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# A New Type of Phase-Transfer Catalysts (PTC). Reaction of Substrates in the Inner Organic Phase with the Outer Aqueous Anions Catalyzed by PTC Grafted on the Capsule Membrane[1,2]

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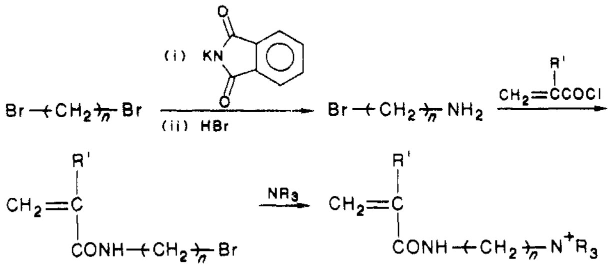
A large, ultrathin nylon capsule membrane with surface-grafted polymers having hydrophobic onium salts or poly(ethylene oxide) was prepared. The onium salt or poly(ethylene oxide) acted as a phase-transfer catalyst (PTC) across the porous capsule membrane, accelerating reactions between benzyl bromide in the inner organic phase and sodium azide in the outer aqueous phase. The reactivity was largely dependent on the hydrophobic property and the spacer chain length of onium salts, the ionic strength (concentration of $NaN_3$) of the outer aqueous phase, and the graft amount of polymers on the capsule. The capsule membrane supported PTC showed higher reactivity than usual oil/water PTC systems, because the PTC attached to long graft polymer chains could move freely between the inner organic and the outer aqueous phases.

Phase-transfer properties of onium salts, crown ethers, and poly(ethylene oxide) have found many applications in modern organic syntheses.[3-6] Insoluble polymer-supported phase-transfer catalysts promote various nucleophilic reactions between water-soluble anions and organic substrates under triphase conditions.[7-11] The catalysts can be separated from reaction mixtures without causing emulsification and can be reused. There are also drawbacks to the known triphase, polymer-supported PTC: (i) the most commonly used support for PTC is 2% cross-linked polystyrene, which may be too gelatinous in swelling solvents for repeated uses; (ii) the gel should be swelled before the reaction in order to avoid the induction period for the penetration of reactants; (iii) the reactivity is often less than that of soluble phase-transfer catalysts and largely depends on the diffusion rate of reactant through the swelled polymer matrix; (iv) the highly cross-linked macroporous support shows less reactivity than the swelled polymer matrix. The activity is improved to some extent by introducing a long spacer alkyl chain between onium salts and polymer supports.[12-14]

In this paper, we report a new type of phase-transfer catalyst (PTC) grafted onto the surface of a porous, ultrathin nylon capsule membrane. The graft polymer having hydrophobic onium salts or poly(ethylene oxide) on the capsule membrane accelerated reactions between benzyl bromide in the inner chloroform solution and sodium azide in the outer aqueous phase. A schematic illustration is showw in Figure 1. The capsule membrane supported PTC shows the high reactivity because the PTC attached to long graft polymer chains can move freely between the inner organic and the outer aqueous phase.

## Experimental Section

**Materials.** Acryloyl or methacryloyl monomers having onium salts in side chains ($A-C_n-X^+R_3$, $M-C_n-X^+R_3$) were prepared by the two routes in eq 1 and 2. ω-Bromoalkylamine ($n$ = 6, 10) were prepared by the Gabriel synthesis from α,ω-dibromoalkane and purified as HBr salts. $N$-(ω-Bromoalkyl)acryl- or -methacrylamide was prepared from ω-bromoalkylamine and acryloyl- or methacryloyl chloride in chloroform at 0 °C for 3 h in the presence of triethylamine. The quaternization with trimethylamine or tributylamine was carried out in benzene or ethanol at room temperature for 40-80 h (eq 1). The reaction mixture was evaporated, and the residue was purified by recrystallization or column chromatography: $A-C_2-N^+Me_3$, mp 130-135 °C; $A-C_6-N^+Me_3$, m 173-175 °C; $A-C_{10}-N^+Me_3$, mp 125-127 °C; $M-C_{10}-N^+Me_3$, mp 118-121 °C; $A-C_{10}-N^+Bu_3$ and $A-C_6-N^+Bu_3$, pale yellow, viscous oil.



