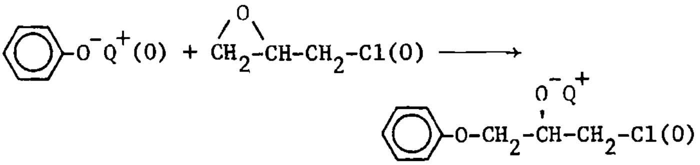
Equations (15-23) represents the essential reaction sequences for PTC bisphenol-A - epichlorohydrin reaction in a biphasic system. In the presence of an alkali metal hydroxide and a suitable PTC, bisphenol-A (represented for convenience as a model phenol) will quantitatively form the quaternary ammonium ion pair (Eq. 15).

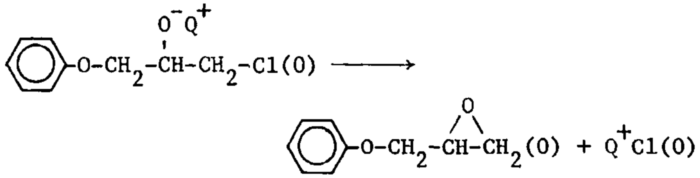

...(15)

Due to its better solubility in the organic phase, the latter will then migrate preferentially into the organic phase (eq. 16).


...(16)

and react with epichlorohydrin to form the intermediates chlorohydrin (eq. 17) and monoepoxide (eq. 18).

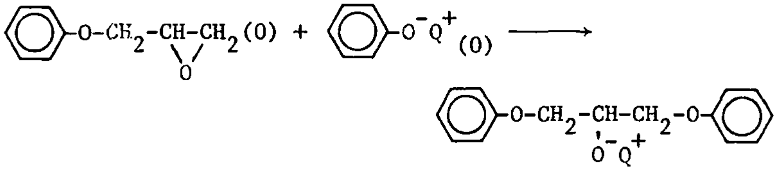

...(17)

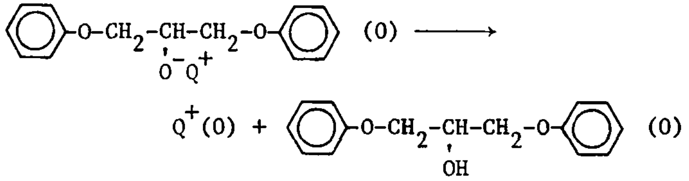

...(18)

the regenerated quaternary salt will be recycled back to the aqueous phase (eq. 19).

$$Q^{+}Cl^{-}(O) \rightleftharpoons Q^{+}Cl^{-}(Aq.) \qquad ...(19)$$

The monoepoxide can further react with quaternary ammonium phenoxide ion-pair to provide the necessary chain extension (eq. 20, 21).

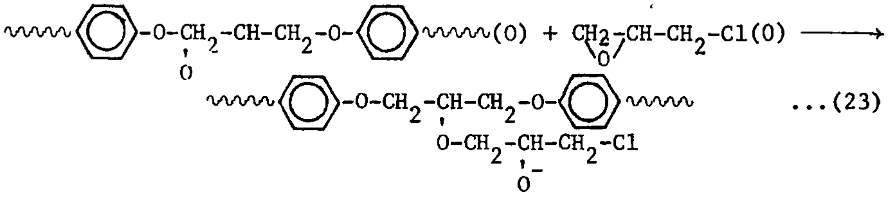

...(20)


...(21)

The quaternary cation will then partition itself between the aqueous and organic phase (eq. 22), the relative position depending upon the characteristics of the particular system in question.

$$Q^+(0) \rightleftharpoons Q^+(Aq.) \quad ...(22)$$

The relatively fast alkylation step (eq. 17) under these mild conditions will ensure that the chain-branching reaction (eq. 23) is at an absolute minimum.


...(23)

Catalysis by micellar [41] and reverse micellar systems [41, 42] are known not to be decisive for the course of reaction in the presence of concentrated alkali. Besides, in the present case quaternary compounds bearing a symmetrical structure and also having small substitutents e.g., small quaternary salts like $(C_2H_5)_4N^+Br^-$, are poor surfactants, but still behaved as good phase transfer catalysts. Similar reactions carried out in the presence of a good surfactant such a sodium lauryl sulfate demonstrated no significant effect on the intrinsic viscosity of the polymer. Considering these factors, no attempt has been made at the moment to consider the micelle-catalyzed reaction mechanism. However, it will be interesting to examine the role of both the large quaternary salts e.g. $(C_{12}H_{25})_4\overset{+}{N}\overset{-}{X}$, which are poor surfactants but are known to be good phase-transfer catalysts along with good surfactants such as $C_{16}H_{33}\overset{+}{N}(CH_3)_3\overset{-}{X}$, which are not always good phase-transfer agents. Furthermore, attempts are being made to utilize a water-immicible solvent by itself or, in combination with a small percentage of water-miscible solvent like THF or dioxane. The approach will test the question of whether use of a separate phase which is a good solvent for polyhydroxyether will permit higher molecular weights to be achieved.

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