SHORT COMMUNICATIONS

Novel Synthesis of Polymeric Phase Transfer Catalyst Containing *N,N*-Dialkylacrylamide Unit

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Phase transfer catalyst (PTC) is useful for organic chemistry and polymer chemistry.¹ Also, its application to polymer-supported PTC has been studied widely, because polymeric PTC is more economical than low molecular weight of PTC.² However, polymeric PTC has some disadvantages such as low stability and low catalytic activity. Recently, polymeric PTCs with high stability such as polymeric cosolvents³ and polymers with aryl onium salts⁴ have been reported. However, these polymeric PTCs seem to be low catalytic activity than the usual PTC.

In the previous paper,⁷ we investigated polymeric PTC containing polar groups such as *p*-nitrophenoxy group and *N,N*-dimethylacrylamide unit, which could cause polarity to increase around the polymer chain and accelerate reactions. However, this polymer did not show satisfactorily high catalytic activity, because solubility was very low for organic solvents.

This communication reports the synthesis of new polymeric PTCs containing *N,N*-dialkylacrylamide units with long alkyl groups such as *N,N*-dipropylacrylamide, *N,N*-dibutylacrylamide, and *N,N*-dihexylacrylamide units, which show high solubility for organic solvents.

Typical polymeric PTC was prepared as follows. The copolymer of CMS with *N,N*-dibutylacrylamide was prepared in 49.4% yield from radical copolymerization of CMS (4.50 g, 30 mmol) with *N,N*-dibutylacrylamide (12.83 g, 70 mmol) using 2,2'-azobis(isobutyronitrile) (0.164 g, 1 mmol) in 20 ml of benzene at 60°C for 5 h and 80°C for 3 h under nitrogen. The addition of the obtained polymer [content of chloromethyl group: 27.5 mol%, 3.50 g (5.5 mmol)] with TBP (1.34 g, 6.6 mmol) was carried out in *o*-dichlorobenzene (10 ml) at room temperature for 24 h and 100°C for 1 h, and poured into *n*-hexane (300 ml) to give 4.24 g of P-3. The degree and content of phosphonium salts of the obtained polymer were 100 mol% and 27.5 mol%, respectively, calculated from halogen analysis. The results are summarized in Table I.

A typical phase transfer catalyzed reaction of benzylchloride with solid potassium acetate is as follows: Benzylchloride (10 mmol), PTC (0.04 mmol as phosphonium salt), and 10 ml of solvent were charged into a 30 ml reaction flask kept by water jacket at 80°C. To the mixture was added potassium acetate (10 mmol) with stirring at 500 rpm, and the reaction mixture was periodically analyzed by GLC.

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Scheme 1. Synthesis of polymeric PTC.

RESULTS AND DISCUSSION

Polymeric PTCs (P-2, P-3, P-4) containing *N,N*-dialkylacrylamide units were prepared from copolymerization of CMS with *N,N*-dialkylacrylamides such as *N,N*-dipropylacrylamide, *N,N*-dibutylacrylamide, and *N,N*-diethylacrylamide followed by reaction of the resulting copolymer with TBP in dimethylformamide (DMF) or *o*-dichlorobenzene according to the synthesis of P-1 containing *N,N*-dimethylacrylamide unit (Scheme 1).⁷ The reactions proceeded smoothly to give the polymeric PTCs with pendant benzyltributylphosphonium chloride and *N,N*-dialkylacrylamide unit (Table I). The obtained polymers were soluble or swelled in toluene, ethyl ether, and *n*-hexane, whereas P-1 and the polymeric PTC (P-5) with styrene unit were insoluble in these solvents.⁷ Therefore, these two long alkyl groups improve the solubility of polymeric PTCs for organic solvents.

