A POLYMER ANALOG OF DIMETHYL SULFOXIDE: CATALYTIC ACTIVITY OF CROSSLINKED POLYMERIC SULFOXIDES IN NUCLEOPHILIC REACTIONS UNDER THE CONDITIONS OF THREE-PHASE CATALYSIS

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An investigation was made of the catalytic activity of polymeric sulfoxides, $P-(-CH_2SOCH_2-)_n-R$ where P is the crosslinked polystyrene matrix (divinylbenzene as the crosslinking agent), R is H or CH_3, and n is 1, 2, or 3, in nucleophilic substitution reactions between alkyl bromides and phenoxides, iodides, thiocyanates and cyanides of alkali metals under the conditions of liquid––solid–liquid (L–S–L) three-phase catalysis (TC). The effect of the structure of polymeric sulfoxides on their activity under the conditions of TC was studied; the strongest catalytic activity was found with polymeric sulfoxides having the optimal ratio between the functional groups and hydrophobic polymer matrix. Extension of the pendant sulfoxide chain has no pronounced effect of the catalytic activity of polymers.

Reactions which proceed with the participation of nucleophiles are often very strongly affected by the nature of the solvent. Dipolar aprotic solvents possess a high solvation power towards cations and a low one towards anions. In nucleophilic reactions, this power is reflected in a strong influence upon the reaction rate and upon the course of these reactions in general. The conception of a catalysis with solid-phase co-solvents[1,2] is based on the view that solvation properties of dipolar solvents remain also in the case of polymers containing structural units analogous to those which cause activation of the anions if dipolar solvents alone are used. Such view involves some other advantages offered by polymers in the three-phase catalysis (easy separation of reaction products, re-use of the polymeric catalyst).[3] Up to now, several cases of catalysis have been described in which various types of solid-phase cosolvents are used in reactions between inorganic nucleophiles and organic halides; application of polymer-bound hexamethylphosphortriamide[2,4–6], linear polyethers derived from ethyleneglycol[1,7–13], N,N-dimethylformamide[14] and N-methylpyrrolidone[15] has been reported. Quite recently, the catalytic activity of polymers containing dimethyl sulfoxide side units has been pointed out by us[16,17] and by Japanese authors[18]. In a preceding paper[19] we described the preparation of crosslinked polymeric sulfoxides *I–III* (Table I) differing in the functionalization of the polystyrene

matrix P (divinylbenzene as the crosslinking component), in the $-(-CH_2SOCH_2-)_n-R$ chain and in the degree of functionalization. This study is concerned with the catalytic activity of polymers $I-III$ in substitution nucleophilic reactions of alkyl bromides with anions A^- (PhO^-, I^-, SCN^-, CN^-), carried out under the conditions of liquid– –solid–liquid (L–S–L) three-phase catalysis (TC),

$$R'-Br + A^- \xrightarrow[\text{catalyst}]{\text{toluene/H}_2\text{O}} R'-A + Br^-.$$
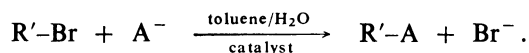
The catalysis with solid-cosolvent polymers proceeds in a complicated multi-component three-phase system. The mechanism of their catalytic action is not exactly known. It is assumed that this mechanism consists in solvation interactions between catalytic groups and salt cations in the aqueous phase and in the transfer of the anion bound with the cation in an ionic pair into the organic phase, and/or in the microhomogenization of the aqueous and organic phases inside the polymer in those domains, where hydrophilic and hydrophobic effects are combined in a favourable way (micellar mechanism).

It follows from the analysis of experimental results (Tables II and III) that the easiness with which the anion of salts is transferred from the aqueous to the organic phase decreases in the series

$$C_6H_5O^{(-)} > I^{(-)} > SCN^{(-)} > CN^{(-)}.$$
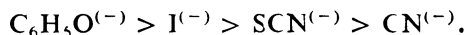
Reactions of sodium phenoxide proceed also in the absence of the catalyst. At high

TABLE I

Crosslinked polymeric sulfoxides $P-(-CH_2SOCH_2-)_n-R$; P denotes the polystyrene matrix with divinylbenzene as the crosslinking agent (M_2), D_f is the degree of functionalization

Polymer	n	R	M_2,%	D_f, %	[S], mmol/g
Ia	1	H	1	98	5·5
Ib	1	H	2	97	5·3
Ic	1	H	2	61	4·1
Id	1	H	2	33	2·8
IIa	2	CH$_3$	1	98	5·5
IIb	2	CH$_3$	2	97	5·3
IIc	2	CH$_3$	2	61	4·1
IIIa	3	CH$_3$	1	98	5·5
IIIb	3	CH$_3$	2	97	5·3
IIIc	3	CH$_3$	2	61	4·1

concentrations of sodium phenoxide in the aqueous phase, differences between the catalyzed and uncatalyzed system are even wiped out — in contrast with the case of 1-bromobutane reported by Japanese authors (extent of the catalyzed reaction was 41% at 100°C for 20 h), we recorded, under similar model conditions, complete conversions of alkyl bromide to butyl phenyl ether, both in presence and in absence of the polymeric catalyst. In reactions of the other anions of the given series, the extent of the reaction in the absence of the polymeric catalyst is negligible. The