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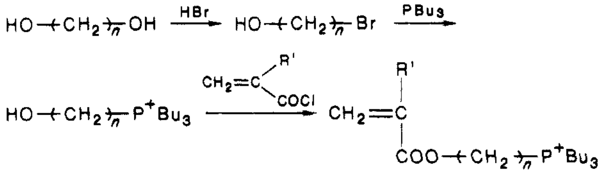

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ω-(Tributylphosphonio)alkyl alcohol, obtained by the quaternization of ω-bromoalkyl alcohol with tributylphosphine, was reacted with acryloyl or methacryloyl chloride in chloroform at 0 °C for 3 h (eq 2). The reaction mixture was purified by column chromatography. All products ($M-C_6-P^+Bu_3$, $M-C_{10}-P^+Bu_3$, $A-C_{10}-P^+Bu_3$) were pale yellow, viscous oil.

The structures and purities of all onium salt monomers were confirmed by TLC with a flame ionization detector, NMR and

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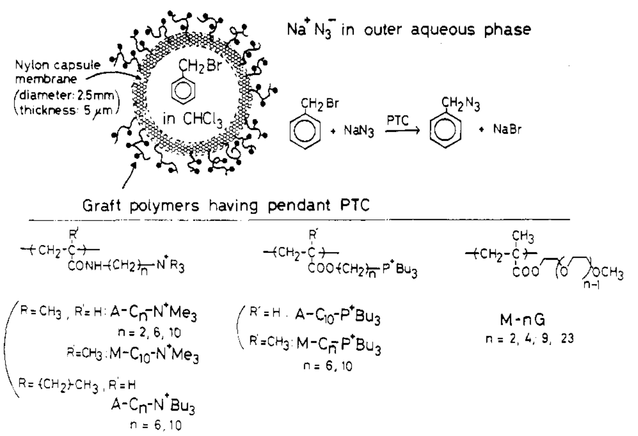

**Figure 1.** Schematic illustration of the capsule membrane supported phase-transfer catalyst (PTC). Graft polymer having onium salts (A– or M–$C_n$–$X^+R_3$) or poly(ethylene oxide) (M-*n*G) in side chains accelerated the reaction between benzyl bromide in the inner chloroform solution and sodium azide in the outer aqueous phase.

IR spectroscopy, and elemental analyses (C, H, N).

Methoxy poly(ethylene glycol) monomethacrylate (M-*n*G; *n* = 2, 4, 9, 23) was presented from Yushi-seihin Co. Ltd. M-2G and M-4G were prepared from the pure diethylene or tetraethylene glycol methyl ether and methyl methacrylate in toluene in the presence of a small amount of concentrated sulfuric acid. M-9G and M-23G were prepared from the crude poly(ethylene glycol) methyl ether (average oxyethylene units are 8.6 and 23.4, respectively) and characterized by gel permeation chromatography (column, TSK-GEL GMH$_6$ × 2; eluent; tetrahydrofuran): M-9G, $M_n$ = 480, $M_w$ = 600, $M_w/M_n$ = 1.25; M-23G, $M_n$ = 1130, $M_w$ = 1260, $M_w/M_n$ = 1.12.

**PTC-Grafted Capsule Membranes.** Large, porous nylon-2,12 capsule membranes were prepared from ethylenediamine and 1,10-bis(chlorocarbonyl)decane by interfacial polycondensation. The details were described in previous papers.[15-17] The capsule diameter and membrane thickness were 2.5 mm and 5 μm, respectively. The dry weight of a capsule was 25 ± 2 μg.

PTC monomers were grafted onto the nylon capsule membrane according to general methods.[2,18-21] A small amount (5–10 μg/capsule) of ethylene glycol dimethyacrylate was first grafted in order to introduce vinyl groups onto the capsule membrane. Twenty pieces of the obtained capsule were soaked in an aqueous and/or ethanol solution (15 mL) of the respective PTC monomer (A–, M–$C_n$–$X^+R_3$ or M–*n*G, 0.2–2.0 g) with the radical initiator (potassium persulfate, 50 mg) and the resultant mixture was kept for 2–3 h at 70 °C under nitrogen. The PTC-grafted capsules were washed and dialyzed against an excess of water, methanol, and then isopropyl alcohol to remove nongrafted polymers and unreacted monomers.

**Characterization of PTC-Grafted Capsules.** The graft amount of polymers on a capsule was determined from the weight of dried capsule membranes before and after polymerization to be 2.5–25 μg/capsule, which could be controlled by the monomer feed in the graft polymerization step.

