

Polymeric analogues of dipolar aprotic solvents as phase transfer catalysts

Shuji Kondo*, Kunihiro Ohta, Yasuhito Inagaki, Makoto Minafuji, Haruhiko Yasui, Nobuo Nakashima, Masaki Iwasaki, Keizo Furukawa and Kazuichi Tsuda

Department of Applied Chemistry, Nagoya Institute of Technology,
Gokisocho, Showa-ku, Nagoya 466 Japan

Abstract - Soluble polymers containing dipolar aprotic solvent moieties such as dimethyl sulfoxide, sulfolane, N,N-dimethylformamide, N,N-dimethylacetamide, N-methylpyrrolidone, tetramethylurea and their analogues were prepared by free-radical polymerization and copolymerization of corresponding monomers. These polymers serve as effective phase transfer catalysts for several reactions under liquid-liquid two-phase condition. The catalytic activity of the copolymers containing styrene units is generally higher than that of homopolymers. It was found that these polymers extract all alkali metal cations more effectively than their monomeric analogues, and that the extraction ability increases with increasing density of active sites, suggesting their cooperative effect. It is reasonable to assume that the catalytic activity is due to both cation extraction ability of the polymers and the activation of anions caused by desolvation in the hydrophobic regions of polymers. Insoluble polymers containing dipolar aprotic solvent moiety as well as partially alkylated poly-L-leucine and Nylon-66 also exhibit phase transfer catalytic activity.

INTRODUCTION

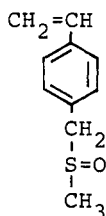
Recently various polymeric phase transfer catalysts have been developed and have become a useful technique in organic synthesis. Most of these polymers were prepared by merely anchoring classical phase transfer catalysts such as ammonium salts, phosphonium salts, crown ethers, cryptands, and linear polyethers on insoluble polymer supports (ref. 1-6). Though the relationship between polymer structure and catalytic activity has been discussed from several viewpoints, the effect of the environment around the active site has not been investigated in a satisfactory way because the distribution of active sites in polymers prepared by polymer reaction is not uniform. In addition, the catalytic activity of insoluble polymers is generally lower than that of soluble catalysts.

On the other hand, polymers containing dipolar aprotic solvents as hexamethylphosphoramide (HMPA) (ref. 7,8), dimethyl sulfoxide (DMSO) (ref. 9-12), sulfolane (ref. 13), N,N-dimethylformamide (DMF) (ref. 14), N,N-dimethylacetamide (DMAc) (ref. 15,16), N-methylpyrrolidone (ref. 17), have been found to display a similar activity to polymeric phase transfer catalysts mentioned above, although the monomeric analogues are ineffective. However, the studies on this type of catalysts have not been performed systematically. In this paper, we wish to review our recent studies which concern polymeric analogues of dipolar aprotic solvents as phase transfer catalysts.

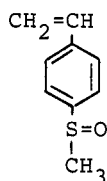
PREPARATION OF MONOMERS

In order to obtain the information about the catalysis in detail, we need the polymers with well-defined structure as well as the number and distribution of functional group. Therefore, we carried out the preparation of catalysts by the free radical polymerization of monomers containing dipolar aprotic solvent structures.

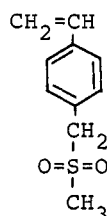
Though many types of monomers possessing dimethyl sulfoxide structure are possible to design, we thought that methyl *p*-vinylbenzyl sulfoxide (BSO) was suitable in terms of the compound with high polymerizability and with no other functional group except for sulfinyl group. BSO