TABLE II

Extent of substitution reactions (ε definition *cf.* Experimental) of alkyl bromides catalyzed with polymeric sulfoxides *I—III*

Polymer			Polymer		
type	amount in mmol S	ε %	type	amount in mmol S	ε %
C_4H_9Br (1·5 mmol) + PhONa (1 mmol), 70°C, 12 h			$C_8H_{17}Br$ (0·6 mmol) + KSCN (17·5 mmol), 100°C, 48 h		
Ia	0·26	15	*Ia*	0·26	4
Ic	0·19	26		0·52	20
Id	0·13	15[a]		0·78	27
IIc	0·27	8	*Ib*	0·25	3
IIIc	0·31	16		0·60	38
—	—	4	*Ic*	0·20	27
$C_8H_{17}Br$ (0·6 mmol) + NaI (3·4 mmol), 90°C, 24 h				0·61	90[c]; 99; 83[d]
Ia	0·26	26			
Ib	0·25	20	*Id*	0·66	32
Ic	0·20	34[b]	*IIa*	0·92	8
Id	0·14	11	*IIb*	0·92	21
IIa	0·31	15	*IIc*	0·82	22
IIb	0·31	17	*IIIa*	1·08	14
IIc	0·27	38	*IIIb*	1·01	35
IIIa	0·36	24	*IIIc*	0·95	26
IIIb	0·33	19	PS[e]	0	0[f]
IIIc	0·31	30	—	—	< 1
—	—	0			

[a] With 8 mmol PhONa and 0·31 g *Id* or without catalyst, ξ is 100% or 98% respectively. [b] In the reaction with KI, ξ = 20%. [c] After 24 h. [d] Second use of the catalyst. [e] Poly[styrene(98)-co-divinylbenzene(2)]. [f] According to ref.[18].

easiness of the transfer obviously depends also on the cation bound in the pair as can be seen in the reactions of iodides (data for KI, note to Table II). A higher temperature under otherwise unchanged conditions increases conversions; as a consequence, the activity of the catalyst may then be compared to that of a polymer analog of hexamethylenephosphortriamide[10].

Kondo and coworkers have found[18] that in the reaction of 1-bromooctane with KSCN an increase by an order of magnitude in soluble polymeric sulfoxides used as catalysts leads to a considerable rise in the yield of octyl thiocyanate, but that the activity of the catalysts decreases with increasing content of sulfoxide groups in the linear chain. In the application of crosslinked polymeric sulfoxides prepared for this study, a distinctly favourable effect on the extent of substitution nucleophilic reactions of 1-bromooctane produced by SCN^- and CN^- anions was observed, already after small changes in the amount of the catalyst. This effect cannot be assigned to a local increase in the concentration of catalytic sites: even if, in the case of polymers with pendant chain $-(-CH_2SOCH_2)_2CH_3$ (e.g., IIIa − c), there is a slight increase in the catalytic effect, compared with polymers containing the $-(-CH_2SOCH_2)_2CH_3$ (IIa − c), polymers with the $—CH_2SOCH_3$ groupings (i.e. Ia − d) always have the same or higher catalytic activity. All these findings suggest that in the reactions under investigation the catalytic activity of polymeric sulfoxides is enhanced by the

TABLE III

Effect of the type and amount of polymeric catalysts I—III (in mmol S) on the extent of the reaction (ξ) between 1-bromooctane (0·6 mmol) and KCN (8 mmol)

Polymer		T	t	ξ	Polymer		T	t	ξ
type	mmol S	°C	h	%	type	mmol S	°C	h	%
Ia	0·26	100	48	5	IIa	0·62	90	33	0
	0·52	90	33	8	IIb	0·61	90	33	0
					IIc	0·55	90	33	6
Ib	0·49	90	33	5	IIIa	1·30	90	33	1
	0·50	100	48	20	IIIb	1·35	90	33	0
					IIIc	1·45	90	33	7
Ic	0·40	90	33	13					
	0·20	100	48	27	PS[a]	—	110	24	0[b]
	0·40	100	48	46					
					—	—	90	33	0
Id	0·41	100	48	15					

[a] Poly(styrene-co-divinylbenzene), 2% of crosslinking component. [b] According to ref.[10].

hydrophobic surroundings of active sites, or, in other words, by the optimal concentration ratio of catalytic groups and hydrophobic regions (cf. the extent of reactions catalyzed with polymers *Ib — d* under similar conditions) which provide a suitable matrix for a close contact with alkyl halides, and thus an immediate contact between the catalytic sites and their partner reagents. The structure of hydrophobic regions also has an important influence on the catalytic activity of crosslinked polymeric sulfoxides[17].