Characterizations of the graft polymer having onium salts or poly(ethylene oxide) units were studied after complete hydrolysis of nylon capsule membranes under strong acidic conditions at 60 °C for 1 day. The residual graft polymer, poly(acrylic or methacrylic acid), was analyzed by gel permeation chromatography [column, TSK-GEL G-6000PW, Toyo Soda Co. Ltd.; eluent, 0.2 M phosphate buffer (pH 6.8) + 20% $CH_3CN$]. It was confirmed that linear polymers whose average degree of polymerization was 300–800 were grafted on capsules.

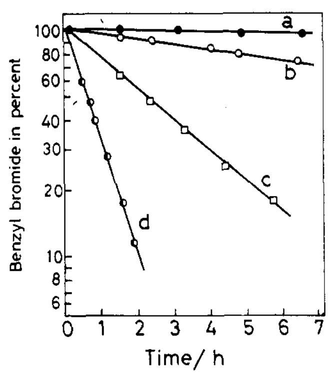

**Figure 2.** Plots of percent of benzyl bromide in the inner chloroform solution as a function of time catalyzed by PTC capsules: (a) nongrafted capsule; (b) A–$C_2$–$N^+Me_3$-grafted capsule; (c) A–$C_6$–$N^+Bu_3$-grafted capsule; (d) M–$C_6$–$P^+Bu_3$-grafted capsule. Conditions: [benzyl bromide], 2.52 × $10^{-6}$ mol in 10 μL of chloroform; [$NaN_3$], 2.55 × $10^{-2}$ mol in 5 mL of the outer aqueous phase; [PTC on the capsule membrane], (2.5 ± 0.2) × $10^{-8}$ mol of the onium monomer unit.

The surface structure of the A–$C_{10}$–$N^+Me_3$-grafted capsule was analyzed by scanning electron microscopy (SEM; instrument, Hitachi H-500) and X-ray photoelectron spectroscopy (XPS; instrument, Shimadzu ESCA 750). Graft polymers were confirmed to exist mainly on the outer surface of the capsule membrane from the SEM observation. XPS spectra were obtained at the take-off angle of 90° that corresponds to the probing depth of 3–6 nm from the surface. The peak of $N_{1S}$ corresponding to ammonium groups of graft polymers was mainly observed on the outer surface, but not the inner surface, of the capsule membrane. These results clearly indicate that PTC polymers grafted on the only outer surface of capsules.

**Rate Measurements.** PTC-grafted capsules containing isopropyl alcohol in the inner core were dialyzed against a chloroform solution of benzyl bromide for 2 days to obtain capsules containing (0.63–2.52) × $10^{-6}$ mol of substrates in the inner core (10 μL). Reactions were started under shaking at 30 °C in 5 mL of an aqueous solution with a large excess of sodium azide [(0.65–25.5) × $10^{-3}$ mol, 0.13–5.10 M], after dropping one PTC-grafted capsule containing benzyl bromide in the inner chloroform phase. Within the prescribed time interval, the capsule was removed from the aqueous solution and crushed in chloroform, and the reduction of benzyl bromide and the production of benzyl azide in the inner phase were monitored by HPLC up to ca. 90% conversion [instrument, Toyo Soda HLC-803C with UV detector; column, TSK gel ODS-120T; eluent, isopropyl alcohol: water = 3:2; flow rate, 0.5 mL min$^{-1}$]. Identification of benzyl azide was made by comparison of the HPLC retention time and IR spectra with that of the authentic sample.

## Results and Discussion

**Phase-Transfer Catalysis.** The production of benzyl azide in the inner organic phase of the PTC-grafted capsule membrane could be followed by HPLC analyses, when the PTC-grafted capsule containing benzyl bromide in the inner chloroform solution was soaked in the aqueous solution of sodium azide azide under shaking at 30 °C (see equation in Figure 1). Figure 2 shows typical examples of semilogarithmic plots of the reduction of benzyl bromide in the inner organic phase of the capsule as a function of time. The reactions followed the pseudo-first-order kinetics up to 90% conversion of substrates in the presence of a large excess amount of $NaN_3$ in the outer aqueous phase. The capsule grafted with (2.5 ± 0.2) × $10^{-8}$ mol of the onium salt unit (or 6–13 μg of graft polymers) per capsule were employed. An induction period for the reaction was not observed, which had frequently been observed in insoluble polymer-supported PTC because of

