

POLYMER SULFOXIDES BASED ON POLY(VINYL ALCOHOL) AS EFFECTIVE CATALYSTS OF NUCLEOPHILIC SUBSTITUTION REACTIONS

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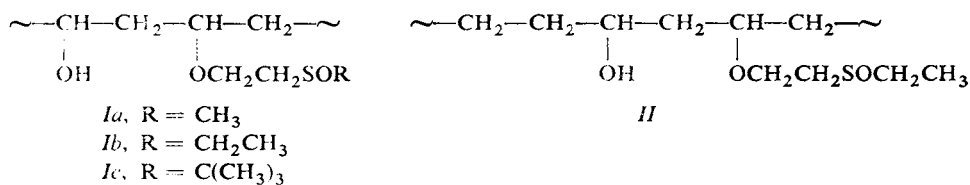
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Using the addition of alcohols to ethyl vinyl sulfoxide, a number of 2-alkoxyethyl ethyl sulfoxides were prepared, containing the following alkyls: methyl, ethyl, isopropyl, benzyl, and cyclohexyl. With a 10 mole % excess of alcohol the extent of the reaction was 70–95%. By a polymer-analogous reaction with poly(vinyl alcohol) and poly(ethylene-co-vinyl alcohol), copolymers poly[1-hydroxyethylene(74 mole %)-co-1-(2-ethylsulfinyloxy)ethylene(26 mole %)] and poly[ethylene(62 mole %)-co-1-hydroxyethylene(35 mole %)-co-1-(2-ethylsulfinyloxy)ethylene(3 mole %)] were prepared; the reaction with polymer alcohols requires the use of excess ethyl vinyl sulfoxide. These polymer sulfoxides were tested as catalysts of nucleophilic substitution reactions, using reactions of 1-bromooctane with sodium phenoxide, sodium iodide and potassium thiocyanate. They are more effective catalysts than polymer sulfoxides based on crosslinked poly(styrene) under the conditions of a two-phase (S-L) and three-phase (L-S-L) catalysis.

It is known that polymers bearing bound sulfoxide units are effective catalysts of nucleophilic substitution reactions¹⁻³. So far, however, only polymers based on soluble or crosslinked poly(styrene) and poly(phosphazene) have been studied. An important factor which affects the activity of these polymer catalysts is the relative content of sulfoxide groupings in the polymer matrix. The effect of the character of the polymer matrix on the catalytic activity of polymer sulfoxides has been demonstrated by using poly(styrene-co-divinylbenzene) and poly(phosphazene) as carriers of sulfoxide units; the favourable effect of a heteroatomic main chain has also been demonstrated³. Poly(vinyl alcohol), a readily commercially available polymer offering a number of chemical modifications, can be considered as the carrier⁴.

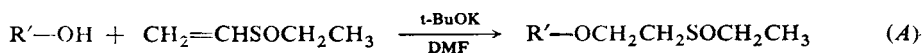
Although the nucleophilic addition of hydroxy compounds on an activated double bond is a well-known reaction, additions to compounds bearing a vinyl sulfoxide grouping have been described only very scarcely and unsystematically^{5,6}. At the same time, one may expect that the strong dipolar character of the S—O group may favourably affect the course of the addition reaction. It has been observed earlier⁷ that in the preparation of ethyl vinyl sulfoxide by the dehydrohalogenation of 2-chloroethyl ethyl sulfoxide with an aqueous solution of potassium hydroxide under the conditions of phase transfer catalysis, ethyl vinyl sulfoxide is readily

formed as the first product, which thereafter is gradually transformed by a consecutive reaction with water to ethyl 2-hydroxyethyl sulfoxide and to other addition products containing alkoxyethyl sulfoxide groupings. This indicates a high reactivity of the double bond of alkyl vinyl sulfoxides in the addition reactions. Recently, also, Imai *et al.*⁸ have investigated a reaction between poly(vinyl alcohol) and alkyl vinyl sulfoxides in an aqueous medium and prepared copolymers of type *I*. To reach a high degree of addition, it was necessary to use a significant excess of alkyl vinyl sulfoxide, obviously due to its competitive reaction with water, accompanied by the formation of alkyl-2-hydroxyethyl sulfoxide.



