

NOTES

Solid-Liquid-Solid Triphase Transfer Reaction of Poly(chloromethylstyrene)

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Recently, phase transfer catalysis has been widely used in polymer chemistry such as polymeric phase transfer catalysts, polymer syntheses, and chemical modification of polymers.^{1,2} Some new phase transfer systems such as triphase systems, which can be used in reaction using gel polymer, have been developed. In the polymeric phase transfer catalyst, the triphase system has been studied in detail.^{3,4} These systems have some advantages such as facile separation and purification of products from the reaction mixture. In the reaction of a polymer, Fréchet *et al.*⁵ reported a liquid-liquid-solid triphase system consisting of an aqueous solution of nucleophilic reagent, an organic solvent, and chloromethylated polystyrene gel.

However, triphase systems of linear polymers have not been studied except for our previous communication.⁶ In that communication, it was found that the phase transfer reaction of linear poly(chloromethylstyrene) (PCMS) with solid nucleophilic reagent proceeds smoothly in solid-liquid-solid triphase system consisting of a solid nucleophilic reagent, an organic solvent, and solid PCMS

under mild conditions using poor solvents such as *n*-hexane, cyclohexane, and diisopropyl ether.

This article reports the reaction mechanism in the solid-liquid-solid triphase transfer reaction of PCMS with nucleophilic reagents in the poor solvents, and discusses in detail suitable quaternary salts used as a phase transfer catalyst (PTC) and effect of stirring rate.

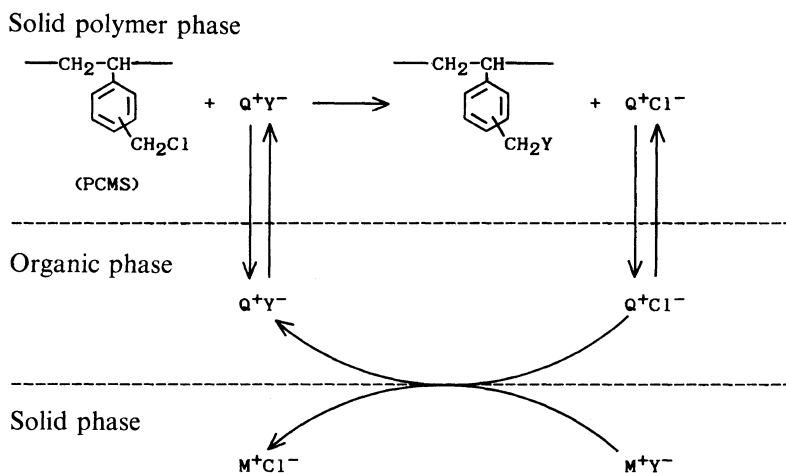
PCMS (the reduced viscosity in *N,N*-dimethylformamide (DMF) was 0.14 dl g⁻¹, measured at a concentration of 0.5 g dl⁻¹ at 30°C) was prepared in 67% yield by radical polymerization of chloromethylated styrene (mixture of 40% of *meta* and 60% *para*). The typical procedure for the solid-liquid-solid triphase reaction of PCMS is described below. 0.610 g (4 mmol) of PCMS, 0.392 g (4 mmol) of potassium acetate, and 0.129 g (0.4 mmol) of tetrabutylammonium bromide (TBAB) were dispersed in 10 ml of *n*-hexane. The mixture was stirred at *ca.* 300 rpm by magnetic stirrer at 30°C for 48 h, and then poured into 300 ml of methanol. The obtained polymer was purified by reprecipitating twice from tetrahydrofuran (THF) into water and from THF into

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methanol, and was finally dried *in vacuo* at 50°C. The yield of the resulting polymer was 0.549 g (the reduced viscosity was 0.15 dl g⁻¹, measured at a concentration of 0.5 g dl⁻¹ in DMF at 30°C). The degree of substitution was 19.8 mol%, calculated from elemental analysis of chlorine. The IR spectrum (film) showed absorptions at 1740 (C=O) and 1240 cm⁻¹ (C-O-C). The ¹H NMR spectrum (CDCl₃) showed δ =2.0 (CO-CH₃) and 4.3 ppm (CH₂-O). These IR and ¹H NMR spectra of the polymer agree with those of the corresponding polymer prepared in solid-liquid two phase system.⁷

