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Syntheses of Some Condensation Polymers by Phase-Transfer Catalyzed Polycondensation

Yoshio Imai

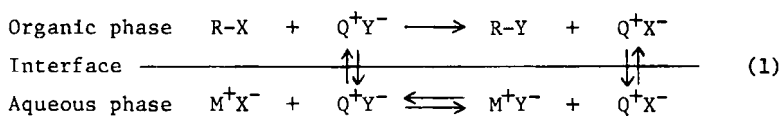
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ABSTRACT

Fundamental studies on the two-phase polycondensation using various phase-transfer catalysts such as quaternary ammonium and phosphonium salts, crown ethers, and poly(ethylene glycol)s yielded information useful for the synthesis of a variety of condensation polymers. We successfully synthesized various types of condensation polymers such as aromatic polysulfonates and polyphosphonates, aromatic polyethers, aliphatic and aromatic polysulfides, and carbon-carbon chain polymers of high molecular weights by the phase-transfer catalyzed polycondensation from combinations of aromatic disulfonyl chlorides, phosphonic dichlorides, activated aromatic dichlorides, and aliphatic dihalides, with bisphenols, aliphatic and aromatic dithiols, and active methylene compounds. The two-phase polycondensation was generally carried out in a water-immiscible organic solvent-aqueous alkaline solution system at room temperature or above. In conclusion, this method of polycondensation offers a highly versatile and convenient synthetic method for a variety of condensation polymers.

INTRODUCTION

Recently phase-transfer catalysts have been widely used for organic synthesis, particularly for nucleophilic substitution reactions [1,2]. In general, those nucleophilic substitution reactions between alkyl halides in an organic phase and anions in an aqueous phase, which do not occur usually because of phase separation, can often be strongly catalyzed by addition of a small amount of quaternary ammonium or phosphonium salts. The catalysis of these onium salts is due to the ability of the organic-soluble cations to repeatedly bring anions into the organic phase in a form suitable for reactions; this effect is termed as "phase transfer catalysis". The outline of the catalysis sequence is expressed by Eq. (1):



Quaternary ammonium salt, $Q^+ = R_4N^+$, selected due to its high solubility in the organic phase, transfers anion Y^- into the organic phase as Q^+Y^- , which then reacts with alkyl halide RX to yield the substitution product RY . The coproduced Q^+X^- is reconverted rapidly to Q^+Y^- by anion exchange with nucleophile M^+Y^- from the aqueous phase. Crown ethers and poly(ethylene glycol) derivatives are also as useful for the phase-transfer catalyzed reactions as onium salts.

Our attention has been focused on the application of phase transfer catalysts to polymer synthesis, since a few studies on the polycondensation using phase transfer catalysts appeared in the literature. Known examples are the syntheses of aromatic polyesters and polysulfonates by interfacial polycondensation in the presence of onium salt accelerators [3] and polycarbonate synthesis by solid-liquid two-phase polycondensation using crown

ethers [4,5]. The present paper summarizes our recent works on the syntheses of various condensation polymers by phase-transfer catalyzed polycondensation, where the following phase transfer catalysts were employed: tetrabutylammonium chloride (TBAC), benzyltriethylammonium chloride (BTEAC), cetyltrimethylammonium chloride (CTMAC), benzyltriphenylphosphonium chloride (BTPPC), cetyltributylphosphonium bromide (CTBPB), 15-crown-5 (15-C-5), 18-crown-6 (18-C-6), dibenzo-18-crown-6 (DB-18-C-6), dicyclohexyl-18-crown-6 (DC-18-C-6), dibenzo-24-crown-8 (DB-24-C-8), and dicyclohexyl-24-crown-8 (DC-24-C-8).

RESULTS AND DISCUSSION

Syntheses of Aromatic Polysulfonates and Polyphosphonates [6-8]

It is known that aromatic polysulfonates of high molecular weights can be prepared from aromatic disulfonyl chlorides and alkaline salts of bisphenols by the interfacial polycondensation technique using onium salt accelerators [3]. However, the function of these onium salts as phase transfer catalysts had not been fully elucidated till 1965. Therefore, we reinvestigated the synthesis of polysulfonates by two-phase polycondensation using various phase transfer catalysts.