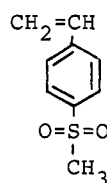
BSO



PSO



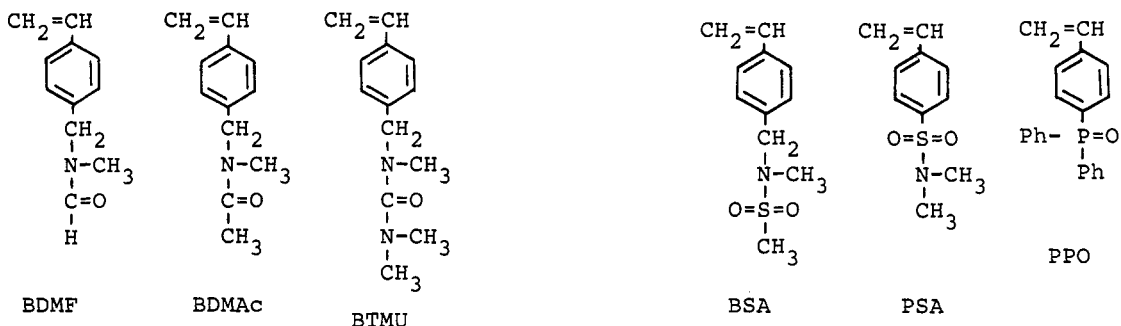
BSO₂



PSO₂

was prepared readily by the selective oxidation of methyl *p*-vinylbenzyl sulfide with sodium metaperiodate (ref. 18,19). However, this monomer has an acidic hydrogen at benzylic position which is not always stable under phase transfer reaction conditions. In order to overcome this disadvantage, other sulfoxide monomer, methyl *p*-vinylphenyl sulfoxide (PSO) was prepared by the similar method to the case of BSO. Methyl *p*-vinylbenzyl sulfone (BSO₂) and methyl 4-vinylphenyl sulfone (PSO₂) as model monomers of sulfolane were prepared by the oxidation of corresponding sulfides with hydrogen peroxide.

N-Methyl-*N*-(*p*-vinylbenzyl)formamide (BDMF) as a monomer having *N,N*-dimethylformamide structure was prepared readily from the reaction of *p*-chloromethylstyrene with *N*-methylformamide in the presence of sodium hydride. Similarly, *N*-methyl-*N*-(*p*-vinylbenzyl)acetamide (BDMac) and *p*-vinylbenzyl-trimethylurea (BTMU) were prepared as corresponding monomers of *N,N*-dimethylacetamide and tetramethylurea respectively.



As analogous compounds of dipolar aprotic solvents, sulfonamides are interesting (ref. 20). A monomer containing sulfonamide structure, *N*-methyl-*N*-(*p*-vinylbenzyl)methanesulfonamide (BSA), was prepared from the reaction of *p*-chloromethylstyrene with *N*-methylmethanesulfonamide. *N,N*-Dimethylstyrenesulfonamide (PSA) was prepared by the treatment of *p*-styrenesulfonyl chloride with dimethylamine.

Dipolar aprotic solvents are regarded as compounds having polar double bond which contain an oxygen atom with high electron density. From this viewpoint, we hoped that phosphine oxides might show similar behavior to dipolar aprotic solvents. Thus, diphenyl-*p*-vinylphenylphosphine oxide (PPO) was prepared.

All these monomers are readily homopolymerized in benzene or dimethyl sulfoxide in the presence of azobisisobutyronitrile (AIBN). From the copolymerization with styrene, *Q* and *e* values of these monomers were calculated (Table 1).

PREPARATION OF SOLUBLE POLYMER CATALYSTS

Based on the copolymerization parameters, various types of copolymers of a functional monomer and styrene were prepared. General formula of these copolymers is expressed as follows. In this formula, *x* and *y* show the mol fraction of each monomer in percent in copolymers.

G	Abbreviation
CH_2SOCH_3	PBSO(<i>x</i>)
SOCH_3	PPSO(<i>x</i>)
$\text{CH}_2\text{SO}_2\text{CH}_3$	PBSO ₂ (<i>x</i>)
SO_2CH_3	PPSO ₂ (<i>x</i>)
$\text{CH}_2\text{N}(\text{CH}_3)\text{CHO}$	PBDMF(<i>x</i>)
$\text{CH}_2\text{N}(\text{CH}_3)\text{COCH}_3$	PBDMac(<i>x</i>)
$\text{CH}_2\text{N}(\text{CH}_3)\text{CON}(\text{CH}_3)_2$	PBTMU(<i>x</i>)
$\text{PO}(\text{C}_6\text{H}_5)_2$	PPPO(<i>x</i>)

Extraction of alkali metal ions

Polymeric sulfoxides (PBSO, PPSO) and sulfones (PBSO₂, PPSO₂) are soluble in benzene, toluene, and methylene chloride, but insoluble in water. Therefore, phase transfer of metal ions from water into these organic phases should be possible if the polymers are effective phase transfer catalysts. In order to assess the ability of these polymers as phase transfer catalysts, we have determined the extraction of picrate salts from water to benzene in the presence of these polymers and monomeric analogues of these polymers. The results are summarized in Table 2.