The solid-liquid-solid triphase reaction of PCMS with some nucleophilic reagents was carried out in the poor solvents using TBAB as a PTC at 30°C for 48 h. As summarized in Table I, the reaction of PCMS with reagents took no place without PTC in *n*-hexane; how-

ever, the addition of PTC caused the reaction to proceed smoothly. The polymers with relatively high degree of substitutions were obtained from the reaction of PCMS with some reagents such as potassium azide, potassium ethyl xanthate, and potassium thiophenolate in the triphase system. This suggests that the reaction occurs inside the polymer phase as well as on the surface of PCMS. In addition, the degree of substitution tended to decrease with increasing polarity of the solvent in the order: *n*-hexane > cyclohexane > diisopropyl ether. This may be attributed to the decreasing amount of PTC with a nucleophilic anion distributed from the organic phase to the polymer phase in that order. Therefore, PTC works between the non-polar organic phase and the relatively polar solid polymer phase as shown in the following scheme.



M⁺ metal ion; Q⁺ quaternary ion; Y⁻ nucleophilic ion.

Scheme 1. PTC works between the non-polar organic phase and the relatively polar solid polymer phase.

Stirring is an important factor in phase transfer reactions. The rate of reaction is independent of stirring over 200 rpm in two phase system⁸⁻¹⁰ and 800 rpm¹¹ or 400-500 rpm¹² in triphase system using polymeric phase transfer catalyst. However, this solid-liquid-solid triphase reaction was greatly affected by

the stirring rate and the degree of substitution decreased with increase of stirring above 300 rpm as shown in Figure 1. The polymer was observed to leap out of the reaction system by stirring and to become attached to the surface of reaction flask when the stirring was too fast. Therefore, the other experiment was conduct-

Table I. Substitution reaction of PCMS with nucleophilic reagents in a solid-liquid-solid triphase system

No.	Nucleophilic reagent	Solvent	PTC	Degree of substitution
				mol%
1	CH ₃ COOK	<i>n</i> -Hexane	None	0
2	CH ₃ COOK	<i>n</i> -Hexane	TBAB	19.8
3	CH ₃ COOK	Cyclohexane	TBAB	12.5
4	CH ₃ COOK	DIPE ^a	TBAB	42.4
5	N ₃ K	<i>n</i> -Hexane	None	0
6	N ₃ K	<i>n</i> -Hexane	TBAB	70.6
7	N ₃ K	Cyclohexane	TBAB	68.1
8	N ₃ K	DIPE ^a	TBAB	22.9
9	Ph _t . K ^b	<i>n</i> -Hexane	None	0
10	Ph _t . K ^b	<i>n</i> -Hexane	TBAB	13.9
11	NCSK	<i>n</i> -Hexane	None	0
12	NCSK	<i>n</i> -Hexane	TBAB	43.3
13	NCSK	Cyclohexane	TBAB	35.7
14	NCSK	DIPE ^a	TBAB	22.9
15	KSCSOEt	<i>n</i> -Hexane	None	0
16	KSCSOEt	<i>n</i> -Hexane	TBAB	56.1
17	KSCSOEt	Cyclohexane	TBAB	68.1
18	KSCSOEt	DIPE ^a	TBAB	47.1
19	Ph-COSK	<i>n</i> -Hexane	None	0
20	Ph-COSK	<i>n</i> -Hexane	TBAB	32.2
21	Ph-SK	<i>n</i> -Hexane	None	9.6
22	Ph-SK	<i>n</i> -Hexane	TBAB	79.8

The reaction was carried out with 4 mmol of PCMS, 4 mmol of the nucleophilic reagent, and 0.4 mmol of PTC at 30°C for 48 h.

^a Diisopropyl ether.

^b Potassium phthalimide.

ed by stirring at *ca.* 300 rpm.