Simultaneously with ref.⁸ we obtained original data on reactions of low-molar mass alcohols, poly(vinyl alcohol) (PVA), and poly[ethylene(62 mole %)-*co*-vinyl alcohol(38 mole %)] (PEVA) with ethyl vinyl sulfoxide in an anhydrous medium, carried out in the presence of strong bases ($\text{KOC}(\text{CH}_3)_3$, $\text{KCH}_2\text{SOCH}_3$, NaH), and also on the catalytic activity of polymer sulfoxides based on PVA (*Ib*) and PEVA (*II*) in nucleophilic-substitution reactions performed under the conditions of two-phase (*L-S*) and three-phase (*L-S-L*) catalysis.

To verify the reactivity of the hydroxy group in the additions to ethyl vinyl sulfoxide, we investigated reactions of low-molar mass hydroxy compounds ($\text{R}'\text{-OH}$). They were carried out in a solution in *N,N*-dimethylformamide (DMF) in the presence of potassium *tert*-butoxide (10 mole % calculated to OH groups) at room temperature (Table I). The corresponding alkyl 2-(ethylsulfinyl)ethyl ethers were isolated,



as the only products of the addition of alcohol to the activated double bond of ethyl vinyl sulfoxide. No significant excess of one of the components is needed in order to reach a satisfactory conversion to the required 2-alkoxyethyl ethyl sulfoxides. It was proved, at the same time, that in the case of phenol no addition reaction takes place, obviously due to the low basicity of the phenoxide anion.

So far, the addition of poly(vinyl alcohol) and unsaturated compounds has been reported for the cases of acrylamide⁹, methyl vinyl ketone¹⁰, and acrylonitrile¹¹. We examined a similar polymeranalogous transformation using reactions of PVA

and PEVA with ethyl vinyl sulfoxide in DMF and DMSO as the anhydrous medium (Table II). The composition of the products was determined by analysis (C, H, S) and by ^1H NMR spectroscopy. The transformation of OH groups to 2-(ethylsulfinyl)-ethoxy groups does not depend on the type of the strong base too much, because the change of the O^- base to the C^- and H^- bases does not lead to any important changes in the extent of the addition reaction. This suggests that the limiting factor in this reaction is not the transformation of OH groups on the polymer to the alkoxide form, but structural factors. Unlike the addition of low-molar mass alcohols to ethyl vinyl sulfoxide, the extent of the addition reaction of polymeric alcohols is strongly dependent on the ratio of the reaction components; the highest extent (about 25%) is reached at a twofold molar excess of ethyl vinyl sulfoxide with respect to OH groups (a higher excess is not effective).

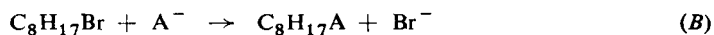
The catalytic activity of modified polymers was investigated using a reaction between sodium phenoxide and 1-bromooctane in an anhydrous 1,4-dioxan (L-S system) at 75°C , when the polymer acts as a solid cosolvent (Table III), and in reactions of sodium iodide and potassium thiocyanate with 1-bromooctane in the system H_2O -toluene (L-S-L system) at 100°C , when the polymer is operative as the catalyst of reactant transfer through the interface (Table IV, Eq. (B)).

