Phase Transfer Catalyzed Polycondensation of α, α'-Dichloro-p-xylene with 2,2-Bis(4-hydroxyphenyl)propane II. Some Aspects of Phase Transfer Catalyzed Polycondensation Reaction in the Tetrahydrofuran-Dimethyl Sulfoxide/Aqueous Sodium Hydroxide System

Noboru YAMAZAKI and Yoshio IMAI

*Department of Textile and Polymeric Materials,
Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152, Japan*

ABSTRACT: Phase transfer catalyzed (PTC) polycondensations of α, α'-dichloro-p-xylene with 2,2-bis(4-hydroxyphenyl)propane were carried out in a THF–DMSO (3 : 1)/aqueous sodium hydroxide system at 60°C in the presence of quaternary ammonium halides. For both tetra-n-butylammonium bromide and hexadecylammonium bromide, the following rate equation was obtained: polymerization rate $= k[Q^+X^-]^{0.57}[NaOH]^{2.3}$ where $[Q^+X^-]$ and $[NaOH]$ stand for the concentrations of a phase transfer catalyst in an organic layer and sodium hydroxide in an aqueous layer, respectively. The catalytic activity for the PTC polycondensation was in the increasing order of $(CH_3)_4NBr < (C_2H_5)_4NBr < C_6H_{13}(CH_3)_3NBr < C_8H_{17}(CH_3)_3NBr < C_{10}H_{21}(CH_3)_3NBr \approx C_{12}H_{25}(CH_3)_3NBr \approx C_{14}H_{29}(CH_3)_3NBr < C_{16}H_{33}(CH_3)_3NBr < (C_3H_7)_4NBr < (C_4H_9)_4NBr < (C_5H_{11})_4NBr$. The counter halide anions for benzyltriethylammonium cation also affected the polycondensation rate, which decreased in the order of chloride > bromide > iodide. The addition of sodium chloride to the PTC polycondensation system in the presence of benzyltriethylammonium chloride caused little change in the polymerization rate but always gave a white, soluble polyether even when some drastic reaction conditions were applied.

KEY WORDS   Phase Transfer Catalyst / Quaternary Ammonium Halides / Phase Transfer Catalyzed Polycondensation / Polycondensation Reaction / Polyether / α, α'-Dichloro-p-xylene / 2,2-Bis(4-hydroxylphenyl)propane /

Phase transfer catalyzed (PTC) polycondensation is a novel type of interfacial polycondensation for moderately reactive monomer pairs, and is generally carried out in the presence of a phase transfer catalyst in a two phase system of an aqueous alkaline solution and immiscible organic solvent.

Several polymers nearly impossible or difficult to prepare by conventional interfacial and/or solution polycondensations can be obtained easily by the PTC method without expensive monomers and/or solvents. Typical examples are polycarbonates,[1] polysulfones,[2] polysulfonates,[3] polyamines,[4] polyphospho-nates,[5] polysulfides,[6] polyesters,[7] polyethers,[9-13] and C–C chain polymers.[14,15]

The synthesis of a polyether by the PTC polycondensation of α, α'-dichloro-p-xylene (DCPX) with 2,2-bis(4-hydroxyphenyl)propane (BPA) was reported independently by N'Guyen and Boileous,[8,9] Cameron and Law,[10] and our group.[12] We reported that the addition of DMSO to the PTC polycondensation system not only enhanced reactivity but suppressed side reactions to give a completely soluble, high molecular weight polyether from DCPX and BPA, and that the optimal solvent system at 60°C was tetrahy-

drofuran (THF)–dimethyl sulfoxide (DMSO) (3 : 1)/or nitrobenzene–DMSO (3 : 1)/50% aqueous sodium hydroxide, which gave a polymer having an inherent viscosity greater than $0.5 \, \mathrm{dl} \, \mathrm{g}^{-1}$.

In this connection, further study on the PTC polycondensation of DCPX with BPA has been carried out in a THF–DMSO (3 : 1)/ aqueous sodium hydroxide system to understand the reaction mechanism involved. Reaction variables such as alkaline concentration, alkyl chain length of a tetraalkylammonium salt as a phase transfer catalyst, counter anions for tetraalkylammonium cations, and inorganic salts in the aqueous phase were investigated in detail. In the present study, the rate of the increases in the inherent viscosity of the resulting polymers, which roughly correlate with the polymerization rates, were measured and compared one another to discuss these factors.