The effects of counter ion and length of the alkyl chains in tetraalkylammonium salts were investigated in the reaction of PCMS with potassium azide in *n*-hexane. As shown in Figure 2, the catalytic activity was markedly affected by the hydrophilicity of counter ions, which decreased in the following order: HSO₄⁻ > Cl⁻ > Br⁻ > I⁻ > ClO₄⁻.¹³ Although the quaternary ammonium salts containing hydrophilic HSO₄⁻ and lipophilic ClO₄⁻ anions showed low activity, TBAB had the highest activity in tetrabutylammonium salts. This agrees well with the result for the two phase transfer reaction of PCMS.⁹

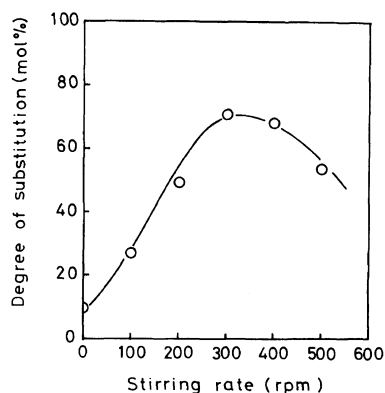


Figure 1. Effect of stirring rate by a magnetic stirrer on the solid-liquid-solid triphase reaction of PCMS with potassium azide in *n*-hexane using TBAB as a PTC at 30°C for 48 h.

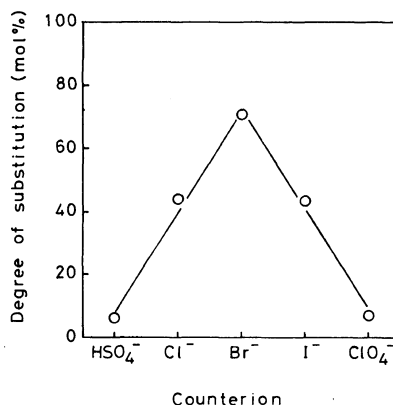


Figure 2. Relation between the degree of substitution and counter ion of tetrabutylammonium salt by the solid-liquid-solid triphase reaction of PCMS with potassium azide in *n*-hexane using TBAB as a PTC at 30°C for 48 h.

Furthermore, TBAB showed the highest catalytic activity of tetraalkylammonium bromides in the triphase system, whereas tetrapentylammonium bromide (TPeAB) was the best PTC in the two phase transfer reaction of PCMS,⁹ as shown in Figure 3. It is well-known that a tetraalkylammonium salt with lipophilic long alkylchains shows high catalytic activity as a PTC.¹⁴ However, the catalytic activity of quaternary ammonium salt interfered with steric hindrance between the quaternary am-

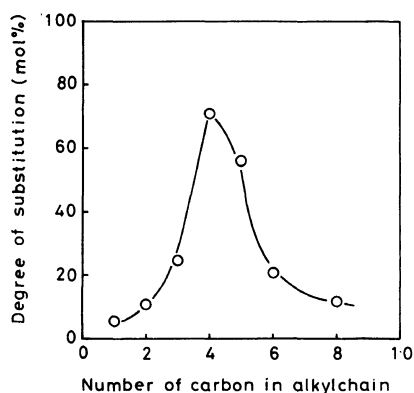


Figure 3. Relation between the degree of substitution and chain length in tetraalkylammonium bromides by the solid-liquid-solid triphase reaction of PCMS with potassium azide in *n*-hexane using TBAB as a PTC at 30°C for 48 h.

monium salt and polymer chain. Therefore, a tetraalkylammonium bromide which has good balance between lipophilicity and steric hindrance shows maximum catalytic activity, which depends on the structure of the polymer containing chlorine.^{9,10,15} In this case, it seems that the mobility of the bulky quaternary ammonium salts was strongly restricted by steric hindrance between the quaternary salts and the polymer chain in the solid polymer phase. Accordingly, a bulky quaternary ammonium salt such as TPeAB showed relatively lower catalytic activity in the solid-liquid-solid triphase system, compared with the solid-liquid two phase system.⁹ This suggests

that the activity of quaternary ammonium salts is also influenced by the surroundings of the polymer.

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