TABLE I

Reaction of alcohols ($\text{R}'\text{—OH}$) with ethyl vinyl sulfoxide (mol. ratio 1:1) in DMF in the presence of potassium tert-butoxide (room temperature, 24 h), giving rise to 2-alkoxyethyl ethyl sulfoxides (extent of reaction according to GLC)

R'	Extent of reaction, %	Yield %	Formula (molar mass)	Calculated/found		
				% C	% H	% S
Methyl	83	56	$\text{C}_5\text{H}_{12}\text{O}_2\text{S}$	44.09	8.89	23.56
			(136.1)	44.22	8.77	23.12
Ethyl	80	51	$\text{C}_6\text{H}_{14}\text{O}_2\text{S}$	47.94	9.40	21.34
			(150.2)	48.21	9.12	21.00
Isopropyl	94 ^a	53	$\text{C}_7\text{H}_{16}\text{O}_2\text{S}$	51.16	9.82	19.52
			(164.2)	51.09	9.66	19.42
Cyclohexyl	73	56	$\text{C}_{10}\text{H}_{20}\text{O}_2\text{S}$	58.77	9.87	15.70
			(204.2)	58.49	9.60	15.47
Benzyl	69	53	$\text{C}_{11}\text{H}_{16}\text{O}_2\text{S}$	62.21	7.60	15.11
			(212.2)	62.00	7.39	14.98

^a 68% after 10 h.



The reaction between sodium phenoxide and 1-bromooctane under L-S conditions in the absence of the polymer or in the presence of unfunctionalized poly-[(styrene(98 mole %)-*co*-divinylbenzene (2 mole %)] (PS) proceeds only very slowly (Table III). A larger extent of the reaction is reached by using PVA and PEVA as the catalysts, which means a favourable effect of the presence of heteroatoms on the C—C chain of the polymer. This has also been shown earlier in the case of PVA under other reaction conditions¹². The effect of transition from PVA to polymeric sulfoxide *Ib* was much more pronounced. The use of a major amount of the catalyzing polymeric sulfoxide raises the observed rate constant *k* accordingly. A similar phenomenon for polymeric sulfoxides *Ib* differing in the content of sulfoxide groupings can be seen also after passing to the polymer with a higher content of sulfoxide units in the chain. However, the specific activity expressed as a specific rate constant (the observed rate constant related to the unit concentration of sulfoxide units in the reaction mixture), $k_{\text{sp}} = k/c_{\text{u}}$, remains the same. This suggests that sulfanyl groups

TABLE II

Conversion of OH groups to 2-(ethylsulfanyl)ethoxy groups in reactions of poly(vinyl alcohol) and poly[ethylene(62 mole %)-*co*-vinyl alcohol(38 mole %)] in the presence of KOC(CH₃)₃ (DMF, 70°C, 40 h), KCH₂SOCH₃ (DMSO, 50°C, 15 h) or NaH (DMF, 70°C, 40 h)

Reaction components, mmol		Base		Product	Conversion
—OH	—C=C—	type	mmol	mass % S	mole %
Transformation of PVA to copolymer <i>Ib</i>					
1	1	KOC(CH ₃) ₃	0.07	1.23	1.8
1	1	KOC(CH ₃) ₃	0.12	1.55	2.2
1	1	KOC(CH ₃) ₃	0.60	4.38	7.0
1	2	KOC(CH ₃) ₃	0.60	12.10	27.4
1	1	KCH ₂ SOCH ₃	0.10	1	1.4
1	1	KCH ₂ SOCH ₃	0.50	7.50	13.6
1	2	KCH ₂ SOCH ₃	0.50	11.10	23.9
1	2	NaH	0.60	11.50	25.2
Transformation of PEVA to copolymer <i>II</i>					
1	1.4	KOC(CH ₃) ₃ ^a	0.36	2.70	8.3

^a Reaction in DMSO at 70°C for 115 h.