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**Table I. Rates of the Reaction Catalyzed by PTC-Grafted Capsule Membranes at 30 °C**[a]

| PTC grafted on capsules | graft amt/capsule[b]/μg | $k_{obsd}/10^{-6}$ $s^{-1}$ | rate enhancement |
|---|---|---|---|
| ungrafted | | 3.5 | 1 |
| $A-C_2-N^+Me_3$ | 6.0 | 12.1 | 3.4 |
| $A-C_6-N^+Me_3$ | 7.3 | 20.6 | 5.9 |
| $A-C_{10}-N^+Me_3$ | 8.5 | 51.2 | 15 |
| $M-C_{10}-N^+Me_3$ | 9.0 | 60.5 | 17 |
| $A-C_6-N^+Bu_3$ | 10 | 116 | 33 |
| $A-C_{10}-N^+Bu_3$ | 12 | 174 | 50 |
| $M-C_6-P^+Bu_3$ | 11 | 239 | 68 |
| $A-C_{10}-P^+Bu_3$ | 12 | 167 | 48 |
| $M-C_{10}-P^+Bu_3$ | 13 | 146 | 42 |
| $C_{10}-P^+Bu_3$ in capsule[c] | 10 | 53.7 | |
| $(C_8)_3-N^+Me$ in capsule[c] | 10 | 43.4 | |
| $(C_8)_3-N^+Me$ in oil/water[e] | 10 | 48.2 | |
| M-2G | 12[d] | 8.68 | 2.5 |
| M-4G | 12[d] | 19.7 | 5.6 |
| M-9G | 9.3[d] | 40.2 | 12 |
| M-23G | 8.0[d] | 30.3 | 8.6 |

[a] Benzyl bromide, 2.52 × $10^{-6}$ mol in the inner chloroform solution (10 μL) of a capsule; $NaN_3$, 2.5 × $10^{-2}$ mol in the outer aqueous solution (5 mL). [b] Onium salt, (2.5 ± 0.2) × $10^{-8}$ mol/capsule. [c] Dodecyltributylphosphonium bromide ($C_{10}-P^+Bu_3$, 10 μg, 2.4 × $10^{-8}$ mol) or trioctylmethylammonium chloride ($(C_8)_3-N^+Me$, 10 μg, 2.5 × $10^{-8}$ mol) was dissolved in the inner chloroform solution of the ungrafted capsule. [d] Ethylene oxide unit, (1.5 ± 0.2) × $10^{-7}$ mol/capsule. [e] $(C_8)_3-N^+Me$ (2.5 × $10^{-8}$ mol) was dissolved in usual $CHCl_3$/water two-phase systems.

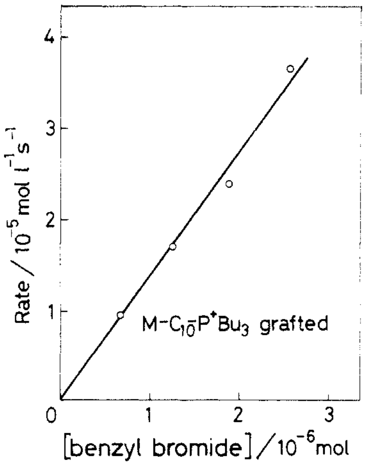


**Figure 3.** Effect of concentration of benzyl bromide in the inner organic phase (10 μL) on the reaction rate catalyzed by the capsule grafted with $M-C_{10}-P^+Bu_3$ (2.5 × $10^{-8}$ mol/capsule): $[NaN_3]$ = 2.55 × $10^{-2}$ mol in 5 mL of the outer aqueous phase.

swelling of the resin.[7-11] The $k_{obsd}$ values obtained from the slope of Figure 2 are summarized in Table I, together with those of other capsule membrane supported PTC.

The effect of the concentration of benzyl bromide in the inner organic phase on the reaction rate is shown in Figure 3 when the capsule grafted with $M-C_{10}-P^+Bu_3$ was employed. The rate increased linearly with increasing the concentration of substrate in the presence of a large excess amount of $NaN_3$ in the outer aqueous phase (eq 3.) The

$$\text{rate} = k_{obsd}[\text{substrate}] \qquad (3)$$

similar results were observed when other PTC-grafted capsule membranes were employed. These results indicate that the rate-limiting step is the nucleophilic substitution process, but not the phase-transfer process of $N_3^-$ anions from the aqueous to the organic phase.

