Capsule Membrane-supported Phase-transfer Catalysts[1]

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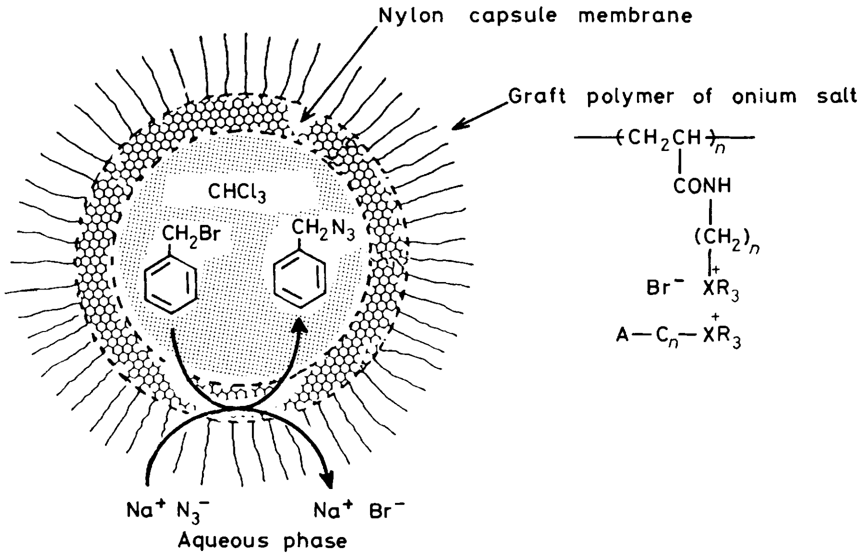
Quaternary ammonium and phosphonium salts of acryloyl monomers can be grafted onto a large, ultrathin nylon capsule membrane and act as phase-transfer catalysts accelerating reactions between substrates in the inner organic phase and water-soluble anions in the outer phase.

Phase-transfer properties of onium salts and crown ethers have found wide application in modern organic syntheses. Insoluble polymer-supported phase-transfer catalysts (PTC) promote reactions between water-soluble anions and organic substrates under triphase conditions.[2—4] The catalysts can be easily separated from the reaction mixtures and can be reused; however, their activity is often less than that of soluble phase-transfer catalysts. The activity is improved to some extent by introducing a long spacer alkyl chain between the onium salt and polymer support.[4]

We describe here a new type of phase-transfer catalyst (PTC) grafted onto the surface of a porous nylon capsule membrane.

The capsule membrane-supported PTC accelerated reac-



n = 2,6,10
X = N,P
R = Me, Bu

Scheme 1. Membrane diameter 2 mm, thickness 1 μm.

tions between substances in the inner organic phase and water-soluble anions in the outer aqueous phase. A schematic illustration is shown in Scheme 1.

Large, porous ultrathin nylon-2,12 capsule membranes were prepared according to established methods.[5] The onium salts of the acryloyl monomer ($A\text{-}C_n\text{-}X^+R_3$) were synthesized from the *N*-bromoalkylacrylamide and the trialkylamine or trialkylphosphine. Their structures were confirmed by t.l.c., n.m.r. spectroscopy, and elemental analyses (C, H, and N). Graft polymerization of the onium salts ($A\text{-}C_n\text{-}X^+R_3$) onto the capsule membrane was carried out in an aqueous solution of acidic cerium(IV) ammonium nitrate at room temperature for 4 h in a nitrogen atmosphere, as described previously.[6] The polymer-grafted capsules obtained were washed with excess water and then iso-propyl alcohol to remove non-grafted polymers and unreacted monomers. Elemental analyses, weighing before and after polymerization, and direct ESCA analyses of the polymer-grafted capsules confirmed that 7—10 μg (5×10^{-8} mol of onium units) of linear polymers (average degree of polymerization 10^3) were grafted onto the surface of a capsule membrane of dry weight 20 ± 2 μg.