EXPERIMENTAL

Materials

Commercial benzyltriethylammonium chloride (BTEAC), benzyltriethylammonium bromide (BTEAB), benzyltriethylammonium iodide (BTEAI), tetramethylammonium bromide (TMAB), tetraethylammonium bromide (TEAM), tetra-*n*-propylammonium bromide (TPAB), tetra-*n*-butylammonium bromide (TBAB), tetra-*n*-amylammonium bromide (TAAB), *n*-hexyltrimethylammonium bromide (HTMAB), *n*-octyltrimethylammonium bromide (OTMAB), *n*-decyltrimethylammonium bromide (DTMAB), *n*-dodecyltrimethylammonium bromide (DDTMAB), *n*-tetradecyltrimethylammonium bromide (TDTMAB), *n*-hexadecyltrimethylammonium bromide (HDTMAB), sodium chloride (NaCl), sodium sulfate (Na_2SO_4), and sodium *p*-toluene sulfonate (PTS-Na) were used as received. α, α'-Dibromo-*p*-xylene (DBPX), DCPX, and BPA were recrystallized from dry benzene.

Synthesis of α, α'-Ditosyloxy-p-xylene (DTPX)

In a 500-ml flask, 15 g (0.11 mol) of *p*-xylene glycol, 55 g (0.29 mol) of *p*-toluenesulfonyl chloride, 6.0 g (0.02 mol) of tetra-*n*-butylammonium chloride, and 150 ml of benzene were placed and the mixture was heated at 60°C. With vigorous stirring, 150 ml of 10 wt% aqueous sodium hydroxide was added and the reaction was continued for 1.5 h at 60°C. The benzene layer was separated and combined with the ether washings of the aqueous layer; this combined solution was washed successively with diluted hydrochloric acid and water. After drying over magnesium sulfate overnight, the benzene and ether were evaporated under reduced pressure. The crude product was recrystallized three times from ethanol to give 10.5 g (21% yield) of DTPX, white plates, mp 108°C. NMR (CDCl$_3$) δ ppm: 2.40 (s, 6H (CH$_3$)), 4.94 (s, 4H (CH$_2$O)), 7.10—7.35 (m, 8H (phenylene)), 7.60—7.80 (m, 6H (phenylene)). *Anal.* Calcd for $C_{22}H_{22}O_6S_2$: C, 59.19%; H, 4.93%; S, 14.35%. Found: C, 58.87%; H, 4.87%; S, 14.43%.

Polymerization

In a 50-ml flask equipped with a mechanical stirrer and a condenser, 0.88 g (5.0 mmol) of DCPX, 1.14 g (5.0 mmol) of BPA, 0.28 g (1.0 mmol) of TPAB, and 20 ml of a THF–DMSO (3 : 1 by volume) mixture were placed. The mixture was heated at 60°C, and 20 ml of 50% aqueous sodium hydroxide solution was added with vigorous stirring. After 1 h of reaction at 60°C, the mixture was neutralized with diluted hydrochloric acid and the precipitate was filtered off. The crude polymer was washed successively with water and acetone to remove inorganic salts, monomers, and oligomers. The polymer was purified by dissolution in *N*-methyl-2-pyrrolidone (NMP) followed by precipitation in methanol. The inherent viscosity of the polymer in NMP was $0.49 \, \mathrm{dl} \, \mathrm{g}^{-1}$, measured at a concentration of $0.5 \, \mathrm{g} \, \mathrm{dl}^{-1}$ at 30°C. The IR spectrum (KBr) showed absorptions at 1250 and 1020 cm^{-1} ($=$C–O–C). *Anal.*

Calcd for $C_{23}H_{22}O_2$: C, 83.64%; H, 6.67%. Found: C, 82.90%; H, 6.72%.