TABLE 1. Q and e values of monomers containing dipolar aprotic solvent structures and their analogues

Monomer	Q	e
BSO	1.03	0.28
PSO	1.19	0.58
BSO ₂	0.93	0.21
PSO ₂	1.53	0.45
BDMF	0.80	-0.38
BDMAc	0.83	-0.22
BTMU	0.61	-0.35
BSA	1.50	-0.71

TABLE 3. Phase transfer halogen exchange reactions of octyl bromide with alkali metal iodides catalyzed by polymeric sulfoxides and sulfones

Metal iodide	Catalyst	Yield (%)
KI	Me ₂ SO	trace
KI	PhSOMe	trace
KI	PhCH ₂ SOMe	trace
KI	sulfolane	trace
KI	PhCH ₂ SO ₂ Me	trace
KI	PPSO(30)	62
NaI	PPSO(30)	77
LiI	PPSO(30)	89
NaI	PBSO(49)	73
NaI	PPSO ₂ (33)	38
NaI	PBSO ₂ (31)	61

[n-C₈H₁₇Br] = 0.55 M in toluene, 3 ml;
[MI] = 4.0 M in H₂O, 5 ml; catalyst 0.3 mmol (based on active group); 100°C, 20 h.

TABLE 2. Extraction or adsorption of picrate salts by polymeric sulfoxides and sulfones

Catalyst	Picrate salt extracted (%)		
	Li ⁺	Na ⁺	K ⁺
PhSOMe	0	0	0
PhCH ₂ SOMe	0	0	0
PhCH ₂ SO ₂ Me	0	0	0
PPSO(100)	14	9	13
PPSO(67)	12	6	10
PPSO(55)	7	2	5
PPSO(30)	2	1	2
PBSO(49)	6	5	5
PBSO ₂ (100)	-	4	-
PBSO ₂ (47)	-	3	-
PBSO ₂ (25)	-	1	-
CPSO(75-23-2)	17	7	9
CPSO(48-50-2)	13	3	3
CPSO(33-65-2)	4	1	2
CPSO(50-48-2)	-	3	-
CPSO(49-46-5)	-	2	-
CPSO(44-46-10)	-	2	-

Solvent system H₂O/benzene (5 ml/20 ml); [Picric acid] = 5.0 × 10⁻⁵ M; [MOH] = 1.0 × 10⁻² M (M: Li, Na, K); 6.3 × 10⁻⁶ mol catalyst (based on active group); CPSO particle size 100-200 mesh

TABLE 4. Phase transfer reaction of benzyl bromide with sodium phenoxide

Catalyst	Total yield (%)	Product distribution (%)	
		O-Alkylation	C-Alkylation
PPSO(55)	98	100	0
PPSO ₂ (47)	26	97	3
PBDMF(57)	85	100	0
PBDMAc(56)	82	100	0
PBTMU(100)	59	100	0

[PhCH₂Br] = 0.55 M in toluene, 3 ml; [PhONa] = 2.0 M in H₂O, 5 ml; Catalyst 0.3 mmol (based on active group)

As can be seen from Table 2, polymeric sulfoxides and sulfones extract alkali metal ions such as Li⁺, Na⁺, and K⁺, but monomeric sulfoxides and sulfone, such as methyl phenyl sulfoxide, benzyl methyl sulfoxide, and methyl benzyl sulfone do not to any detectable degree. Further, the cation extraction ability increases with increasing active site density in the polymer. This result can be explained in terms of cumulative chelation of metal ions with several sulfinyl or sulfonyl groups. Similar tendency was obtained for the extraction with polymeric formamides, acetamides, ureas, and phosphoramides (ref. 7,12,13,14,16). Though Li⁺ and K⁺ seem to be extracted to a somewhat higher degree than Na⁺, a clear selectivity with respect to alkali metal ions was not found.