In a study reported by Japanese authors[18], an extent of 70% was reached in the reaction of 1-bromooctane with KSCN in presence of the most active soluble polymeric sulfoxide (mol.ratio S/Br 1·82, 100°C, 20 h). In our case, with the crosslinked polymeric sulfoxide *Ic* used in the given reaction under similar conditions (mol. ratio S/Br 1·01, 100°C, 24 h), the extent of the reaction was 90%. Thus, a distinct improvement in efficiency is brought about by crosslinking. This obviously leads in turn to the formation of such structures which favour the role of the micellar and/or complex-forming mechanism of catalysis.

Generally, for crosslinked polymers which catalyze reactions under conditions of the TC arrangement an important factor for the reactions usually consists in the degree of crosslinking, as the latter determines the porosity, pore size and swelling of the material. It is difficult to discuss the effect of the degree of crosslinking on the catalytic activity of polymeric sulfoxides in detail, since in the synthesis of the catalysts due to the initial chloromethylation of poly(styrene-co-divinylbenzene) the nominal degree of crosslinking (as given by the content of the crosslinking component, *i.e.*, divinylbenzene) may be increased by methylene bridges. Moreover, the catalysts under study were prepared by a sequence of reactions which proceed to a satisfactory degree of refunctionalization only if the chlorine atom is replaced with methylsulfinyl, while in all the other cases the final step of the synthesis (oxidation of polymeric sulfides) probably leads to an additional crosslinking by disulfidic groups[19]. Nevertheless, it can be seen from the extent of the reactions investigated in this study (Tables II, III) that the catalytic activity of polymeric sulfoxides possessing a different nominal degree of crosslinking at approximately the same degree of functionalization by the pendant methylsulfinylmethyl group (*Ia,b*) is similar. This fits in with the view that up to a certain critical degree of crosslinking, the catalytic sites in the polymer are freely accessible to reagents.

It may be said, in conclusion, that in the three-phase L–S–L system the activity of polymeric sulfoxides is comparable to that of other solid-phase cosolvents, but lower than that of polymers based on ammonium and phosphonium salts[10]. Of course, in relation to their soluble analogs the polymeric sulfoxides have an advantage in being readily available and in their easy separation from reaction products.

EXPERIMENTAL

Methods

Gas-chromatographic measurements were performed with a CHROM 51 apparatus (flame-ionization detector. column 3 mm in diameter, length 2·5 m, Chromaton N-AW-HMDS with 6% OV17 as packing), with chlorobenzene as the internal standard.

Chemicals

Crosslinked polymeric sulfoxides were prepared as reported in the literature[19] from poly(styrene--co-divinylbenzene), grain size 0·2—0·4 mm. 1-Bromobutane (Fluka) and 1-bromooctane (Fluka) were used without previous purification. The solvents were purified prior to use by the usual procedures. The other chemicals were also commercial products and were used without further treatment.

Reaction of 1-Bromobutane with Sodium Phenoxide

To 0·050 g of polymeric sulfoxide, 1 ml of a 1·5M solution of 1-bromobutane in toluene was added, and the mixture was kept with stirring in a closed test tube at 100°C for 15 min. After that, 1 ml of a solution of sodium phenoxide prepared by dissolving 0·940 g phenol (10 mmol) in 10 ml of aqueous 2·5M-NaOH was added. The reactions were carried out with stirring with a magnetic stirrer at $70 \pm 1°C$. On completion of the reaction time, the upper organic layer was analyzed by gas chromatography; the tabulated data on the extent of the reaction were calculated as the average from the relative loss of 1-bromobutane and from its conversion to butyl phenyl ether (difference between the values was below 3%).

Reaction of 1-Bromooctane with Iodides, KSCN and KCN

To a chosen amount of polymeric sulfoxide (0·050—0·220 g), 1 ml of 0·6M solution of 1-bromooctane in toluene was added and the mixture was maintained with stirring in a closed test tube at 100°C for 15 min. After that, 1 ml of the solution of a chosen inorganic salt was added, prepared by dissolving 2·50 g NaI (17 mmol) in 5 ml water, 2·82 g KI (17 mmol) in 5 ml of water, 17·00 g KSCN (175 mmol) in 10 ml of water, or 5·20 g KCN (80 mmol) in 10 ml of water. The reactions were carried out with stirring with a magnetic stirrer at 90 or 100°C ($\pm 1°C$). On completion of the reaction time, the upper organic layer was analyzed by gas chromatography, and the extent of the reaction was evaluated as described.

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