In a THF–DMSO (3:1)/aqueous sodium hydroxide system, the polymer began to precipitate when its inherent viscosity reached about $0.2\,dl\,g^{-1}$ during the reaction. This means that the polycondensation proceeds homogeneously at the beginning and then heterogeneously to give a high molecular weight polymer.

To determine the rate of the increase in inherent viscosity of the resulting polymer (polymerization rate), five or six polycondensations in each case were carried out for different periods during the initial 60 min at 60°C. The polymerization rate was calculated from the initial linear part of a time–dependence curve of the inherent viscosity. The relative polymerization rate was also calculated on the basis of the polymerization rate in a THF–DMSO (3:1)/50% aqueous sodium hydroxide system without a phase transfer catalyst at 60°C.

RESULTS AND DISCUSSION

Effects of Alkaline Concentration

A THF–DMSO (3:1)/aqueous sodium hydroxide system exhibits good phase separation

behavior, similar to the benzene–DMSO (3:1)/aqueous sodium hydroxide system reported previously.[12]

Figure 1 shows the time-dependence of the inherent viscosity of the polymers obtained in the polycondensation of DCPX with BPA in the presence of BTEAC in THF–DMSO (3:1)/aqueous sodium hydroxide systems at 60°C using 20, 30, 40, and 50% aqueous sodium hydroxide solutions as aqueous phases. The polymerization rates obtained from the slopes of the curves in the initial
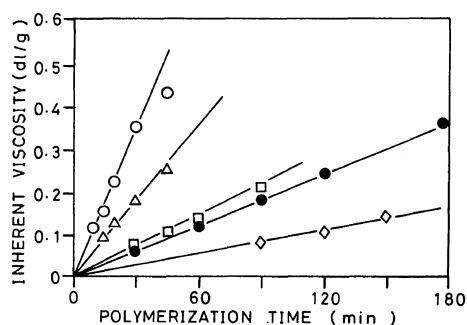

Figure 1. Time–dependence of the inherent viscosity of the resulting polymers in THF–DMSO (3:1)/aqueous sodium hydroxide systems at 60°C. The PTC polycondensations were carried out with BTEAC using 20% (◇), 30% (□), 40% (△), and 50% (○) aqueous sodium hydroxide and without BTEAC using 50% (●) aqueous sodium hydroxide.

Table I. PTC polycondensation rates in the THF–DMSO (3:1)/50 wt% aqueous sodium hydroxide system at 60°C

Run	Monomer	Concentration of NaOH %	Catalyst	Polymerization rate[a] $dl\,g^{-1}\,min^{-1}$	Relative polymerization rate
1-1	DCPX	50	—	1.94×10^{-3}	1.0
1-2	DCPX	20	BTEAC	0.873	0.45
1-3	DCPX	30	BTEAC	2.72	1.4
1-4	DCPX	40	BTEAC	6.21	3.2
1-5	DCPX	50	BTEAC	11.6	6.0
1-6	DBPX	20	BTEAC	3.46	1.8
1-7	DBPX	30	BTEAC	13.4	7.0
1-8	DBPX	40	BTEAC	27.3	14.2
1-9	DBPX	50	BTEAC	44.6	23.0

[a] Polymerization rates $(d\eta_{inh}/dt)$ were calculated from the time–dependence curves of the inherent viscosity of the resulting polymers such as the slopes of the curves in Figure 1.

stage of the polycondensation are given in Table I. A high concentration of sodium hydroxide (50%) gave a high polymerization rate and high molecular weight polymer in an almost quantitative yield within a short reaction time (run 1-5, $\eta_{inh} = 0.50$ after 1 h). However, a low concentration (20%) resulted in only a low molecular weight polymer even for a sufficient reaction time (run 1-2, $\eta_{inh} = 0.25$ after 24 h). DBPX always gave polymerization rates higher than DCPX at any concentration of sodium hydroxide. DBPX resulted in a higher molecular weight polymer (run 1-9, $\eta_{inh} = 0.78$) than DCPX (run 1-5, $\eta_{inh} = 0.4$) within 20 min in the THF–DMSO (3:1)/50% aqueous sodium hydroxide system at 60°C.

