Polymeric Sulphones as Phase Transfer Catalysts

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Polymeric sulphones prepared by radical polymerization of sulphone monomers with styrene serve as effective phase transfer catalysts, and their catalytic activity markedly depends on both cation binding ability and lipophilicity around the active sites in the polymer.

Polymeric phase transfer catalysts (PTCs) have recently been developed because of the ease of work-up procedures. Most were prepared by merely anchoring soluble classical PTCs such as onium salts, crown ethers, cryptands, and linear polyethers to insoluble polymer supports.[1] However, the catalytic activity is generally lower than that of soluble catalysts. Polymers containing dipolar aprotic solvents as the active sites have been found to display a similar activity to the polymeric PTCs mentioned above,[2] although the monomeric analogues are ineffective. In this article, we describe a new type of soluble polymeric PTC, polymeric sulphones.

Catalysts (**1**) and (**2**) were prepared by free radical polymerization or copolymerization of the corresponding sulphone monomers and styrene. Polymerizations were carried out in dimethyl sulphoxide in the presence of azoisobutyronitrile at 60 °C by the method reported previously.[3] The monomer composition ratios (*n*/*m*) and intrinsic viscosity (η) of the polymers employed here are given below the structural formulae.

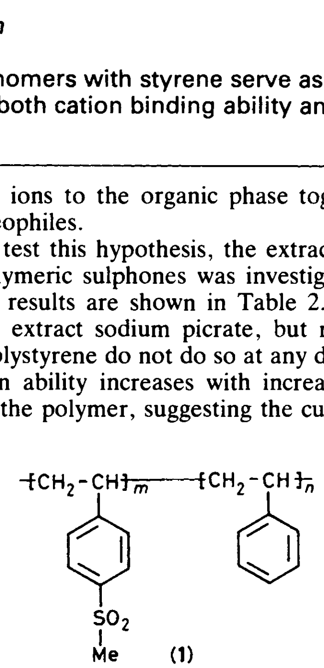
The catalytic activity of these polymers was tested in the reaction (1) of n-octyl bromide with iodide anions. This reaction was carried out in a toluene–water two-phase system and the results are shown in Table 1.

$$\text{n-}C_8H_{17}Br + MI \xrightarrow[100\,°C]{\text{Cat.}} \text{n-}C_8H_{17}I + MBr \qquad (1)$$

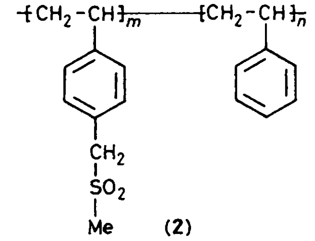
$$M = Li, Na, \text{ or } K$$

The reaction with sodium iodide in the presence of (**1c**) or (**2c**) gave the corresponding iodide in moderate yields, but was not catalysed by monomeric analogues such as methyl phenyl sulphone and benzyl methyl sulphone. The polymeric sulphones are soluble in toluene, but insoluble in water in spite of the presence of the sulphonyl group which strongly interacts with water.[4] Therefore, we think that the sulphonyl group in the polymer interacts with alkali metal ions at the interface to transfer metal ions to the organic phase together with the resulting nucleophiles.

In order to test this hypothesis, the extraction of sodium cations by polymeric sulphones was investigated by Smid's method.[5] The results are shown in Table 2. All polymeric sulphones can extract sodium picrate, but monomeric sulphones and polystyrene do not do so at any detectable level. This extraction ability increases with increasing density of active sites in the polymer, suggesting the cumulative chela-


(1)

	(**1a**)	(**1b**)	(**1c**)	(**1d**)	(**1e**)
n/*m*	0	1.0	2.2	2.9	3.8
$[\eta]/(dl\,g^{-1})$	0.71	0.26	0.32	0.21	0.25


(2)

	(**2a**)	(**2b**)	(**2c**)	(**2d**)	(**2e**)
n/*m*	0	0.9	2.0	3.0	4.3
$[\eta]/(dl\,g^{-1})$	0.26	0.15	0.15	0.17	0.18

Monomer composition ratio (*n*/*m*) and intrinsic viscosity (η) of the polymeric catalysts (**1**) and (**2**).

Table 1. Halogen exchange reactions under phase-transfer conditions[a] at 100 °C.