Furthermore, in an extraction experiment, the concentration of monomeric sulfone in benzene decreased after addition of sodium picrate to the aqueous solution. From this observation we believe that monomeric species is also able to interact with sodium ions at the interface to form the complex, which is quickly transferred into the aqueous phase. The low-molecular sulfone complex is soluble in water, in contrast to the polymeric sulfone complex. Thus, the essential difference in extraction ability between polymeric and monomeric species might be due to the difference of lipophilicity.

Phase transfer reactions catalyzed by soluble polymers

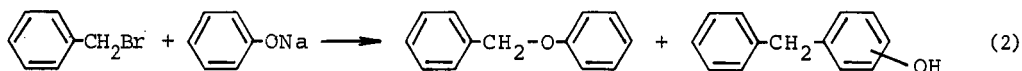
The catalytic activity of soluble polymeric sulfoxides and sulfones was tested in the reaction of octyl bromide with iodide anion.



These reactions were carried out in a toluene-water two-phase system, and the results are shown in Table 3. As can be seen from this table, these reactions are accomplished in the

presence of polymer catalysts PPSO(30), PBSO(49), PPSO₂(33), and PBSO₂(31), but are not catalyzed by monomeric sulfoxides and sulfones such as dimethyl sulfoxide, methyl phenyl sulfide, benzyl methyl sulfoxide, sulfolane, and benzyl methyl sulfone. It should be noted that the catalytic activity of polymers is superior to that of their monomeric analogues. These results may be due to the extraction ability of alkali metal ions. Polymeric formamides, acetamides, ureas, and phosphine oxides display the catalytic activity for these reactions although the monomeric analogues are ineffective.

It is well known that the reaction of benzyl bromide with phenoxide affords C-alkylation product in water, whereas in organic solvents having no ability of hydrogen bond, O-alkylation occurs (ref. 21). In order to obtain the information about the reaction phase, we examined this reaction using polymeric catalysts (Table 4).



The reaction proceeded in the presence of PPSO(55) to give O-alkylation product, benzyl phenyl ether exclusively. Other catalysts gave the same result except for PPSO₂(40). In the case of PPSO₂(40), a small amount of C-alkylation product was observed. Thus, it was established that most of the reactions occur in organic phase.

In order to obtain further information about the reaction phase, the reaction of octyl methanesulfonate with sodium halides was investigated (Table 5).

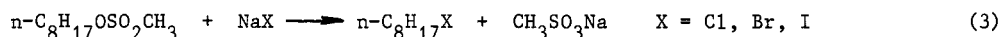


TABLE 5. Phase transfer reaction of octyl methanesulfonate with sodium halides catalyzed by PBTMU(100)

Sodium halide	$k_{\text{obsd}} \text{ (s}^{-1}\text{)}$
NaCl	2.8×10^{-6}
NaBr	9.1×10^{-6}
NaI	3.8×10^{-5}

[$n\text{-C}_8\text{H}_{17}\text{OSO}_2\text{CH}_3$] = 1.65 M in toluene, 1.67 ml; [NaX] = 4.0 M in H₂O, 15 ml; catalyst 0.5 mmol (based on active group); 100°C.

Polymeric urea PBTMU(100)-catalyzed reaction showed that the reactivity of nucleophile decreases in the order $\text{I}^- > \text{Br}^- > \text{Cl}^-$. This order does not coincide with the order in anhydrous chlorobenzene, indicating the existence of water in reaction phase (ref. 22).

From the found data, we believe that the catalytic activity of these polymers can be attributed to the initial coordination of metal cation to oxygen atom of active site in polymers at the interface and subsequent transfer of the cation together with the anion from aqueous phase to organic phase. The anion would attack the substrate in organic phase where a small amount of water exists which might come to organic phase with hydrated anion.

Dependence of catalytic activity on polymer structure

In order to obtain the relationship between structure and activity, the reaction of octyl bromide with sodium iodide was examined kinetically using polymeric sulfoxides of different composition. The reactions were monitored by GLC analysis and followed pseudofirst-order kinetics.