The phase transfer catalyzed reaction of benzylchloride with potassium acetate was carried out in solid-liquid two-phase system consisting of solution of benzylchloride and P-3 in a solvent and solid potassium acetate at 80°C. Although the reaction took no place without PTC or with poly(*N,N*-dibutylacrylamide), the addition of the polymeric PTC caused the reaction to proceed. The reaction obeyed first-order kinetics by high conversion,

Table I. Typical polymeric PTC

Polymer	Phosphonium content/mol%	Acrylamide unit content/mol%	η_{sp}/c^a
P-1	25.0	75.0	0.36 ^{b,c}
P-2	34.7	65.3	0.37 ^c
P-3	27.5	72.5	0.62 (0.10) ^d
P-4	26.7	73.3	0.49 (0.08) ^d

^a Measured at 0.5 g dl⁻¹ in nitrobenzene at 30°C.

^b Measured at 0.5 g dl⁻¹ in DMF at 30°C.

^c Polymer was insoluble in nitrobenzene-toluene (1:9) at 30°C.

^d Measured at 0.5 g dl⁻¹ in nitrobenzene-toluene (1:9) at 30°C.

and catalytic activity was evaluated using observed first-order constant (k_{obsd}). Insoluble polymeric phosphonium salt⁵ and polymeric cosolvent⁶ show the maximum catalytic activity with around 20 mol% of phosphonium salts and 50 mol% of cosolvent units, respectively. We reported⁷ that P-1 containing about 25 mol% of phosphonium salt showed maximum catalytic activity using the mixed solvent of toluene with 90 vol% nitrobenzene. However, P-3 did not show maximum catalytic activity, and was less effective than P-1, P-5, and the corresponding low molecular weight PTC benzyltributylphosphonium chloride (BTBPC) using the mixed solvent of toluene with 90 vol% nitrobenzene (Figure 1). When the mixed solvent with 10 vol%

Figure 1. Effects of phosphonium content in P-3 on catalytic activity for the reaction of benzylchloride with potassium acetate in mixed solvent of toluene with (▲) 10 vol% and (●) 90 vol% of nitrobenzene.

nitrobenzene was used, maximum catalytic activity, which was much higher than that of BTBPC, was observed using P-3 with 27 mol% of phosphonium salt. k_{obsd} of the obtained polymeric PTCs containing 25–35 mol% of phosphonium salt is summarized in Table II. k_{obsd} of P-2, P-3, and P-4 was higher than that of BTBPC and P-5 in toluene. These results suggest that the polymeric PTCs containing dialkylacrylamide unit are more effective in a low polar solvent. In addition, the viscosity of the polymeric PTC in the solvent was much lower than that in nitrobenzene. It is proposed that the polar acrylamide units of the polymer shrunk in a low polar solvent caused polarity around the polymer chain to become higher than that of the solvents, and apparent catalytic activity to increase.

The catalytic activity increased in the order of alkylchain length of the acrylamide unit in toluene: P-2 < P-3 < P-4, whereas P-1 did not show catalytic activity, because this polymer was insoluble in the solvent. The catalytic activity of P-4 in a mixed solvent with 50 vol% *n*-tridecane was about 2 times that observed in toluene, although the nucleophilicity of acetate anion was lower in the mixed solvent than that

Table II. Catalytic activity of polymeric PTC

Solvent (volume ratio)	$k_{\text{obsd}} \times 10^5/\text{s}^{-1}$				
	P-1	P-2	P-3	P-4	BTBPC
Toluene	very slow	1.08	1.21	1.79	0.48 (0.83) ^a
Toluene- <i>n</i> -tridecane (9:1)	—	1.06	1.12	2.93	0.46
(1:1)	—	—	1.10	3.67	0.30
Toluene-nitrobenzene (9:1)	2.11	1.97	2.47	2.58	0.37
(1:9)	8.98	—	4.59	—	10.02 (8.22) ^a

^a P-5: polymeric PTC containing styrene comonomer unit (phosphonium content: 13 mol%).

in toluene. P-4 was 12 times more active than that of BTBPC using a mixed solvent with 50 vol% *n*-tridecane, although P-5 hardly showed catalytic activity under these conditions. P-4 thus shows high catalytic activity in low polar solvents such as mixed solvents of toluene-*n*-tridecane. Therefore, the polymeric PTC containing lipophilic long chains such as hexyl group is desirable for polymeric PTC.

Further studies on the synthesis of polymeric phase transfer catalysts containing *N,N*-dialkylacrylamide units with long alkyl chains and their catalytic activity are now in progress.

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