Run	Reagent	Cat.	Time/h	Yield of octyl iodide (%)
1	NaI	None	48	trace
2	NaI	$PhSO_2Me$	48	trace
3	NaI	$PhCH_2SO_2Me$	48	trace
4	NaI	Polystyrene	48	trace
5	LiI	**(1c)**	48	38
6	NaI	**(1c)**	48	43
7	NaI	**(1c)**	160	82
8	NaI	**(2c)**	48	61
9	KI	**(1c)**	48	53

[a] [Substrate] = 0.55 M in toluene, 3 ml [reagent] = 4.0 M in H_2O, 5 ml, cat. = 0.3 mmol based on the sulphone group.

Table 2. Extraction of sodium picrate[a] by monomeric and polymeric sulphones.

Sulphone	Sodium picrate extracted (%)
$PhSO_2Me$	0.0
(1a)	2.3
(1b)	2.1
(1c)	1.6
(1d)	1.5
(1e)	0.4
$PhCH_2SO_2Me$	0.0
(2a)	4.0
(2b)	2.4
(2c)	2.3
(2d)	1.9
(2e)	0.4

[a] Solvent system H_2O–benzene (5 ml/20 ml), [picric acid] = 5.0×10^{-5} M, [NaOH] = 1.0×10^{-2} M, cat. = 6.25×10^{-3} mmol based on the sulphone group.

tion of metal ions by several sulphonyl groups. Furthermore, it can be seen from Table 2 that the extraction ability of the polymeric sulphone **(2)** is generally higher than that of **(1)**. This may be caused by the difference of electron density on the oxygen atom.

On the other hand, in extraction experiments, the concentration of the monomeric sulphones in benzene decreased after addition of sodium picrate to the aqueous solution.

From these observations we believe that the monomeric species displays no catalytic activity for the following reason. The monomeric sulphone is also able to interact with sodium cations at the interface to form a complex, but this is quickly transferred into the aqueous phase because the complex is soluble in water, in contrast to the polymeric sulphone complex. Thus, the essential difference in catalytic activity between polymeric and monomeric species might be due to the difference of lipophilicity.[6]

Next, in order to study the relationship between the catalytic activity and the microenvironment around the active site, the kinetics of the halogen exchange reaction were studied for polymers having various composition ratios. The reaction followed pseudo-first-order kinetics, and no appreciable side reaction was detected. The results are shown in Figure 1. Interestingly, in both cases there are maxima at certain composition ratios of sulphone to styrene unit. In the n/m = 0—2 range, the rate constants are inversely related to

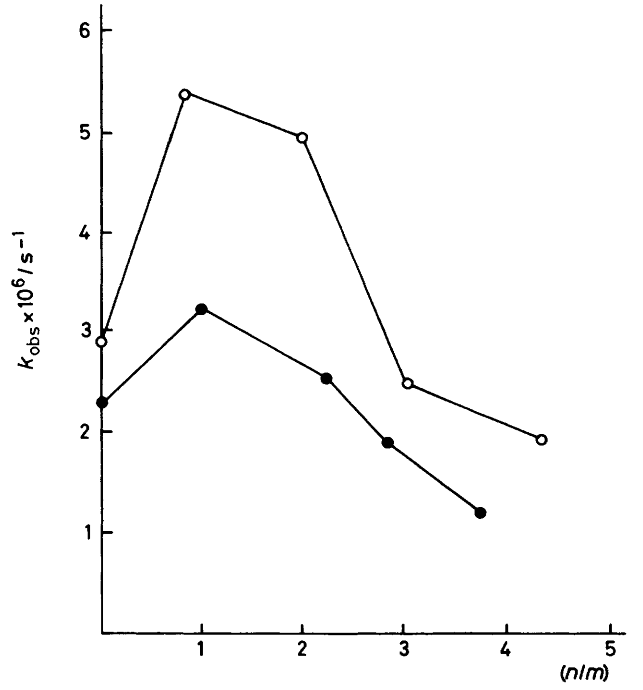


Figure 1. Dependence of the observed pseudo-first-order rate constants ($k_{obs.}$) on composition ratio (n/m) in copolymers **(1)** (●) and **(2)** (○). [$n\text{-}C_8H_{17}Br$] = 0.55 M in toluene, 5 ml, [NaI] = 4.0 M in H_2O, 15 ml, cat. = 0.5 mmol based on the sulphone group.

the extraction ability. This finding strongly indicates the importance of lipophilicity around the active sites, and further suggests the activation of nucleophiles by desolvation. For $n/m > 2$, the rate follows the extraction ability. Thus the catalytic activity of polymeric sulphone was found to depend strongly on extraction ability and lipophilicity around the active sites.

In addition, these polymeric sulphones were readily recovered quantitatively by reprecipitating from the toluene solution with light petroleum.

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