**Effect of Structure of PTC Polymers.** The $k_{obsd}$ values of the substitution of benzyl bromide by $N_3^-$ catalyzed by the capsule membrane supported PTC are summarized in Table I. The PTC capsules were employed whose concentration of onium salts or ethylene oxide units was (2.5 ± 0.2) × $10^{-8}$ or (1.5 ± 0.2) × $10^{-7}$ mol/capsule, respectively.

When the ungrafted, original nylon capsule was employed, the reaction was very slow at 30 °C ($k_{obsd}$ = 3.50 × $10^{-6}$ $s^{-1}$, $t_{1/2}$ = 55 h). In the case of the capsule grafted with A– or $M-C_n-X^+R_3$ having onium salts in the side chain, the $k_{obsd}$ value was increased by a factor of 3–68 compared with that of the ungrafted capsule. The extent of the rate acceleration of the reaction largely depended on both the spacer chain length ($C_n$) and the hydrophobic nature of onium salts ($-X^+R_3$). Thus, when the capsules grafted with a series of $A-C_n-N^+Me_3$ having trimethylammonium salt in side chains were employed, the reactivity was increased with increasing the spacer chain length form $C_2$ to $C_{10}$. The similar trend was observed in the catalysis of the capsule grafted with $A-C_n-N^+Bu_3$ ($n$ = 6, 10) polymers. In the comparison of $A-C_{10}-X^+R_3$-grafted capsules, the reactivity increased with increasing the hydrophobicity of onium salts in the order of $P^+Bu_3$ = $N^+Bu_3$ > $N^+Me_3$. When the capsule grafted with the hydrophobic tributylphosphonium monomer (A–, M–$C_n-P^+Bu_3$) was employed, the reactivity was decreased with increasing the spacer chain length from $C_6$ to $C_{10}$ and with increasing the hydrophobicity of a polymer main chain from acrylate (A–) to methacrylate (M–). Thus, the suitable extent of hydrophobicity of the onium salt is required to give the high reactivity as a phase-transfer catalyst, and the $M-C_6-P^+Bu_3$ polymer showed the highest reactivity ($k_{obsd}$ = 2.39 × $10^{-4}$ $s^{-1}$, 68 times larger than the ungrafted capsule).

The relative reactivity of the PTC capsule was compared with a monomeric PTC (decyltributylphosphonium bromide, $C_{10}-P^+Bu_3$, trioctylmethylammonium chloride, $(C_8)_3N^+Me$) dissolved in the inner organic phase of the ungrafted capsule or a monomeric PTC dissolved in usual oil/water two phases (see Table I). The capsule grafted with $M-C_6-P^+Bu_3$ showed 4–5 times higher reactivity than those of the ungrafted systems. Insoluble polymer-supported PTC, triphase catalysts, usually show the reduced reactivity compared with soluble PTC, the extent depending on the spacer chain length between onium salts and supports and on the swelling of the resin.[7,12-14] In the case of the PTC capsule, however, onium salts attached to long graft-polymer chains (degree of polymerization, 300–800) would be able to exist and move freely in the interface of the inner organic and the outer aqueous phases and hence would show the high reactivity.

When the capsule grafted with methoxy poly(ethylene glycol) monomethacrylate (M-$n$G) was employed, the reactivity increased only by a factor of 2.5–12 times relative to that of the ungrafted capsule. The extent of the rate acceleration of the reaction was not as large as that of the onium polymer grafted capsule, and it depended on the length of the poly(ethylene oxide) side chain of the polymer. Thus, the $k_{obsd}$ value increased with increasing the poly(ethylene oxide) chain length from 2G to 9G and slightly decreased in the case of M-23G. The poly(ethylene oxide) units in side chains interact with $Na^+$ in the outer aqueous phase and bring $N_3^-$ as a counteranion to the oil/water interface or the inner organic phase. The shorter poly(ethylene oxide) unit of grafted monomers cannot strongly interact with $Na^+$ and hence show the lower reactivity. In the case of the capsule grafted with M-23G, the graft polymer having 23 units of ethylene oxide in side chains, may be too hydrophilic to bring $N_3^-$ anions to the inner organic phase. As a result, the M-9G showed the