If the polymerization rate is a function of both the m-th power of the concentration of a phase transfer catalyst ($[Q^+X^-]^m$) in an organic layer and the n-th power of the concentration of sodium hydroxide ($[NaOH]^n$) in an aqueous layer, the rate may be expressed as

$$\text{polymerization rate} = k[Q^+X^-]^m[NaOH]^n \quad (1)$$

When the polymerization rate at a constant concentration of the phase transfer catalyst is plotted against the concentration of sodium hydroxide, linear relations with the slope of 2.3 are obtained in the both cases (Figure 2). Although the actual mechanism is not clear yet, the alkaline concentration rather than the phase separation seems to affect the PTC polycondensation; that is, the higher the reaction rate becomes, the higher the molecular weight becomes. BPA is supposedly forced to transfer into the organic phase when the alkaline concentration is high, probably due to the salting-out effect. The reaction between DCPX or DBPX and BPA thus proceeds much faster than DCPX or DBPX reacts with hydroxide anion (hydrolysis of DCPX or DBPX).

Catalytic Activity of Tetraalkylammonium Bromides

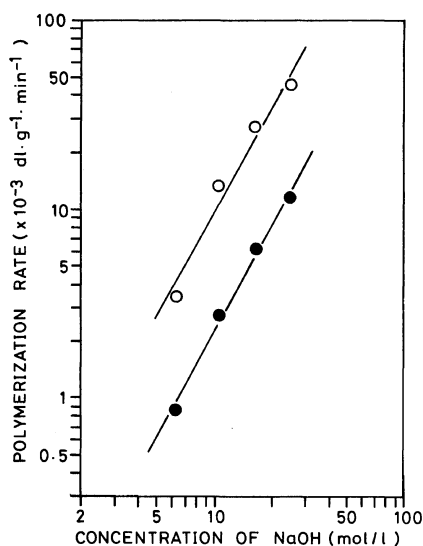The PTC polycondensations of DCPX with

Figure 2. Relations between polymerization rate and concentration of sodium hydroxide. The PTC polycondensation of DCPX (●) or DBPX (○) with BPA was carried out in a THF–MDSO (3:1)/aqueous sodium hydroxide system in the presence of BTEAC at 60°C. Polymerization rates were plotted against sodium hydroxide concentrations according to eq 1 to give $n = 2.3$.

BPA were carried out in the presence of various tetraalkylammonium bromides in the THF–DMSO (3:1)/50% sodium hydroxide system at 60°C. Figure 3 shows the time dependence of the inherent viscosity of the resulting polymers. All the catalysts examined in this work gave good linear relations in the initial stage of the polycondensation. The polymerization rates determined from Figure 3 are summarized in Table II. The catalytic activity was in the increasing order of TMAB < TEAB < HTAB < OTMAB < DDTMAB < TDTMAB < HDTMAB < TPAB < TBAB < TAAB.

Figure 4 shows the relative polymerization rate as a function of total carbon number in tetraalkylammonium bromides. In the case of tetra-n-alkylammonium bromides, catalytic activity became obvious at total carbon number greater than 12 (TPAB) and increased almost linearly with respect to the total carbon number. The catalytic activity of TMAB or TEAB was not so obvious as that of TPAB,
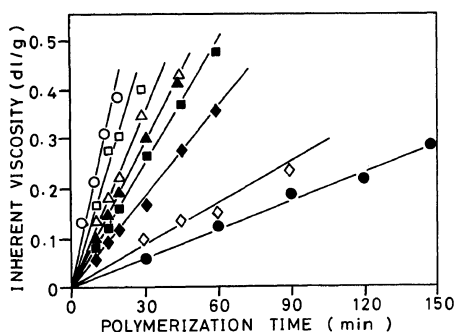
Figure 3. Catalytic activities of the tetra-*n*-alkylammonium and *n*-alkyltrimethylammonium bromides in the PTC polycondensation of DCPX with BPA in the THF–DMSO (3:1)/50 wt% sodium hydroxide system at 60°C. Without a phase transfer catalyst (●), TEAB (◇), TPAB (△), TBAB (□), TAAB (○), HTMAB (◆), OTMAB (■), DTMAB (▲), DDTMAB (▲), TDTMAB (▲), HDTMAB (▲).
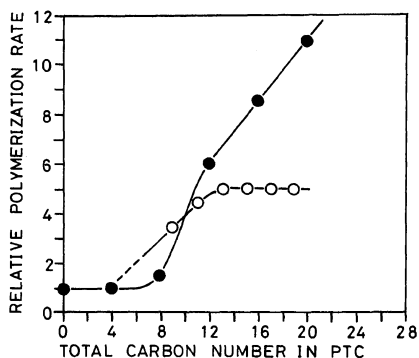