TABLE III

Rate constants (k , $k_{sp} = k/c_u$) of the reaction of sodium phenoxide (0.25 mmol) with 1-bromooctane (1 mmol) in anhydrous 1,4-dioxan (total volume 1 cm³) at 75°C. Symbols: c_u concentration of sulfoxide units in the reaction mixture, ξ extent of reaction after 23 h

Catalyst		c_u mol l ⁻¹	$k \cdot 10^5$ l mol ⁻¹ s ⁻¹	$k_{sp} \cdot 10^5$ l ² mol ⁻² s ⁻¹	ξ %
type	mmol S/g				
—	—	—	—	—	9
PS	0	0	—	—	9
PEVA	0	0	—	—	17
PVA	0	0	—	—	28
<i>Ib</i>	0.83	0.075	0.86	11.5	42
<i>Ib</i>	0.83	0.15	1.69	11.3	71
<i>Ib</i>	3.08	0.28	3.44	12.3	92
<i>Ib</i>	4.27	0.19	2.61	13.7	84
<i>Ib</i>	4.27	0.38	5.10	13.4	100
<i>Ib</i>	—	—	5.05 ^a	13.4 ^a	100 ^a
<i>Ib</i>	4.27	0.76	10.0	13.2	100
<i>II</i>	0.84	0.042	3.06	72.5	89
PS—DMSO ^b	4.45	0.22	0.51	2.32	37
(CH ₃) ₂ CHO CH ₃ CH ₂ SOCH ₂ CH ₂	6.08	0.25	3.05	12.2	88

^a In the third use of recycled catalyst. ^b Functionalized ($D_f = 70\%$) poly[styrene(98 mole%)-*co*-divinylbenzene(2 mole%)] prepared according to ref.².

TABLE IV

Reaction of 1-bromooctane (0.3 mmol in 0.5 ml toluene solution) with NaI and KSCN (6 mmol in 1 ml aqueous solution) under conditions of three-phase catalysis (100°C, 48 h)

Catalyst (C)		Amount of C		Extent of reaction, %	
Type	mmol S/g	mg	mmol S	C ₈ H ₁₇ I	C ₈ H ₁₇ SCN
—	—	—	—	1	0
PVA	0	25	0	1	2
PEVA	0	25	0	15	16
<i>Ib</i>	1.84	25	0.046	25	40
<i>II</i>	0.84	25	0.021	100	100

behave independently of each other as regards their ability to activate the anion. This is also indicated by the fact that the k_{sp} value found when using these polymers lies close to the k_{sp} value measured in the reaction catalyzed by their low-molar mass model. Dramatic differences can be seen in the activities of polymeric sulfoxides based on PS and PEVA (*II*). While the specific activity of the polymer analog of dimethyl sulfoxide based on crosslinked poly(styrene) (PS-DMSO), which is the most active member of its series under three-phase conditions (*cf. ref.*²), is very low, copolymer *II* having a relatively low content of sulfoxide groupings (3 mole %) possesses a high specific activity, distinctly the highest of all the tested catalysts, and even higher than that of dimethyl sulfoxide¹³. This confirms conclusions reached by other authors¹⁴ and concerning the great importance of hydrophilic-hydrophobic relations operative inside the polymer matrix in the polymer catalysis.

In the reactions of NaI and KSCN with 1-bromooctane under the L-S-L conditions, the more hydrophobic copolymer *II* also is the more active catalyst of the pair *Ib* and *II*, in spite of the fact that the content of catalytically active groups is much lower (Table IV). It is remarkable, moreover, that already the original (unmodified) PEVA shows a distinct ability to transfer reactants through the interface, while PVA shows none.

Investigations of the catalytic activity of polymer sulfoxides based on PVA and PEVA indicate that these polymer catalysts are active under conditions of both the two-phase and three-phase catalysis. Under the two-phase S-L conditions the polymer sulfoxide based on PVA or PEVA is more suitable for the activation of the anion than the polymer based on crosslinked PS. A comparison with the results reported earlier² reveals that also in the three-phase conditions polymeric sulfoxides based on PVA and PEVA are more active than similar polymers based on crosslinked PS. Further aspects of the catalysis with polymer sulfoxides based on PVA and PEVA are being investigated, and the results will be published.

EXPERIMENTAL

Gas-chromatographic measurements were carried out using a CHROM 51 apparatus (flame-ionization detector, column 3 mm in diameter and 2.5 m long, packed with Chromaton N-AW-HMDS with 6% OV17). The IR spectra were recorded with Perkin-Elmer 580B. The ¹H NMR spectra were measured with a JEOL PS 100 apparatus.

