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POLYMER-SUPPORTED CRYPTANDS AS CATALYSTS FOR PHASE-TRANSFER REACTIONS

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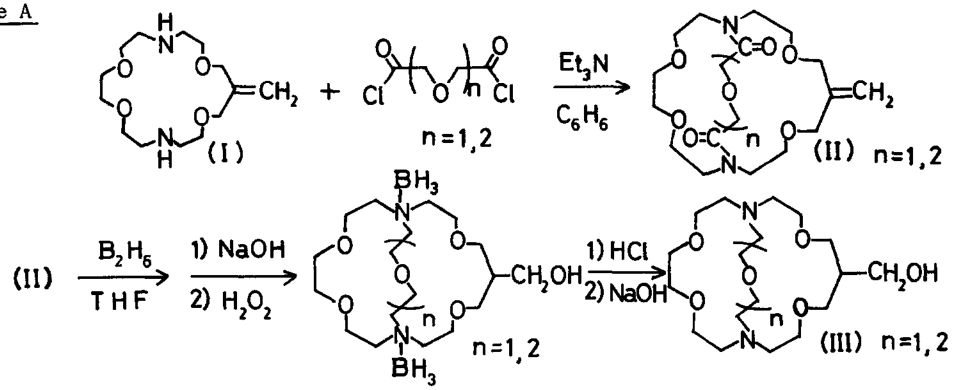
Polymer-supported cryptands were prepared by the reaction of hydroxyl-containing cryptands and chloromethylated polystyrene resin. The polymer-supported cryptands were effective catalysts for aqueous organic two-phase reactions.

It is well-known that cryptands[1] containing hydrophobic groups catalyze aqueous organic two-phase reactions. Moreover, polymer-supported cryptand [2.2.2] have been prepared and successfully used as a catalyst for the two-phase reactions.[2] The polymer-supported cryptand can be removed at the end of the reaction by simple filtration and reused.

We wish to report the synthesis of new cryptands containing hydroxyl group, and the immobilization of the cryptands on a polymer support. The cryptands with hydroxyl group were prepared by the method as shown in Scheme A. Bicyclic diamides (II) with methylene group were prepared by the reaction of methylene-19-diazacrown-6 (I)[3] and diglycolyl chloride[4] or triglycolyl chloride.[4] The diamides (II) could be converted to hydroxymethyl-cryptands (III)[5] by reduction[4] and hydroboration—oxidation.[6]

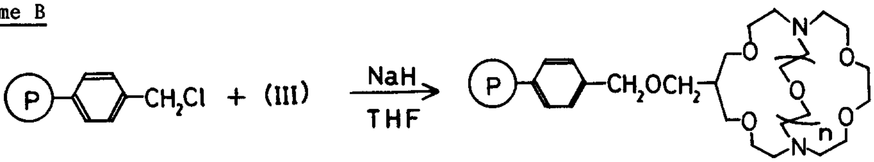
Scheme A



Polymer-supported cryptands (IV) were prepared by the reaction of (III) and chloromethylated polystyrene resin cross-liked with 10% divinylbenzene (macroreticular type; 4.7 mequiv of Cl per g of polymer), in the presence of NaH, in refluxing THF (Scheme B). Compounds (IVa) and (IVb) contained 0.83 and 1.14 mmol of cryptand unit per g of polymer, respectively. This is a convenient method for the immobilization of cryptands.

The aqueous organic two-phase reactions (halogen exchange and cyanation) were carried out, under magnetic stirring, in the presence of the polymer-supported cryptands (See Table). The polymer-supported cryptands were found to be highly effective catalysts for the two-phase

Scheme B



(IVa) n=1; (IVb) n=2

reactions. In the case of the halogen exchange the reused catalyst showed very low catalytic activity, but the activity was restored by the treatment of the catalyst with $Na_2S_2O_3$. Such an inhibition of the catalytic effect must have been caused by triiodide ion.[7] The activity of the reused catalyst (treated with $Na_2S_2O_3$) was slightly higher than that of the original one. It may be due to the increase in surface area of the catalyst since the catalyst was ground during the reaction with magnetic stirring.[3,8] The activity of the polymer-supported cryptands for the cyanation was dependent on the species of alkali cations used. Using the CPK model approach, it is evident that polymer-supported cryptands (IVa) and (IVb) have cavity sizes suited for the ionic diameters of sodium ion and potassium ion, respectively. The result of the cyanation could be explained in terms of the fact that (IVa) is more specific for sodium ion than potassium ion, while (IVb) is more specific for potassium ion. In the case of the halogen exchange, however, the activity was largely independent of the species of the alkali cations.

Table. PHASE-TRANSFER REACTIONS CATALYZED POLYMER-SUPPORTED CRYPTANDS[a)]

Reagent[b)]	Catalyst	[Cryptand unit]/[Substrate]	Time(hr)	Yield(%)[c)]
KI	(IVa)	0.01	6	77
"	(IVb)	"	"	77
"	(IVb)[d)]	"	"	5
"	(IVb)[e,g)]	"	"	80
"	(IVb)[f,g)]	"	"	88
NaI	(IVa)	"	"	80
"	(IVb)	"	"	78
KCN	(IVa)	0.02	4	50
"	(IVb)	"	"	76
NaCN	(IVa)	"	"	100
"	(IVb)	"	"	63

a) Substrate, octyl bromide; temp, 80°C. b) Saturated aq soln, 7.0 mol equiv.
c) By g.l.c. analysis. d) Reused catalyst (not treated with sodium thiosulfate).
e) Reused (1st) catalyst. f) Reused (2nd) catalyst. g) Treated with sodium thiosulfate and sodium chloride.

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