The polycondensation of 4,4'-oxybisbenzenesulfonyl chloride (I) with 2,2-bis(4-hydroxyphenyl)propane (II, bisphenol A) was carried out in a dichloromethane-aqueous alkaline solution system at room temperature under the standard Schotten-Baumann's reaction conditions [Eq. (2)].

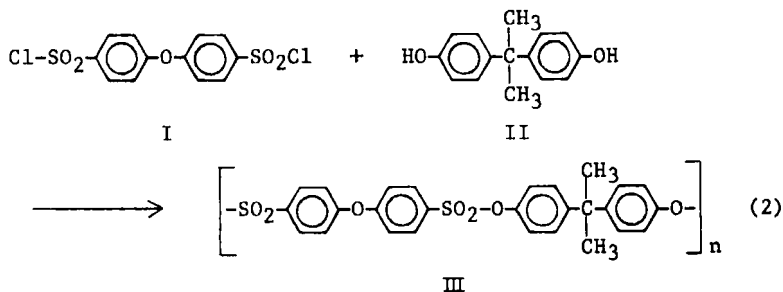
The results of the polycondensation are summarized in Table 1. In the absence of the catalyst, only low-molecular polysulfonate III was obtained even though the reaction was continued for 24 hr, whereas the addition of these quaternary ammonium salts and crown

TABLE 1. Synthesis of Aromatic Polysulfonate III with Various Phase Transfer Catalysts in Dichloromethane-Water System^a

Catalyst	Reaction time (hr)	η_{inh} of polymer (dl/g) ^b	
		Alkaline component	
		NaOH	KOH
None	24	0.20	-
TBAC	2	1.44	-
BTEAC	2	1.02	-
CTMAC	2	1.19	-
15-C-5	3	1.31	1.28
18-C-6	3	0.99	1.11
DB-18-C-6	3	0.95	1.02
DC-18-C-6	3	1.28	1.48
DB-24-C-8	3	1.03	1.09
DC-24-C-8	3	0.80	1.13

^aThe polymerization was carried out with 2.5 mmol of I and II in the presence of 0.05 mmol of the catalyst in 3.5 ml of dichloromethane and 5 ml of the aqueous alkaline solution (1.01M) at 20°C.

^bMeasured at a concentration of 0.5 g/dl in *sym*-tetrachloroethane at 30°C.



ethers increased the average molecular weight of the polymer remarkably. These catalysts react with bisphenol II to form such compound that are more soluble in the organic phase than the alkali salts of the bisphenol. Thus, the contact of II with I in the

organic phase is accelerated and the polymer of higher molecular weight is obtained.

Among these catalysts, TBAC and DC-18-C-6 were found to be highly efficient, leading to the formation of the polysulfonate with an inherent viscosity of as high as 1.4 dl/g. In the crown ether catalyzed system, potassium hydroxide was generally more effective as alkaline component than sodium hydroxide for preparing the polymer of high molecular weights.

The relationship between inherent viscosities of the resulting polymer and reaction time in the polycondensation with crown ether catalyst is shown in Figure 1. The phase-transfer catalyzed polycondensation proceeded fairly rapidly at 20°C and was essentially completed after 2 hr.

As the next step to the phase-transfer catalyzed synthesis of aromatic polysulfonates, we synthesized structurally related aromatic polyphosphonates. The polycondensation of phenylphosphonic dichloride (IV) with bisphenol A (II) leading to polyphosphonate (V) was conducted with various phase transfer catalysts in a dichloromethane-aqueous alkaline solution system at a temperature

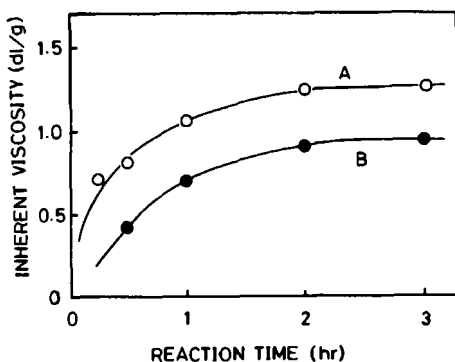


FIG. 1. Polycondensation of I and II in dichloromethane-aqueous KOH system at 20°C with DC-18-C-6 (A) and DB-18-C-6 (B) catalysts. Reaction conditions, see Table 1.

range of lower than 0°C, because IV is known to be highly susceptible to alkaline hydrolysis [Eq. (3)].