PTC-grafted, porous capsules containing iso-propyl alcohol in the inner phase were immersed in a chloroform solution of benzyl bromide to obtain capsules containing 2.52×10^{-6} mol substrate in the inner chloroform solution (10 μl). Reactions were carried out at 30 °C in 5 ml aqueous solution with a large excess of NaN_3 [$(5.0$—$25) \times 10^{-3}$ mol, 1—5 M], by dropping into the solution one PTC-grafted capsule containing benzyl bromide in the inner organic phase. The capsule was removed from the aqueous solution, crushed in chloroform, and the production of benzylazide in the inner phase was monitored by h.p.l.c. The reactions followed the pseudo-first order kinetics up to 90% conversion of substrates in the presence of a large excess of NaN_3. An induction period for the reaction was not observed, which has frequently been observed in insoluble polymer-supported PTC because of swelling of the resin.[2—4] The $k_{obs.}$ values obtained are summarized in Table 1.

Table 1. Rates of reaction catalysed by PTC-grafted capsule membranes at 30 °C.[a]

	$k_{obs.}/10^{-6}\,s^{-1}$	
PTC-grafted capsules	1 M NaN_3	5 M NaN_3
Ungrafted	0.73	3.50
$A\text{-}C_2\text{-}N^+Me_3$ grafted	57.3	12.1
$A\text{-}C_6\text{-}N^+Me_3$ grafted	55.3	20.6
$A\text{-}C_{10}\text{-}N^+Me_3$ grafted	50.6	51.2
$A\text{-}C_{10}\text{-}N^+Bu_3$ grafted	162	174
$A\text{-}C_{10}\text{-}P^+Bu_3$ grafted	170	167
$3C_8\text{-}N^+Me$ in a capsule[b]	41.4	43.4
$C_{10}\text{-}P^+Bu_3$ in a capsule[b]	68.2	50.8

[a] Catalysts: 5×10^{-8} mol of onium monomer grafted per capsule, benzyl bromide: 2.52×10^{-6} mol in the inner chloroform solution (10 μl) of a capsule, NaN_3: 1 or 5 M in the outer aqueous solution [(5 or 25) $\times 10^{-3}$ mol in 5 ml, respectively]. [b] The PTC was dissolved in the inner chloroform phase of the ungrafted capsule.

When the polymer-ungrafted capsule was employed, the nucleophilic substitution reaction between benzyl bromide in the inner chloroform solution and excess of NaN_3 in the outer aqueous solution was very slow at 30 °C {$k_{obs.}$ 0.73—$3.50 \times 10^{-6}\,s^{-1}$, [$NaN_3$] = 1—5 M}. However the extent to which PTC-grafted capsules accelerate the reaction depends on both the spacer chain length and the hydrophobicity of onium salt monomers. In the presence of a relatively low concentration of NaN_3 (1 M), the spacer chain length of $A\text{-}C_n\text{-}N^+Me_3$ monomers hardly affected the reactivity. The capsule grafted with $A\text{-}C_{10}\text{-}N^+Bu_3$ or $A\text{-}C_{10}\text{-}P^+Bu_3$, relatively hydrophobic onium salts showed the three times higher reactivity than the presence of a soluble PTC (trioctylmethylammonium chloride, $3C_8\text{-}N^+Me$, or decyltributylphosphonium bromide, $C_{10}P^+Bu_3$) in the inner organic phase. Insoluble polymer-supported PTC (triphase catalysts) usually show reduced reactivity compared with soluble PTC, the extent depending on the spacer chain length and the swelling of polymer supports.[2—4] In the case of PTC-grafted capsules, however, onium salts attached to long graft-polymer chains would be able to move freely between the inner organic and the outer aqueous phase, and hence show high reactivity.

In the presence of a high concentration of NaN_3 (5 M) in the outer phase, the reactivity of the catalyst with the short spacer chains ($A\text{-}C_n\text{-}N^+Me_3$, $n = 2, 6$) was considerably reduced by comparison with $A\text{-}C_{10}\text{-}N^+R_3$. The grafted polymer chain may shrink in the high concentration of NaN_3 aqueous solution owing to the salting-out effect.

In conclusion, the capsule membrane-supported PTC has the following features: (i) the high reactivity due to onium salts attached as long graft-polymer chains; (ii) there is no induction period for the reaction caused by swelling of supports; and (iii) easy separation of the catalyst and the inner organic phase from the outer aqueous phase. PTC-grafted capsule membranes should be useful in many heterogeneous reactions.

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