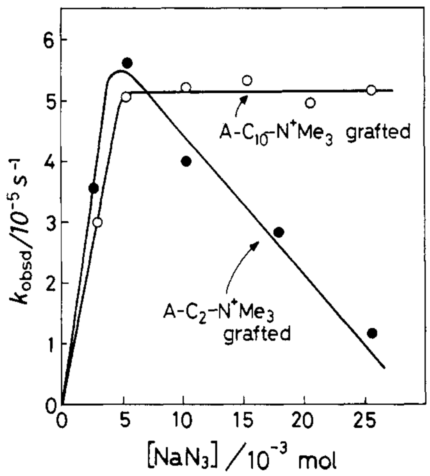


**Figure 4.** Effect of the concentration of $NaN_3$ in the outer aqueous phase on $k_{obsd}$ values at 30 °C: [benzyl bromide] = $2.52 \times 10^{-6}$ mol in chloroform (10 $\mu$L); [onium salt] = $(2.5 \pm 0.2) \times 10^{-8}$ mol/capsule.

highest reactivity because of the suitable length of ethylene oxide units to interact with $Na^+$ and the suitable hydrophobicity of monomers.

The M-$n$G polymer showed the lower reactivity than the onium polymer did. It was reported that onium salts and crown ethers gave the high reactivity in liquid–liquid and solid–liquid two-phase-transfer systems, respectively.[7] Since the M-$n$G-grafted capsule did not show the high reactivity in this liquid–liquid two-phase systems, the detailed study of M-$n$G-grafted capsule was not carried our further more.

**Effect of Ionic Strength.** The effect of the concentration of $NaN_3$ in the outer aqueous phase on the $k_{obsd}$ value is shown in Figure 4. In the case of the capsule grafted with $A-C_{10}-N^+Me_3$, the $k_{obsd}$ value increased linearly with increasing the concentration of $NaN_3$ below $5 \times 10^{-3}$ mol in 5 mL of aqueous phase and was independent of the $NaN_3$ concentration in the range of $(5–25) \times 10^{-3}$ mol. This clearly indicates that the exchange of the counteranion in the aqueous phase has no effect on reaction rates when $5 \times 10^{-3}$ mol of $NaN_3$ exists in 5 mL of the outer aqueous phase (1.0 M). The concentration of onium salts on a capsule surface is estimated to be 0.8 M when $5 \times 10^{-8}$ mol of onium salts is grafted onto $6 \times 10^{-11}$ m$^3$ of the capsule membrane (capsule diameter, 2.5 mm; membrane thickness, 5 $\mu$m). Thus, the concentration of $NaN_3$ giving the saturated velocity ($5 \times 10^{-3}$ mol in 5 mL = 1.0 M) is roughly consistent with the concentration of onium salts on a capsule ($5 \times 10^{-8}$ mol in $6 \times 10^{-11}$ m$^3$ = 0.8 M).

In the case of the capsule grafted with $A-C_2-N^+Me_3$, however, the reactivity decreased with an increase in concentration of $NaN_3$ above $5 \times 10^{-3}$ mol. It is explained that the PTC having the short, $C_2$ spacer chain may be easily sealed in the entangled, salted-out polymers in the high concentration of $NaN_3$ and the reactivity decreased with increasing the ionic strength. In contrast, the reactivity of the $A-C_{10}-N^+Me_3$-grafted capsule was not affected even in the high ionic strength of the outer phase, probably because the PTC having the long $C_{10}$ spacer chain can move freely if polymer main chains are entangled. The hydrophobic PTC having a long spacer chain may form a micellar-like structure in the oil/water interface, and the reactivity may not be reduced in the high ionic strength condition.

**Effect of Graft Amounts of PTC Polymers.** Figure 5 shows the effect of the graft amount of onium polymers per capsule on $k_{obsd}$ values. When the monomeric PTC, $(C_8)_3N^+Me$, was dissolved in the inner organic phase of the ungrafted capsule, the $k_{obsd}$ value increased linearly with increasing PTC concentration. On the contrary, when capsules grafted with $M-C_{10}-P^+Bu_3$ and $A-C_{10}-N^+Me_3$ were employed, the $k_{obsd}$ values increased with an increase in the graft amount on the capsule membrane and reached a plateau at $(2–3) \times 10^{-8}$ mol of onium salts per capsule. This indicates that over $(2–3) \times 10^{-8}$ mol of onium salt on the capsule membrane cannot work as effectively as PTC because of the limiting surface area of a capsule membrane.