Figure 4. Relations between relative polymerization rate and total carbon number in the tetra-*n*-alkylammonium bromides (●) and *n*-alkyltrimethylammonium bromides (○). PTC polycondensations were carried out in the THF–DMSO (3:1)/50 wt% aqueous sodium hydroxide system at 60°C.

Table II. Polymerization rates in the THF–DMSO (3:1)/50 wt% aqueous sodium hydroxide system in the presence of various tetraalkylammonium bromides at 60°C

Catalyst	Polymerization rate[a] $dl\,g^{-1}\,min^{-1}$	Relative polymerization rate
—	1.94×10^{-3}	1.00
TMAB	2.52	1.30
TEAB	2.86	1.50
TPAB	11.7	6.0
TBAB	16.5	8.5
TAAB	21.2	10.9
HTMAB	6.38	3.4
OTMAB	8.54	4.4
DTMAB	9.31	4.8
DDTMAB	9.30	4.8
TDTMAB	9.32	4.8
HDTMAB	9.31	4.8

[a] Polymerization rates $(d\eta_{inh}/dt)$ were calculated from the time–dependence curves of the inherent viscosity of the resulting polymers.

TBAB, or TAAB (Figure 4). The former (TMAB or TEAB) dissolves in water very much but the latter (TPAB, TBAB, or TAAB) has poor solubility. Thus quaternary ammonium halides must be soluble in the organic phase but not in the aqueous phase to show high catalytic activity. This is because water soluble quaternary ammonium salts are considered, not to have enough ion-extraction ability, which is very important for PTC polycondensation. The catalytic activity of tetra-*n*-alkylammonium bromides having total carbon numbers greater than 24 (tetra-*n*-hexylammonium bromide) have not been examined yet. However, their activity will probably decrease with an increase in the total carbon number, since bulkiness around the nitrogen atom probably suppresses it.[16] In the case of *n*-alkyltrimethylammonium bromides, the activity increased with an increase in *n*-alkyl chain length and leveled off at a total carbon number greater than 13 (DTMAB).

For the PTC polycondensation reaction of DCPX with BPA in the THF–DMSO (3:1)/50% sodium hydroxide system, tetraalkylammonium bromides with four alkyl chains longer than *n*-propyl showed superior catalytic activity to *n*-alkyltrimethylammonium bromides with only one long *n*-alkyl chain. The *n*-alkyltrimethylammonium bromides supposedly have almost the same effective ion radii around the nitrogen atom as TMAB, while the effective ion radii of the tetra-*n*-alkylammonium bromides increases with increasing *n*-

alkyl chain length.[17] The tetra-n-alkylammonium bromides have greater bulkiness and lipophilicity (larger effective ion radii) than the n-alkyltrimethylammonium bromides at the same total carbon number, and this bulkiness around the nitrogen atom and lipophilicity plays important roles in the catalytic activity in PTC polycondensation, as in the case of known PTC reactions.[18]

Another difference between the n-alkyltrimethylammonium bromides and tetra-n-alkylammonium bromides is that the former form micells but not the latter.[19] If PTC polycondensation takes place in the micelles, the polymerization rate will probably change at a certain n-alkyltrimethylammonium bromide concentration. The polymerization rate was measured in the THF–DMSO (3:1)/50% sodium hydroxide system at 60°C in the presence of TBAB or HDTMAB (CMC=1.0×10^{-3} mol l^{-1} at 60°C). Figure 5 shows the results as a function of concentration of TBAB or HDTMAB. In either case, parallel linear relations (slope, 0.57) were obtained. TBAB and HDTMAB, therefore, are considered to catalyze the polycondensation by the same mechanism at one of the concentrations examined in this work.