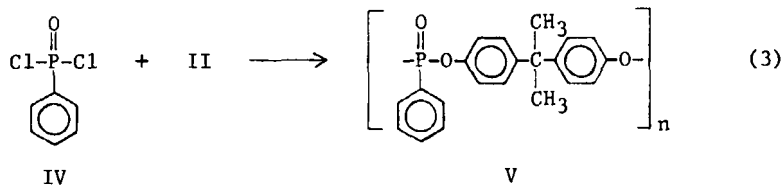


Figure 2 shows the plots of inherent viscosities of the polyphosphonate against reaction time in the polycondensation with BTPPC catalyst. The two-phase polycondensation proceeded very rapidly at -5°C and was almost completed in 20 min. Thus, phenylphosphonic dichloride was found to be more reactive with alkaline salt of bisphenol A than aromatic disulfonyl chlorides.

The results of the polycondensation are summarized in Table 2. In the absence of any catalyst, only low molecular weight polymer V was produced, whereas the addition of the quaternary onium salts

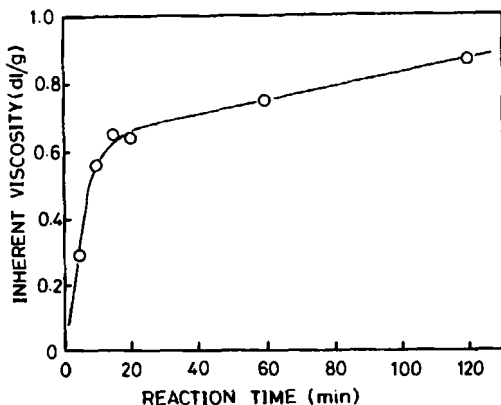


FIG. 2. Polycondensation of II and IV with BTPPC catalyst in dichloromethane-aqueous KOH system at -8~-5°C. Reaction conditions, see Table 2.

TABLE 2. Synthesis of Aromatic Polyphosphonate V with Various Phase Transfer Catalysts in Dichloromethane-Water System^a

Catalyst	η_{inh} of polymer (dl/g) ^b	
	Alkaline component	
	NaOH	KOH
None	0.05	0.05
TBAC	0.58	0.36
BTEAC	0.21	0.21
CTMAC	0.60	0.70
BTPPC	0.59	0.88
CTBPB	0.33	0.28
15-C-5	0.09	0.21
18-C-6	0.14	0.30
DB-18-C-6	0.09	0.59
DC-18-C-6	0.19	0.64
DB-24-C-8	0.10	0.17
DC-24-C-8	0.24	0.50

^aThe polymerization was carried out with 2.5 mmol of II and IV in the presence of 0.05 mmol of the catalyst in 1.3 ml of dichloromethane and 5 ml of the aqueous alkaline solution (1.01 M) at $-8 \sim -5^\circ\text{C}$ for 2 hr.

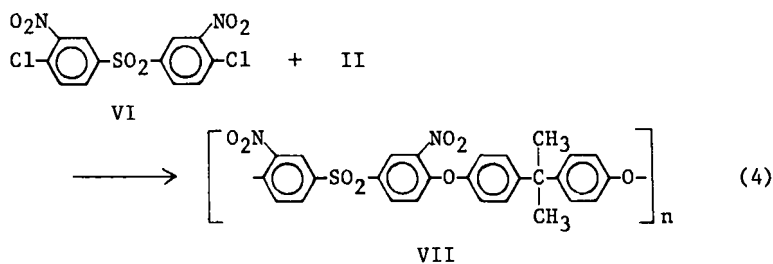
^bMeasured at a concentration of 0.5 g/dl in sym-tetrachloroethane at 30°C .