Compounds

Poly(vinyl alcohol), commercial Fluka product m.m. 128 000. Weakly crosslinked poly[ethylene-(62 mole %)-*co*-vinyl acetate(38 mole %)], commercial BASF product, hydrolyzed with ethanolic KOH in toluene at 125°C to poly(ethylene-*co*-vinyl alcohol). The solvents were reperfired by employing the usual procedures and stored over a 3A molecular sieve. Sodium phenoxide was prepared as described earlier² by reacting equimolar amounts of phenol and sodium ethoxide in ethanol. 1-Bromooctane (Fluka) was used without further purification. The reaction of bromo-

ethane (Fluka) with 2-mercaptoethanol (Fluka) gave ethyl 2-hydroxyethyl sulfide, which in turn was reacted with thionylchloride to yield 2-chloroethyl ethyl sulfide²; both the intermediate and the product possessed the expected physical characteristics (b.p., ¹H NMR spectra).

2-Chloroethyl ethyl sulfoxide. To a solution of 15.30 g 2-chloroethyl ethyl sulfide (123 mmol) in 50 ml methanol, 14.32 g of an aqueous solution (30%) of hydrogen peroxide (126 mmol) was added dropwise with stirring and cooling (water bath). After 30 min the heterogeneous mixture was homogenized, after 2 h GLC did not reveal the presence of the starting sulfide. The volatile fractions were evaporated *in vacuo* at 50°C, 100 ml of dichloromethane was added to the dry residue, and the solution was dried 24 h over anhydrous Na₂SO₄. The solvent was removed by distillation, and 16.50 g of raw product was obtained and subjected to dehydrohalogenation without further purification.

Ethyl vinyl sulfoxide. To 16.50 g 2-chloroethyl ethyl sulfoxide (117.4 mmol) in 40 ml benzene, 0.81 g α -hydrogen- ω -hydroxyhepta(oxyethylene)¹⁵ (2.5 mmol) was added, and after that, 40 ml of an aqueous solution (60%) KOH was also added at once, with cooling and vigorous stirring. After 30 min the light-yellow organic layer was separated, the aqueous layer was extracted four times with 40 ml benzene, and after that, with 40 ml dichloromethane. The combined organic layers were dried 24 h over anhydrous Na₂SO₄. The solvent was evaporated, and 7.20 g of the product was obtained by distillation *in vacuo* (yield 70%, b.p. 79–81°C) 1 730 Pa; no impurities detected by GLC. The ¹H NMR spectrum (deuteriochloroform): 6.40 (m, 3 H, CH₂=CH—), 2.65 (m, 2 H, CH₂SO), 1.10 (t, 3 H, CH₃).