Effects of Counter Ions for Tetraalkylammonium Cations

Considering the PTC reaction mechanism proposed by Starks,[20] ion-exchange reactions seem most important in PTC polycondensations. Thus counter ions may possibly affect the reaction rate of the PTC polycondensation. The affinity of certain anions toward the benzyltrimethylammonium cation is known to be the following decreasing order[21]; $I^- > C_6H_5O^- > Br^- > CN^- > NO_3^- > Cl^- > IO_3^- > CH_3CO_2^- > OH^- > F^-$. The phenolate anion is thus replaced by a bromide or chloride anion but not an iodide anion. The catalytic activity has the decreasing order of BTEAC > BTEAB > BTEAI.
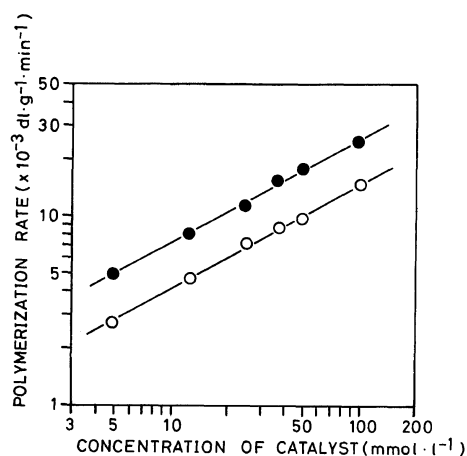
PTC polycondensations of DCPX with BPA

Figure 5. Relations between polymerization rate and concentration of TBAB (●) or HDTMAB (○). PTC polycondensations were carried out in the THF–DMSO (3:1)/50 wt% sodium hydroxide system at 60°C and the polymerization rates were plotted against the phase transfer catalyst concentration according to eq 1 to give $m = 0.57$.
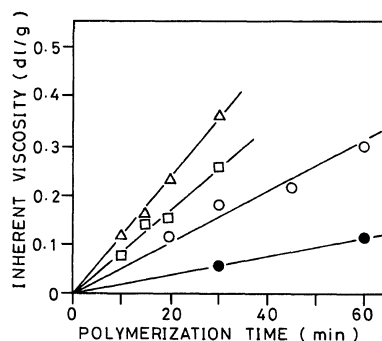
Figure 6. Effects of the counter anions toward benzyltriethylammonium cation on the PTC polycondensation of DCPX with BPA. PTC polycondensations were carried out in the THF–DMSO (3:1)/50 wt% aqueous sodium hydroxide system at 60°C with BTEAC (△), BTEAB (□), or BTEAI (○), and without a phase transfer catalyst (●).

were carried out in the presence of BTEAC, BTEAB, and BTEAI in the THF–DMSO (3:1)/50% sodium hydroxide system at 60°C. The inherent viscosities of the resulting polymers are plotted against reaction time (Figure 6), and the calculated values of the polymerization rate are summarized in the Table III.

Table III. Effects of counter anions toward benzyltriethylammonium cation and
the addition of inorganic salts to the PTC polycondensation system

Run	Monomer pair	Catalyst[a]	Salt[b]		Polymerization rate[a]	Relative polymerization rate
			mmol		$dl\,g^{-1}\,min^{-1}$	
3-1	DCPX-BPA	—	—		1.94×10^{-3}	1.0
3-2	DCPX-BPA	BTEAC	—		11.7	6.0
3-3	DCPX-BPA	BTEAB	—		8.57	4.4
3-4	DCPX-BPA	BTEAI	—		5.25	2.7
3-5	DCPX-BPA	BTEAC	Na_2SO_4	1.0	11.6	5.9
3-6	DCPX-BPA	BTEAC	PTS-Na	1.0	7.70	4.0
3-7	DCPX-BPA	BTEAC	NaI	1.0	7.73	4.0
3-8	DCPX-BPA	BTEAI	NaCl	1.0	7.70	4.0
3-9	DBPX-BPA	—	—		38.3	20
3-10	DBPX-BPA	BTEAC	—		44.6	23
3-11	DTPX-BPA	—	—		15.5	8.0
3-12	DTPX-BPA	BTEAC	—		10.1	5.2
3-13	DCPX-BPA	BTEAC	NaCl	2.0	11.3	5.8
3-14	DCPX-BPA	BTEAC	NaCl	3.0	10.9	5.6
3-15	DCPX-BPA	BTEAC	NaCl	10.1	10.9	
3-16	DCPX-BPA	BTEAC	NaCl	20.1	10.9	5.6

[a] PTC polycondensations were carried out in the THF–DMSO (3 : 1)/50 wt% aqueous sodium hydroxide system with or without a phase transfer catalyst in the presence or absence of a salt at 60°C.