and crown ethers increased more or less molecular weight of the polymer. Among them, the two-phase polycondensation was strongly catalyzed by some lipophilic phase transfer catalysts such as TBAC, CTMAC, BTPPC, DB-18-C-6, DC-18-C-6, and DC-24-C-8, leading to the formation of the polyphosphonate with high inherent viscosities of more than 0.5 dl/g. In these crown ether catalyzed systems, potassium hydroxide was generally more effective as alkaline component in the aqueous phase than sodium hydroxide for producing the polymer of higher molecular weights. On the other hand, the polycondensation was not affected by the alkaline components in

the quaternary onium salt catalyzed systems with regard to inherent viscosity of the resulting polymer.

Synthesis of Aromatic Polyethers [9]

It is known that aromatic polyethers with high molecular weights were generally prepared by the aromatic nucleophilic substitution polymerization of activated aromatic dihalides with alkaline salts of bisphenols in anhydrous polar aprotic solvents at elevated temperatures [10-13]. We successfully synthesized similar aromatic polyether (VII) by the phase-transfer catalyzed polycondensation of bis(4-chloro-3-nitrophenyl) sulfone (VI) and bisphenol A (II) using such catalysts as quaternary ammonium salts, crown ethers, and poly(ethylene glycol)s [Eq. (4)]. Very recently, we have learnt the phase-transfer catalyzed synthesis of another type of polyethers [14].



Our polycondensations were carried out in a water-immiscible organic solvent-aqueous alkaline solution system at room temperature. Figure 3 shows the course of the polycondensation with DC-18-C-6 catalyst in terms of inherent viscosity of the resulting polyether. The phase-transfer catalyzed polycondensation proceeded fairly slowly at 20°C in a dichloromethane-water system and went essentially to completion in 24 hr.

The influence of catalysts on the polycondensation in a dichloromethane-water system is given in Table 3. All of these

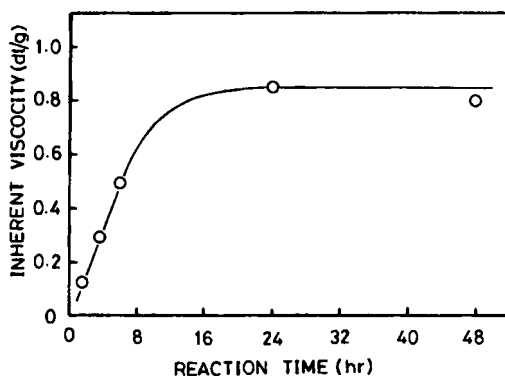


FIG. 3. Polycondensation of II and VI with DC-18-C-6 catalyst in dichloromethane-aqueous KOH system at 20°C. Reaction conditions, see Table 3.

TABLE 3. Synthesis of Aromatic Polyether VII with Various Phase Transfer Catalysts in Dichloromethane-Water System^a

Catalyst	Alkaline component	Reaction time (day)	Polymer η_{inh} (dl/g) ^b
TBAC	NaOH	2	0.42
CTMAC	NaOH	6	0.26
BTEAC	NaOH	6	0.15
15-C-5	KOH	6	0.36
DB-18-C-6	KOH	4	0.37
DC-18-C-6	KOH	1	0.84
DC-18-C-6	NaOH	6	0.31

^aThe polymerization was carried out with 2.5 mmol of II and VI in the presence of 0.05 mmol of the catalyst in 3.5 ml of dichloromethane and 5 ml of the aqueous alkaline solution (1.01 M) at 20°C.

^bMeasured at a concentration of 0.5 g/dl in DMF at 30°C.

crown ethers and quaternary ammonium salts except BTEAC were effective for yielding aromatic polyether VII with reasonable molecular weights. Above all, DC-18-C-6 was the most suitable for the preparation of the highest molecular weight polymer under these conditions.