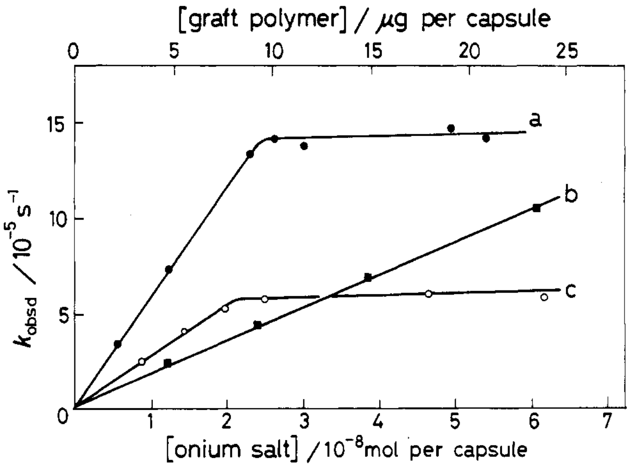


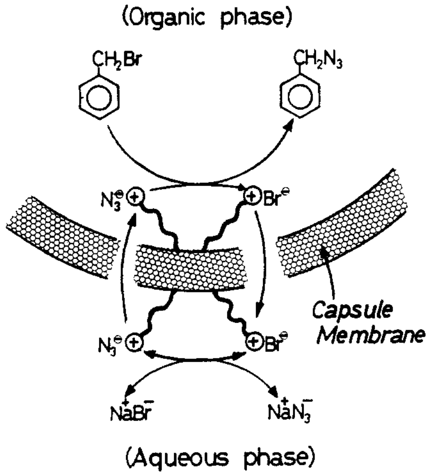
**Figure 5.** Effect of graft amount of PTC polymers on $k_{obsd}$ values at 30 °C: (a) $M-C_{10}-P^+Bu_3$-grafted capsule; (b) $(C_8)_3-N^+Me$ dissolved in the ungrafted capsule; (c) $A-C_{10}-N^+Me_3$-grafted capsule. Conditions: [benzyl bromide] = $2.52 \times 10^{-6}$ mol in 10 $\mu$L of the inner chloroform; [$NaN_3$] = $2.55 \times 10^{-2}$ mol in 5 mL of the outer aqueous phase.

**Reaction Mechanism and Microstructure of PTC Capsules.** Nylon-2,12 capsule membranes are reported[16] to have the asymmetrical structures: the very thin inner layer and the macroporous, thick part of the outer side. A large number of pores in the sponge layer arise naturally during the formation of capsule membranes by the interfacial polymerization. PTC polymers may be grafted in the thick sponge part of capsule membranes.

PTC capsules showed the saturated reactivity when $(2–3) \times 10^{-8}$ mol of onium salts (7–12 $\mu$g of graft polymers) exists on a capsule membrane (see Figure 5). This value roughly corresponds that $3 \times 10^{13}$ polymer chains whose degree of polymerization is 300–800 (ca. 70–200-nm length) are grafted on $6 \times 10^{-11}$ m$^3$ of sponge layer of capsules (capsule diameter, 2.5 mm; membrane thickness, 5 $\mu$m). Thus, one polymer chain having 300–800 pendant onium salts is calculated to be grafted per $2 \times 10^3$ nm$^3$ of the 5-$\mu$m-thick sponge layer of the capsule.

The interface between the outer chloroform and the inner aqueous phases would exist in the sponge layer of the capsule, in which PTC polymer is grafted. If onium salts on graft polymers act as a true phase-transfer catalyst between two phases, the reaction mechanism can be written as shown in Scheme I. The first step is the exchange of the counteranions of the PTC capsule from $Br^-$ to $N_3^-$ in the outer aqueous phase. The second step is the phase transfer of $N_3^-$ from the outer aqueous to the inner organic phase across the capsule membrane. The third, rate-limiting step is the nucleophilic substitution of benzyl bromide by $N_3^-$ anions in the inner organic phase or the oil/water interface. For another possibility, hydrophobic onium polymers may form the micellar-like oil/water interface in the sponge layer of the capsule, in which catalysts act more micellar than phase transfer. Benzyl bromide (or benzyl azide) and $N_3^-$ anions did not exist in the outer

Scheme I



aqueous and the inner organic phases, respectively, after a capsule was crushed. This denies the possibility of the micellar formation or the emulsion-like environment in the interface of the capsule membrane. Kinetic results were properly consistent with the usual phase-transfer catalysis mechanism: the concentration of $NaN_3$ in the outer phase giving the saturated value is roughly consistent with the concentration of onium salts on a membrane surface, and the reactivity reaches a plateau when the concentration of onium salts increases on a capsule surface. These results indicate that onium-polymers act as a true phase-transfer catalyst but not a micellar-like catalyst at the interface of the capsule membrane.