[b] Concentration of salt in the aqueous layer.

The catalytic activity has, as expected, the decreasing order of BTEAC > BTEAB > BTEAI. However, this order was not so obvious for the PTC polycondensation of DBPX with BPA, since the reaction rate was too fast to measure accurately.

Anions readily soluble in an organic phase, such as p-toluenesulfonate anion, seem to affect the PTC polycondensation, since by-product molecules must be excluded from the system immediately after being produced so as to promote the polycondensation smoothly.

Two possible cases were examined, the addition of PTS-Na to the PTC polycondensation system, and the use of DTPX, liberating p-toluenesulfonate anions during the reaction, instead of DCPX. The results of the PTC polycondensation are also listed in Table III. The presence of PTS-Na obviously decreased the polymerization rate to about half that without PTS-Na (runs 3-2 vs. 3-6). However, Na_2SO_4, insoluble in an organic phase, did not

decrease the polymerization rate (runs 3-2 vs. 3-5). Furthermore, in the case of DTPX, the presence of a phase transfer catalyst such as BTEAC decreased the polymerization rate to about half that without BTEAC (runs 3-11 vs. 3-12).

Such influence of anions soluble in an organic phase probably arises from the fact that benzyltriethylammonium cations form complexes both with phenolate and p-toluenesulfonate anions to promote the polycondensation and competitive side reactions, respectively, in the reaction system.

Effects of Addition of Inorganic Salts

Anions in the aqueous phase may also affect the PTC polycondensation. Two possible cases of the PTC polycondensation, one catalyzed by BTEAC in the presence of sodium iodide and the other by BTEAI in the presence of NaCl, were carried out in the THF–DMSO (3 : 1)/50% sodium hydroxide at 60°C. In each

case, an equal molar amount of inorganic salt was added to the reaction mixture. The polymerization rates are shown in Table III. Both (runs 3-7 and 3-8) show almost the same polymerization rate, probably because an equilibrium exists in the system (eq 2).

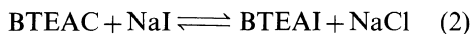$$BTEAC + NaI \rightleftharpoons BTEAI + NaCl \quad (2)$$

Table III also shows the results of PTC polycondensations carried out in a system with excess NaCl. The polycondensation proceeded smoothly even when a saturated amount of NaCl was present in an aqueous phase; the polymerization rate was $11 \times 10^{-3} \, dl \, g^{-1} \, min^{-1}$. Although the NaCl produced during the polycondensation reaction precipitated immediately from the system, the presence of the saturated amount of NaCl in the aqueous phase always resulted in the formation of a white soluble polymer even if extreme reaction conditions such as the addition of a hot aqueous alkaline solution were employed.

Since the affinity of chloride anions to benzyltriethylammonium cations (Q^+) is much higher than that of hydroxide anions as mentioned before, the formation of Q^+OH^-, which probably causes dehydrochlorination from DCPX to give the xylylidene structures, is possibly suppressed according to eq 3, when a large amount of chloride anion exists in the system.

$$Q^+OH^- + Cl^- \rightleftharpoons Q^+Cl^- + OH^- \quad (3)$$
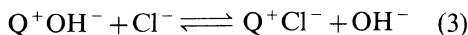
Although exact mechanism for this has not been clarified, both the ion-exchange reaction as shown in eq 3 and salting-out effect probably suppressed side reactions such as the formation of xylylidene structures in the polymer backbone. If DCPX is homopolymerized under the same reaction conditions, yellow, insoluble poly(p-xylylidene) is obtained in good yield as reported previously.[22]

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