The effect of solvents on the two-phase polycondensation is shown in Table 4. Chlorinated hydrocarbons, such as chloroform and 1,2-dichloroethane, as well as some aromatic solvents like nitrobenzene, acetophenone, and anisole were all effective as the polymerization media to produce moderate molecular weight polymer VII. In these solvents, the aromatic polyether was readily soluble or at least partially soluble. In the polycondensation in a nitrobenzene-water system, an increase in reaction temperature brought about a marked reduction in reaction time; the polycondensation at 80°C for 2 hr afforded the polyether with an inherent viscosity of 0.5 dl/g.

TABLE 4. Synthesis of Aromatic Polyether VII in Various Organic Solvent-Water System with DC-18-C-6 Catalyst^a

Solvent	Reaction temperature (°C)	Reaction time (hr)	Polymer η_{inh} (dl/g) ^b
Dichloromethane	20	24	0.84
Chloroform	20	24	0.53
1,2-Dichloroethane	20	24	0.42
Nitrobenzene	20	24	0.47
Nitrobenzene	80	2	0.51
Nitrobenzene	100	1	0.42
Acetophenone	20	24	0.33
Anisole	20	24	0.31

^aThe polymerization was carried out with 2.5 mmol of II and VI in the presence of 0.05 mmol of DC-18-C-6 in 3.5 ml of the organic solvent and 5 ml of 1.01 M aqueous potassium hydroxide.

^bMeasured at a concentration of 0.5 g/dl in DMF at 30°C.

We also found that poly(ethylene glycol)s (PEGs) catalyzed the two-phase polycondensation in a manner similar to those with crown ethers leading to aromatic polyether VII of moderately high molecular weights. As can be seen from Table 5, PEG with molecular weight of 2,000 was found to be the most efficient catalyst among these PEGs. The polycondensation using PEG catalysts in a dichloromethane-water system proceeded much more slowly than the polymerization with crown ether catalysts. This may provide the first successful application of poly(ethylene glycol)s to polymer synthesis, which are both inexpensive and nontoxic compared with crown ethers.

Syntheses of Aliphatic and Aromatic Polysulfides [15-17]

In the early 1950s, aliphatic polysulfides were synthesized by the aliphatic nucleophilic substitution polymerization of dibromoalkanes with sodium salt of dithiols under anhydrous conditions [18]. Recently, we developed a convenient method for the preparation of polysulfides by the two-phase polycondensation in

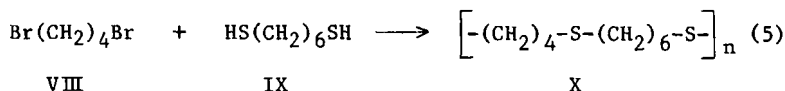
TABLE 5. Synthesis of Aromatic Polyether VII with Poly(ethylene glycol) Catalysts in Dichloromethane-Water System^a

Catalyst	η_{inh} of polymer (dl/g) ^b			
	Reaction time (day)			
	1	3	5	7
PEG-600	0.10	0.28	0.27	0.29
PEG-1,000	0.19	0.31	0.33	0.36
PEG-2,000	0.16	0.33	0.41	0.47
PEG-3,000	0.18	0.33	0.29	0.32
PEG-20,000	0.14	0.25	0.26	0.34

^aThe polymerization was carried out with 2.5 mmol of II and VI in the presence of 0.5 g of PEG catalyst in 3.5 ml of dichloromethane and 5 ml of 1.01 M aqueous potassium hydroxide at 20°C.

^bMeasured at a concentration of 0.5 g/dl in DMF at 30°C.

a potassium hydroxide aqueous solution. The polycondensation of 1,4-dibromobutane (VIII) and 1,6-hexanedithiol (IX) leading to polysulfide (X) was first carried out in various organic solvent-water system with DC-18-C-6 catalyst at 80°C [Eq. (5)].



The results of the polycondensation are summarized in Table 6. All of these polymerization media employed afforded the polysulfide with moderately high inherent viscosities, whereas the polymer with the highest viscosity was produced in the absence of organic solvents. Thus, the polycondensation proceeded readily in a melt-water two-phase system at 80°C, since polysulfide X has a polymer-melting temperature of 75°C.