A comparison of the efficiency of the polymeric sulfoxides PPSO is provided in Fig. 1. The catalytic activity of homopolymer is very low, but the pseudofirst-order rate constant increases significantly when the percentage of sulfoxide unit in copolymer decreased from 100 to approximately 30. This means that in the composition range the catalytic activity is inversely related to the cation extraction ability mentioned above. Especially, it is worth noting that the reaction rate increases almost 200 fold if the catalyst contains styrene as a co-unit, although the cation extraction ability decreased slightly. This finding strongly suggests that the catalytic activity is not affected by the cation extraction ability, but also by the hydrophobic environment of the active sites. Based on these results, we think that the phase-transferred anions are scarcely solvated in copolymers with styrene units in contrast to homopolymer PPSO(100). This difference in solvation seems to be the cause of the catalytic activity.

In the percentage range of sulfoxide units below 30, the catalytic activity decreased with decreasing density of sulfoxide units, which is consistent with the cation extraction ability.

Dependence of catalytic activity on polymer composition was also investigated for other polymeric sulfoxides and sulfones. The results are also shown in Fig. 1. In addition to these polymers, the activity of polymeric formamides and acetamides showed the same tendency as

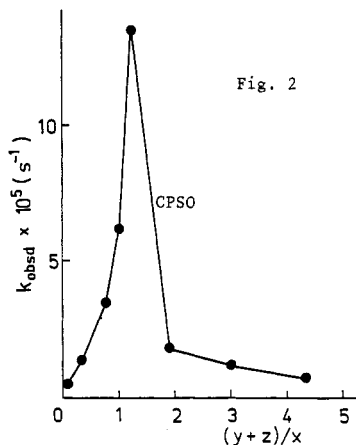
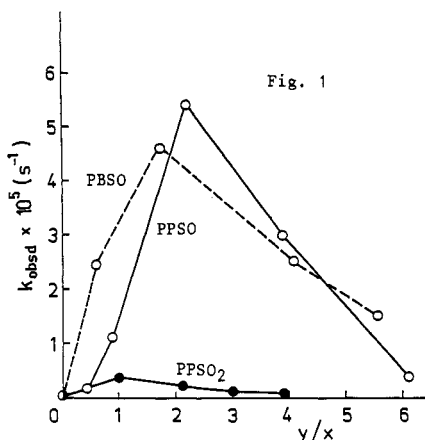
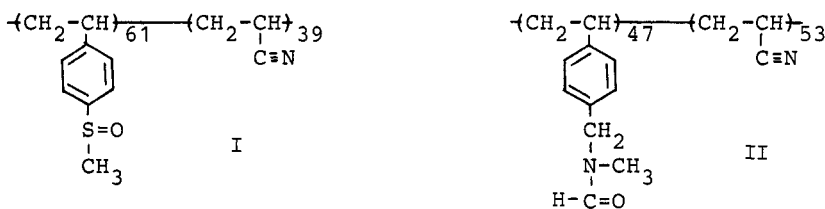


Fig. 1 and 2. Dependence of the observed pseudofirst-rate constant (k_{obsd}) in the reaction of octyl bromide with NaI on composition ratio of catalyst $[\text{n-C}_8\text{H}_{17}\text{Br}] = 0.55 \text{ M}$ in toluene, 5 ml; $[\text{NaI}] = 4.0 \text{ M}$ in H_2O , 15 ml; 0.5 mmol catalyst (based on active groups); CPSO particle size 100-200 mesh; stirring speed 1000 rpm

polymeric sulfoxides PPSO with respect to polymer composition. On the other hand, in polymeric ureas PBTMU, the catalytic activity increases with increasing active site density, in accord with the extraction ability. This finding suggests that the hydrophobicity around the active site is sufficient without the assistance of styrene. The same phenomenon was found for polymeric phosphine oxides PPPO and polymeric phosphoramides (ref. 7).

Furthermore, the importance of hydrophobic environment around the active site was implied from the following experiment. When a polar monomer such as acrylonitrile was employed as comonomer instead of styrene, the resulting copolymers I and II did not catalyze the halogen exchange reaction though they have sufficient extraction ability.