Addition of Low-Molar Mass Alcohols to Ethyl Vinyl Sulfoxide

To a solution of 4.4 mmol of hydroxy compound (R'—OH) in 2 ml N,N-dimethylformamide, 0.045 g potassium tert-butoxide (0.40 mmol) was added, after 10 min 1 ml of a 4 M ethyl vinyl sulfoxide solution in DMF was introduced with stirring, and the stirring continued in a closed flask at room temperature for 24 h. After the addition of 0.1 ml H₂O and evaporation of volatile fractions at 60°C/1 733 Pa, the light-brown dry residue was analyzed by GLC (dodecane as the internal standard), and the addition product, 2-alkoxyethyl ethyl sulfoxide, was isolated chromatographically (SiO₂, acetone); in the analysis by TLC the derivatives have R_F 0.3–0.5 (silufol, acetone). The results of GLC and the yields of isolated products are summarized in Table I. The compounds did not contain any impurities detectable by GLC and had the corresponding IR spectra. ¹H NMR spectra (deuteriochloroform): R' = CH₃, 3.00 (t, 2 H, O—CH₂), 3.50 (s, 3 H, CH₃—O), 2.55 (m, 4 H, CH₂SOCH₂), 1.10 (m, 3 H, CH₃); R' = CH₃CH₂, 3.60 (t, 2 H, O—CH₂), 3.45 (m, 2 H, CH₂—O), 2.55 (m, 4 H, CH₂SOCH₂), 1.10 (m, 6 H, CH₃); R' = (CH₃)₂CH, 3.60 (t, 2 H, O—CH₂), 3.38 (m, 1 H, CH—O), 2.58 (m, 4 H, CH₂SOCH₂), 1.00 (m, 9 H, CH₃); R' = C₆H₁₁, 3.60 (t, 2 H, O—CH₂), 3.35 (m, 1 H, CH—O), 2.58 (m, 4 H, CH₂SOCH₂), 1.4–1.00 (m, 13 H, cycle, CH₃); R' = C₆H₅CH₂, 7.00 (m, 5 H, Ar), 4.2 (s, 2 H, C₆H₅CH₂—O), 3.55 (m, 2 H, O—CH₂), 2.50 (m, 4 H, CH₂SOCH₂), 1.00 (t, 3 H, CH₃).

Reaction Between Poly(vinyl alcohol) and Ethyl Vinyl Sulfoxide

To a solution of 0.10 g PVA (2.2 mmol) in DMF (or DMSO), 0.16 g (1.4 mmol) potassium tert-butoxide (or the same molar amount of KCH₂SOCH₃ or NaH) was added with stirring and under argon, and after that, ethyl vinyl sulfoxide (2.2–4.4 mmol) was added; the reaction mixture was stirred at 50–70°C for the chosen time (for the corresponding conditions *cf.* Table II). On cooling to room temperature and after the addition of 0.3 ml H₂O, the modified polymer was precipitated into diethyl ether, reprecipitated by precipitation from an ethanolic solution, and

dried. IR spectrum: Typical band of valence vibration S—O at $1\,020\text{ cm}^{-1}$. ^1H NMR spectrum ($^2\text{H}_2\text{O}$): 4.15 (m, —CH—O, —CH₂—O), 2.92 (m, CH₂SO), 1.75 (m, CH₂—C), 1.16 (t, CH₃).

Reaction of Poly(ethylene-*co*-vinyl alcohol) with Ethyl Vinyl Sulfoxide

To 0.20 g PEVA (11.1 mmol OH/g; 2.2 mmol) in 4 ml DMSO, 0.85 ml of a solution of potassium tert-butoxide (0.85 mmol) in DMSO, and after that, 0.32 g ethyl vinyl sulfoxide (3.1 mmol) were added. The reaction mixture was stirred at 70°C for 115 h, the swollen copolymer was washed with 1,4-dioxan, heptane, diethyl ether, and dried. Sulfur content: 2.70 mass % (3.15 mole %). IR spectrum: Typical band of S—O valency vibration at $1\,020\text{ cm}^{-1}$.

Reaction of 1-Bromooctane with Nucleophiles

A mixture of the catalyst (40–180 mg) and of a solution of 1-bromooctane in 1,4-dioxan (0.5 ml, 1 mmol) or toluene (0.5 ml; 0.3 mmol) was magnetically stirred (teflon stirrer $1 \times 10\text{ mm}$) at 75°C or 100°C for 30 min. After that, the solution of a nucleophilic compound was added (0.5 ml 0.5M sodium phenoxide in 1,4-dioxan for L–S conditions; 1 ml aqueous 6M-NaI or 6M-KSCN for L–S–L conditions), the reaction mixture was vigorously stirred (600 rpm) at the given reaction temperature and continuously analyzed by GLC (samples 0.05 μl ; dodecane as the internal standard). The extent of the reaction was determined from the concentrations of 1-phenoxyoctane (under L–S conditions) or as the average value determined from the loss of 1-bromooctane and from the concentration of the octyl derivative (under L–S–L conditions). The rate constants k were determined as the average from the calculated values obtained in eight determinations in the reaction range 5–80%.

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