Table 7 shows the effect of catalysts on the polycondensation in an aqueous potassium hydroxide. These general phase transfer catalysts including crown ethers and quaternary ammonium salts, as well as sodium dodecyl sulfate (SDS) which serves as an anionic

TABLE 6. Synthesis of Aliphatic Polysulfide X in Various Organic Solvent-Water System with DC-18-C-6 Catalyst^a

Solvent	Reaction temperature (°C)	Polymer η_{inh} (dl/g) ^b
Dichloromethane	20	0.30
Chloroform	80	0.31
Benzene	80	0.30
Nitrobenzene	80	0.58
Acetonitrile	80	0.58
None	80	0.73

^aThe polymerization was carried out with 2.5 mmol of VIII and IX in the presence of 0.05 mmol of DC-18-C-6 in 2.5 ml of the organic solvent and 5 ml of 1.01 M aqueous potassium hydroxide for 48 hr.

^bMeasured at a concentration of 0.5 g/dl in chloroform at 30°C.

TABLE 7. Synthesis of Aliphatic Polysulfide X with Various Catalysts in Aqueous Potassium Hydroxide^a

Catalyst	Polymer η_{inh} (dl/g) ^b
15-C-5	0.73
18-C-6	0.73
DB-18-C-6	0.93
DC-18-C-6	0.84
DB-24-C-8	0.63
DC-24-C-8	0.49
TBAC	0.83
CTMAC	0.58
SDS	0.63
None	0.51

^aThe polymerization was carried out with 2.5 mmol of VIII and IX in the presence of 0.05 mmol of the catalyst in 5 ml of 1.01 M aqueous potassium hydroxide at 80°C for 24 hr.

^bMeasured at a concentration of 0.5 g/dl in chloroform at 30°C.

surface-active agent, were all effective for producing polysulfide X of high molecular weights. It is interesting to note that the polycondensation proceeded without use of any catalyst in this system, leading to the formation of the polymer with moderately high molecular weight.

Figure 4 shows the course of the polycondensation in an aqueous potassium hydroxide at 80°C in terms of inherent viscosity of the resulting polymer. In the presence of DC-18-C-6 catalyst, the maximum inherent viscosity was reached in 24 hr. On the other hand, the maximum was attained after 48 hr in the absence of the catalyst. Thus, the polycondensation reaction was greatly accelerated by the addition of DC-18-C-6 catalyst in the initial stage. It was also observed that a longer reaction time at 80°C resulted in a slight reduction in inherent viscosity; this is assumed to be caused by alkaline hydrolysis of the resulting polysulfide.

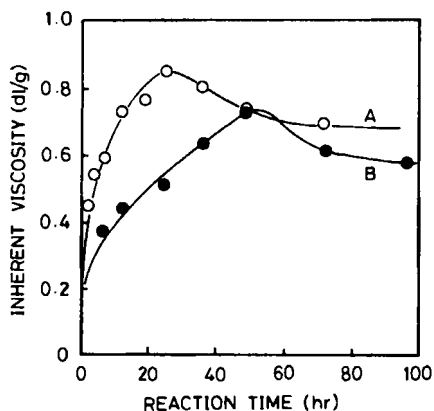
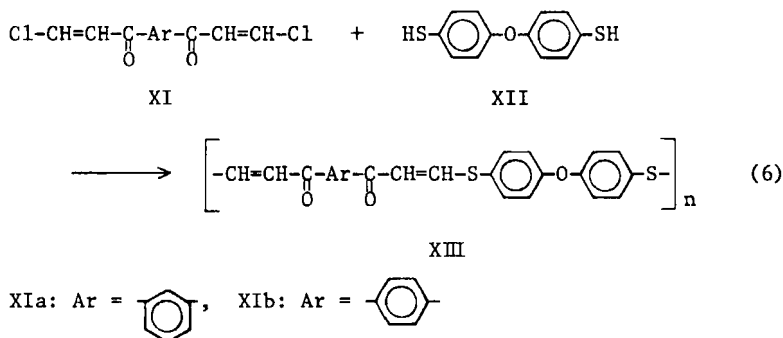


FIG. 4. Polycondensation of VIII and IX in aqueous KOH at 80°C with DC-18-C-6 (A) and without the catalyst (B). Reaction conditions, see Table 7.