Use of conventional monomers for the preparation of phase transfer catalysts

Considering above facts, we hoped that copolymers of styrene and conventional monomers such as acrylamide, *N*-methylacrylamide, *N,N*-dimethylacrylamide, and *N*-vinylpyrrolidone might exhibit the catalytic activity in phase transfer reactions.

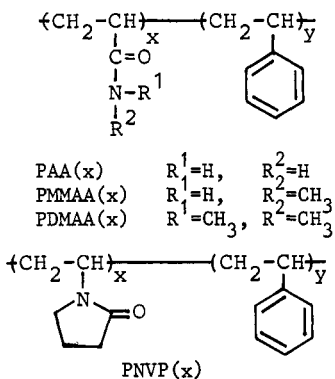


TABLE 6. Phase transfer reaction of octyl bromide with potassium thiocyanate catalyzed by polyacrylamides and polyvinylpyrrolidone

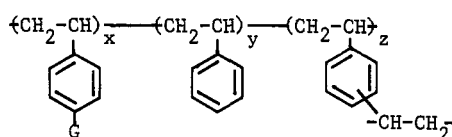
Catalyst	Organic solvent	Yield (%)
CH_3CONH_2	<i>o</i> -dichlorobenzene	trace
$\text{CH}_3\text{CON}(\text{CH}_3)_2$	"	trace
PAA(100)	"	trace
PMMAA(100)	"	17
PDMAA(100)	"	33
PDMAA(33)	"	68
PNVP(100)	toluene	trace
PNVP(39)	"	71

$[\text{n-C}_8\text{H}_{17}\text{Br}] = 0.55 \text{ M}$ in organic solvent, 3 ml; $[\text{KSCN}] = 8.0 \text{ M}$ in H_2O , 5 ml; 0.3 mmol catalyst (based on amide group); 100°C , 20 h.

The catalytic activity was estimated by usual method. The results are provided in Table 6. In polyacrylamides, catalytic activity can be found on the substitution of amino hydrogen with methyl group. Further, it was found that the copolymers with styrene have higher catalytic activity than the homopolymer. Not surprisingly, polymeric analogues of *N*-methylpyrrolidone do indeed function as phase transfer catalysts.

PREPARATION OF INSOLUBLE POLYMER CATALYSTS

Insoluble polymers containing dipolar aprotic solvent structures are of interest for both the easiness of work-up and the reaction mechanism in comparison to soluble catalysts. These polymers were prepared by free-radical terpolymerization of corresponding functional monomers, styrene, and divinylbenzene. The catalysts obtained were crushed and separated with sieves. The structures are shown in next formula where x, y, and z express the mol percentage of each monomer in copolymer.



G	Abbreviation
SOCH ₃	CPSO(x-y-z)
SO ₂ CH ₃	CPSO ₂ (x-y-z)
CH ₂ N(CH ₃)CHO	CDMF(x-y-z)
CH ₂ N(CH ₃)COCH ₃	CDMAc(x-y-z)
CH ₂ N(CH ₃)CON(CH ₃) ₂	CTMU(x-y-z)
SO ₂ N(CH ₃) ₂	CPSA(x-y-z)
CH ₂ N(CH ₃)SO ₂ CH ₃	CBSA(x-y-z)

Phase transfer reactions catalyzed by insoluble polymers

The catalytic activity of insoluble polymeric sulfoxides CPSO was examined in the reaction of octyl bromide and sodium iodide under toluene-water two-phase conditions. In order to obtain the information about the experimental parameters, we firstly examined the dependence of rate on the stirring speed. As can be seen from Table 7, the rate increased upon increasing the stirring speed up to almost 1000 rpm, and remained constant beyond this value. Therefore, reactions were carried out by stirring at 1000 rpm to minimize the influence of diffusion. As shown in Table 7, the rate of the catalytic substitution reaction also depends on particle size. From these results, it was indicated that mass transfer is an important factor in these reactions.