## Summary

The PTC-grafted capsules showed the high reactivity in the reaction between substrates in the inner organic phase and aqueous nucleophilic anions in the outer phase. The reactivity was largely dependent on the hydrophobic property and the spacer chain length of onium salts, the ionic strength (concentration of $NaN_3$) of the outer aqueous phase, and the graft amount of polymers on the capsule. The capsule membrane supported PTC was the following features: (1) the high reactivity due to the onium salts attached as the long graft polymer chains; (2) no induction period for the reaction caused by swelling of supports, which has been frequently observed in the insoluble polymer-supported PTC; (3) easy separation of the catalyst and the inner organic phase from the outer aqueous phase by picking up the PTC capsule. PTC-grafted capsule membranes are the new type of phase-transfer catalysts and may be useful in many heterogeneous reactions.

**Registry No.** $PhCH_2Br$, 100-39-0; $NaN_3$, 26628-22-8; poly(ethylene oxide), 25322-68-3.

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# Host–Guest Complexation. 41. Preorganization of a Host Enhances Its Binding of Aryldiazonium Salts[1]

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Synthetic host 1, a spherand comprised of cyclic urea and aryl ether units, has been designed and examined. It displays markedly superior binding of aryldiazonium tetrafluoroborate salts over previously reported complexing agents. Qualitative experiments indicate a higher degree of stabilization of complexed diazonium salts toward thermal decomposition and azo dye formation than is given by 18-crown-6. Quantitative infrared studies yield an approximate binding free energy of −5.9 kcal mol$^{-1}$ for the complexation of $p$-$(CH_3)_3CC_6H_4N_2BF_4$ by 1 in $ClCH_2CH_2Cl$ at 25 °C, appreciably higher than the −3.6 kcal mol$^{-1}$ determined for 18-crown-6 under identical conditions. Addition of an aqueous solution of $Na_2CO_3$ to a colorless solution of $CH_2Cl_2$ containing $C_6H_5N(CH_3)_2$ and 1 complexed to $p$-$(CH_3)_3CC_6H_4N_2BF_4$ instantaneously released the aryldiazonium ion which coupled to form the azo dye. The alkali metal salts bind 1 much more strongly than does the aryldiazonium salt. Thus the $Na^+$ ion acts as a trigger for dye formation, the system as a whole acting as an indicator for the presence of alkali metal ions.

Following the first report[3,4] in 1973 that corands (crown ether like hosts) lipophilize and stabilize aryldiazonium tetrafluoroborate salts, a variety of studies of coraplexes[5] have been reported.[6] The original evidence[3,4] that complexation occurred by insertion of the $-N_2^+$ group into the macroring was corroborated by the crystal structure determination of 18-crown-6·$C_6H_5N_2PF_6$.[7] Figure 1 provides

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(5) Cram (Cram, D. J. *Angew. Chem.* **1986**, in press) has suggested the general common names podaplex, coraplex, cryptaplex, spheraplex, etc. for denoting the complexes of podands, corands, cryptands, and spherands, respectively.

(6) Bartsch, R. A. *Progress in Macrocyclic Chemistry*; Izatt, R. M., Christensen, J. J., Eds.; Wiley Interscience: New York, 1981; Vol. 2, Chapter 1, pp 1–39.

(7) Haymore and Huffman (Haymore, B. L.; Huffman, J. C. Presented at the 4th *Symposium on Macrocyclic Compounds*, Provo, UT, August 1980) determined this structure. In a personal communication they kindly supplied its Ortep drawing, and the following crystallographic data for 18-crown-6·$C_6H_5N_2PF_6$: a (Å) = 11.091 (3), $b$ (Å) = 8.789 (2), c (Å) = 24.080 (7), $\beta$ = 93.20 (1)°; $Z$ = 4; space group $P2_1/n$; temperature, −170 °C; 2657 reflections, $I > \sigma(I)$; $R(F)$, 0.064; $R_w(F)$, 0.065; N≡N distance (Å), 1.092 (4); effective diameter, 2.86 Å. They also supplied the crystal structure of $C_6H_5N_2BF_4$: a (Å) = 5.636 (2), $b$ (Å) = 8.337 (3), $c$ (Å) = 17.345 (12), $\beta$ = 92.20 (1); Z = 4; space group $P2_1/c$; temperature, −160 °C; 1008 reflections, $I > \sigma(I)$; $R(F)$, 0.057; $R_w(F)$, 0.048; N≡N distance (Å), 1.108 (3).

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