Another type of polysulfides (XIII) were synthesized by the two-phase polycondensation of bis(3-chloroacryloyl)benzenes (XIa and XIb), which are one of the most reactive dichlorides, with 4,4'-oxybisbenzenethiol (XII) [Eq. (6)]. The polycondensation was carried out in a chloroform-water system at room temperature with some phase transfer catalysts.



The course of the polycondensation in terms of inherent viscosity of polysulfide XIIIa formed is shown in Figure 5. Even

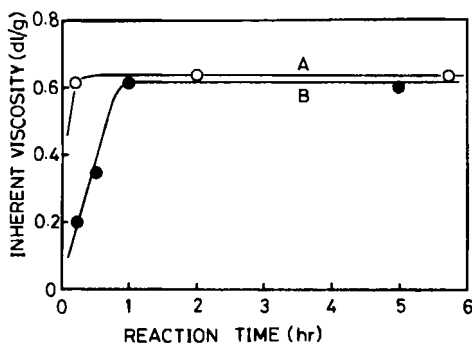


FIG. 5. Polycondensation of XIa and XII in chloroform-aqueous KOH system at 15°C with DC-18-C-6 (A) and without the catalyst (B). Reaction conditions, see Table 8.

without use of any catalyst, the polycondensation proceeded rapidly with precipitation of the polymer and went essentially to completion in 1 hr at room temperature to yield the polysulfide having an inherent viscosity of 0.6 dl/g. The use of DC-18-C-6 increased the initial rate of the polycondensation remarkably and the polymerization was almost completed in 10 min.

Table 8 shows the results of the polycondensation. The polysulfides having inherent viscosities above 0.5 dl/g were readily obtained from two bis(3-chloroacryloyl)benzenes with or without use of phase transfer catalysts. These activated dichlorides are so highly reactive, almost comparable to ordinary dicarboxylic acid chlorides, that the use of catalysts like DC-18-C-6 was not essential to this type of polycondensation for producing high molecular weight polysulfides XIII.

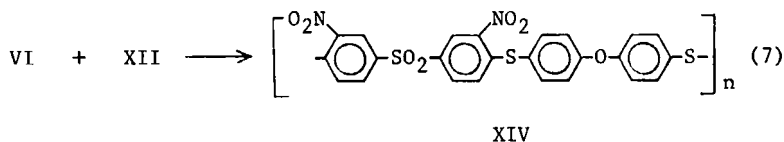
We took a further step to the phase-transfer catalyzed synthesis of aromatic polysulfide (XIV), which is structurally related to the above mentioned aromatic polyether VII. The polycondensation of bis(4-chloro-3-nitrophenyl) sulfone (VI) with 4,4'-oxybisbenzenethiol (XII) was conducted in a nitrobenzene-water system at room temperature by using various phase transfer catalysts [Eq. (7)].

TABLE 8. Synthesis of Polysulfides XIII in Organic Solvent-Water System^a

Dichloride	Solvent	Catalyst	Reaction time (min)	Polymer η_{inh}^b (dl/g)
XIa	Chloroform	None	15	0.21
XIa	Chloroform	None	60	0.61
XIa	Chloroform	DC-18-C-6	10	0.62
XIa	Chloroform	TBAC	60	0.72
XIa	Dichloromethane	DC-18-C-6	60	0.55
XIb	Chloroform	None	60	0.55
XIb	Dichloromethane	None	15	0.42
XIb	Dichloromethane	DC-18-C-6	15	0.51

^aThe polymerization was carried out with 2.5 mmol of XI and XII in the presence of 0.05 mmol of the catalyst in 5 ml of the solvent and 5 ml of 1.01 M aqueous potassium hydroxide at 15°C under nitrogen.

^bMeasured at a concentration of 0.5 g/dl in conc. sulfuric acid at 30°C.