Dependence of the rate on the degree of crosslinking is also shown in Table 7. If the degree of crosslinking is high, the degree of activity would be decreased because the flexibility of active site would be restricted. Although the effect was observed, the extent was very little in the copolymers employed here. Further, the effect of organic solvent was investigated by using hexane, toluene, and chlorobenzene. The results are provided in Table 7. The degree of acceleration by catalyst decreased in the order chlorobenzene > toluene > hexane. This order is in agreement with the order of swelling. These results show that the intraparticle diffusion cannot be ignored in these catalytic reactions.

TABLE 7. The effect of various factors on rate constants of the reaction of octyl bromide with sodium iodide catalyzed by crosslinked polymeric sulfoxides

Stirring speed ^{a,b} (rpm)	$k_{\text{obsd}} \times 10^5$ (s ⁻¹)	Particle size ^{c,d} (mesh)	$k_{\text{obsd}} \times 10^5$ (s ⁻¹)
0	3.4	60 - 100	3.4
500	4.9	100 - 200	4.6
750	5.5	200 - 300	4.7
1000	6.1	300 - 400	4.8
1250	6.2		
1600	6.2		

Crosslinking degree ^{b,d} (%)	$k_{\text{obsd}} \times 10^5$ (s ⁻¹)	Solvent system ^{b,c}	$k_{\text{obsd}} \times 10^5$ (s ⁻¹)
2 ^e	6.1	Dodecane-H ₂ O	2.5
5 ^f	5.9	Toluene-H ₂ O	3.4
10 ^g	5.2	Chlorobenzene-H ₂ O	5.6

[n-C₈H₁₇Br] = 0.55 M in toluene, 5 ml; [NaI] = 4.0 M in H₂O, 15 ml; 0.5 mmol catalyst (based on active groups) ^aCPSO (50-48-2); ^bparticle size 100-200 mesh; ^cCPSO (57-41-2); ^dstirring speed 1000 rpm; ^eCPSO (50-48-2); ^fCPSO (49-46-5); ^gCPSO (44-46-10).

The main object of this study is to understand the relationship between the activity and microenvironment around the active site. For comparison with soluble catalysts, adsorption of alkali metal picrates on crosslinked polymeric sulfoxides was examined. As shown in Table 2,

the polymers employed here have adsorption ability for Li^+ , Na^+ , and K^+ , and the ability increases with increasing active site density in the polymer. Namely, the trend of adsorption ability is parallel to the extraction ability of corresponding soluble polymeric sulfoxides.

The dependence of the activity on the composition of copolymer was also investigated, and the results are shown in Fig. 2. Interestingly, the activity is affected remarkably by composition ratio, and there is maximum at certain composition ratio. This fact indicates the importance of hydrophobicity around the active site (ref. 23). The same phenomena were observed for the reaction of octyl bromide with potassium thiocyanate in the presence of insoluble polymeric formamides and acetamides (CDMF, CDMac) (ref. 24). Based on the above facts, we think that there is no essential difference between the soluble and insoluble polymer catalyzed phase transfer reaction except for the importance of intraparticle diffusion in insoluble polymers.

Polymeric formamides and acetamides are not stable under strong alkali conditions. In order to overcome this disadvantage, polymeric sulfonamides CPSA and CBSA were prepared. The catalytic activity was tested for the reaction of octyl bromide with sodium thiophenoxide. The results are summarized in Table 8. Although these polymers display the catalytic activity, the acceleration effect is not high (ref. 25).

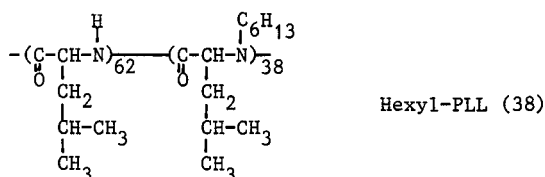
TABLE 8. Phase transfer reaction of octyl bromide with sodium thiophenoxide catalyzed by polymeric sulfonamides

Catalyst	$k_{\text{obsd}} \times 10^5 \text{ (s}^{-1}\text{)}$
-	6
$\text{PhSO}_2\text{N(CH}_3)_2$	7
CPSA(98-0-2)	17
CPSA(55-43-2)	43
CPSA(18-80-2)	12
$\text{PhCH}_2\text{N(CH}_3)_2\text{SO}_2\text{CH}_3$	8
CBSA(98-0-2)	32
CBSA(47-51-2)	51
PBSA(16-82-2)	19

$[\text{n-C}_8\text{H}_{17}\text{Br}] = 0.55 \text{ M}$ in toluene, 5 ml; $[\text{NaSPh}] = 2.0 \text{ M}$ in H_2O , 15 ml; $[\text{catalyst}]/[\text{n-C}_8\text{H}_{17}\text{Br}] = 1:5$; catalyst particle size 60-100 mesh; stirring speed 1000 rpm.