Plots of inherent viscosities of the resulting polysulfide as a function of reaction time is shown in Figure 6. The polycondensation proceeded fairly rapidly without use of DC-18-C-6 catalyst at 15°C with precipitation of polymer XIV and was almost completed in 4 hr. In the presence of the catalyst, the initial rate of the polycondensation was highly accelerated and a gradual increase in inherent viscosity of the polymer with reaction time was observed in a solid polymer-nitrobenzene-water three-phase system.

Table 9 presents the effect of catalysts on the polycondensation in a nitrobenzene-water system. All of these phase transfer

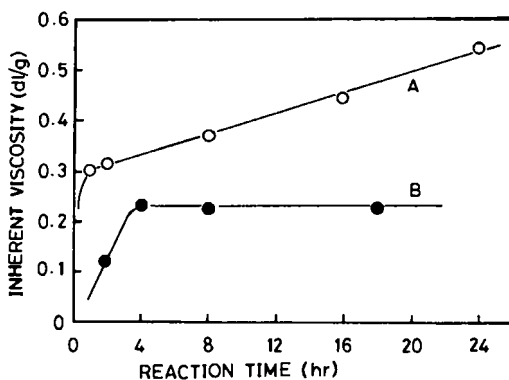


FIG. 6. Polycondensation of VI and XII in nitrobenzene-aqueous KOH system at 15°C with DC-18-C-6 (A) and without the catalyst (B). Reaction conditions, see Table 9.

TABLE 9. Synthesis of Aromatic Polysulfide XIV with Various Catalysts in Nitrobenzene-Water System^a

Catalyst	Polymer η_{inh} (dl/g) ^b
None	0.16
DC-18-C-6	0.54
DB-24-C-8	0.51
BTEAC	0.43
BTTPC	0.57

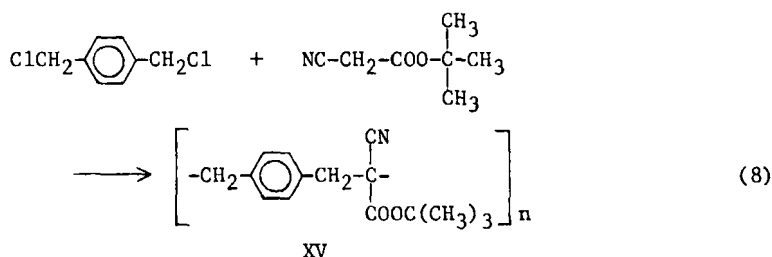
^aThe polymerization was carried out with 2.5 mmol of VI and XII in the presence of 0.05 mmol of the catalyst in 5 ml of nitrobenzene and 5 ml of 1.01 M aqueous potassium hydroxide at 15°C for 24 hr under nitrogen.

^bMeasured at a concentration of 0.5 g/dl in *N*-methyl-2-pyrrolidone at 30°C.

catalysts including onium salts and crown ethers were highly effective for producing the aromatic polysulfide with high molecular weights.

Synthesis of Carbon-Carbon Chain Polymers [19]

On the basis of the results obtained above, we successfully extended phase-transfer catalyzed synthesis to aliphatic nucleophilic substitution polymerization using carbanions as a nucleophile. A typical example is the synthesis of carbon-carbon chain polymer (XV) from α, α' -dichloro-*p*-xylene and *tert*-butyl cyanoacetate [Eq. (8)].



The polycondensation was carried out with a relatively large amount of BTEAC catalyst in a 50% aqueous sodium hydroxide-benzene system at 50°C for 2 hr, and the polymer having an inherent viscosity of 0.7 dl/g was obtained readily. No hydrolysis of *tert*-butyl cyanoacetate or the resulting polymer was observed under these conditions because of a possible steric hindrance of the *tert*-butyl group present. Further studies of this type of polycondensation are now in progress.

CONCLUSION

The conclusion we reached is that phase-transfer catalyzed polycondensation is broadly applicable to syntheses of various

types of condensation polymers by using suitable phase transfer catalysts. A remarkable feature of this method is that it is highly versatile, convenient, and inexpensive (especially in the case of quaternary ammonium salts). Thus, phase-transfer catalyzed synthesis will be extended to much more types of polycondensation and find directly industrial applications in the near future.

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