Catalytic activity of partially alkylated poly-L-leucine

In the case of polyacrylamides, we have already described that the catalytic activity is increased remarkably by substitution of amino hydrogen with methyl group. This finding prompted us to examine the catalytic activity of alkylated poly(amino acids). The alkylation of poly-L-leucine was carried out by the use of hexyl chloride and sodium hydride.



As can be seen from Table 9, alkylated poly-L-leucine Hexyl-PLL (38) is more effective than poly-L-leucine as phase transfer catalyst (ref. 25).

TABLE 9. Phase transfer reaction of octyl bromide with potassium thiocyanate catalyzed by poly-L-leucine

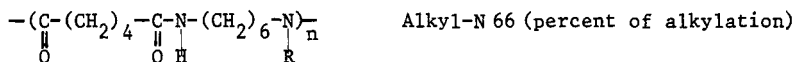
Catalyst	Yield (%)
Poly-L-leucine	8
Hexyl-PLL (38)	85

$[\text{n-C}_8\text{H}_{17}\text{Br}] = 1.65 \text{ M}$ in toluene, 1.5 ml; $[\text{KSCN}] = 8.0 \text{ M}$ in H_2O , 2.5 ml; $[\text{catalyst}]/[\text{n-C}_8\text{H}_{17}\text{Br}] = 1:5$; 100°C, 20 h.

Alkylated Nylon-66 as phase transfer catalysts

Judging from the results obtained with alkylated poly-L-leucine, we hoped that polymeric amides containing the active site along the main chain and their alkylated derivatives might work as phase transfer catalysts. Thus we focused the attention to Nylon-66 because it is

a cheap commercial polymer. The alkylation was carried out by the same method as with poly-L-leucine.



The application of these polymers to organic synthesis was investigated, and the results are summarized in Table 10. Surprisingly, Nylon-66 exhibits the catalytic activity for the reaction of octyl bromide with potassium thiocyanate in two-phase system, although the activity is low. As we expected, the activity was increased enormously by substituting the amino hydrogen with alkyl groups such as octyl and lauryl. These alkylated Nylon-66 are effective as catalysts for the reaction of octyl bromide with sodium thiocyanate, lithium thiocyanate, potassium iodide, sodium phenoxide, and sodium thiophenoxide. The yield of these reactions could be increased by using a large amount of catalyst and longer reaction time (ref. 26).

TABLE 10. Phase transfer reactions of octyl bromide with several nucleophiles catalyzed by partially alkylated Nylon-66

Reagent	Catalyst	[Amide]/[n-C ₈ H ₁₇ Br]	Time (h)	Yield (%)
KSCN	Nylon-66	0.2	24	16
KSCN	Lauryl-N66 (19)	0.2	24	67
KSCN	Lauryl-N66 (33)	0.2	24	70
KSCN	Lauryl-N66 (19)	0.4	24	80
KSCN	Lauryl-N66 (19)	0.8	24	92
KSCN	Octyl-N66 (25)	0.2	24	62
NaSCN	Octyl-N66 (25)	0.2	24	75
LiSCN	Octyl-N66 (25)	0.2	24	24
KI	Octyl-N66 (25)	0.2	48	99
NaOPh	Octyl-N66 (25)	0.2	24	30
NaSPh	Octyl-N66 (25)	0.2	5	99

[n-C₈H₁₇Br] = 1.65 M in toluene, 1.5 ml; [KSCN], [NaSCN], [LiSCN] = 8.0 M in H₂O, 2.5 ml; [KI] = 4.0 M in H₂O, 2.5 ml; [NaOPh], [NaSPh] = 2.0 M in H₂O, 2.5 ml; 100°C.

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