REACTION OF 1-BROMOBUTANE WITH POTASSIUM CYANIDE UNDER CONDITIONS OF THREE-PHASE CATALYSIS: ACTIVITY OF NEW POLYMERIC CATALYSTS

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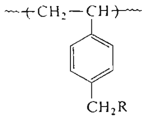
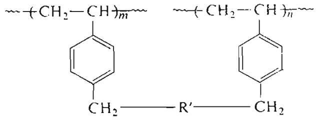
Six new polymeric catalysts active in the reaction between 1-bromobutane and potassium cyanide under conditions of liquid-solid-liquid three-phase catalysis (L-S-L TC) were prepared. The catalysts are based on a crosslinked polystyrene carrier of polar and dipolar functional groups of the type of quaternary ammonium and phosphonium, and also thioether, sulphoxide and sulphone groups. With respect to catalytic activity, an essential difference has been proved to exist between polymers where functional groups of the thio ether, sulphoxide, and sulphone type are bound as pendent on the polymer chain, and those where similar functional groups are part of the network. Compared with the water-toluene system, the water-chlorobenzene system usually gives higher yields.

In recent years, nucleophilic substitution reactions which proceed by transfer of reactants through the phase boundary with the catalytic participation of polymer compounds have aroused an increasing interest of many authors[1-10]. This interest is connected with successful application of catalysts used in the developing phase



I, R = $—SCH_3$
II, R = $—SOCH_3$
III, R = $—SO_2CH_3$
IV, R = $—\overset{(+)}{N}(C_2H_5)_3.Cl^{(-)}$
V, R = $—\overset{(+)}{P}(C_6H_5)_3.Cl^{(-)}$
VI, R = -quinine$^{(+)}$.Cl$^{(-)}$



VII, R′ = —S—
VIII, R′ = —SO—
IX, R′ = $—SO_2—$

transfer catalysis[11] of organic reactions to the field of polymer analogs. An extensive activity in this respect has been mainly developed by Regen's team, who tried to elucidate the mechanism of catalytic effect of the solid phase[3,6]. Studies carried out by other authors provided knowledge on the influence of the structure of polymer catalysts and configuration of groups bound on the polymeric carrier on their catalytic effect expressed through the yields obtained[7–9] and the degree of enantiomeric excess[10,12,13].

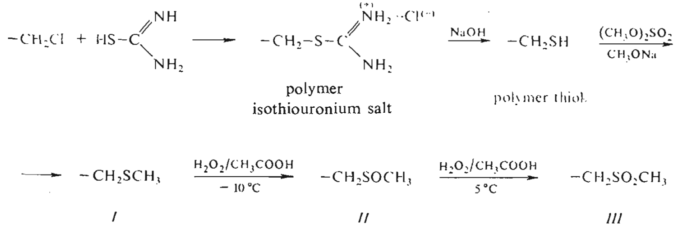
In this work, polymers *I–IX* were prepared, based on crosslinked polystyrene and so far uncharacterized with respect to their catalytic effect.

Their common feature consists in a high content of introduced functional groups. Their catalytic activity was investigated in a nucleophilic substitution reaction of 1-bromobutane with potassium cyanide in the system water–toluene and water–chlorobenzene:

$$CH_3CH_2CH_2CH_2Br + KCN \xrightarrow[80\,°C,\ 10\,h]{} CH_3CH_2CH_2CH_2CN + KBr\,.$$

This reaction does not proceed in the absence of the catalyst in a two-phase arrangement, as has also been confirmed in our cases. The catalytic activity of the polymers was examined as a function of their chemical nature, amount, particle size, and the type of the solvent used. The extent of the reaction was investigated by gas chromatography.

The initial compound used in the preparation of insoluble polymeric catalysts was a chloromethylated copolymer of styrene and divinylbenzene (1% of crosslinking comonomer) with a chlorine content of 24·05% (6·7 mequiv./g). Catalysts *I–III* were prepared according to Scheme 1 (only the chloromethyl group on the carrier is marked).



SCHEME 1

Catalysts *IV*–*VI* were prepared by reacting the chloromethylated polymeric carrier with the corresponding bases in dimethylformamide at elevated temperature. Catalyst *VII* containing thio ether units was obtained by reacting the chloromethylated carrier with Na_2S in dimethylformamide; its oxidation, accompanied by formation of catalysts *VIII* and *IX* containing sulphoxide and sulphone groupings respectively was carried out similarly to that of catalyst *I* (Scheme 1). All the preparation reactions were performed in the presence of the low-molecular reactant in excess; the composition of the products was examined by IR spectroscopy and elemental analysis.

Results of studies performed by other authors[7,14,15] demonstrated a strong effect of the nature of the polymeric catalyst on the course of the substitution reaction under investigation. In our study, another remarkable effect of structure on the activity of a catalyst of basically the same nature has been observed. Crosslinked carriers of pendent thio ether, sulphoxide and sulphone groups exhibit, in solvent systems water–toluene and water–chlorobenzene, either lower catalytic activity or no activity at all, compared with polymeric catalysts which contain analogous groupings of the network structural component. By assuming validity of the suggested mechanism of catalytic effect of polymers consisting in some kind of microhomogenization of both immiscible phases at the phase boundary due to their enveloping by the polymer molecule[6], it may be stated that with all the types of polymers described in this study, this mechanism is effective if functional groups possess a smaller possibility of a "free" motion. Of course, one cannot automatically assign a higher catalytic activity to those polymeric carriers in which the introduction of a functional group has caused an increase in the degree of crosslinking; a certain "fixation" is also induced by the ionic charge of the functional group, as demonstrated by the higher activity of catalyst *IV* compared with that of catalyst *VIII* in the system water–chlorobenzene (Table I). It can be seen, at the same time, that of polymers *VII* to *IX*, the strongest catalytic activity is possessed by that polymer which contains sulphoxide groups where the dipolar character of the bond is stronger than in groups —S— and —SO_2—. Obviously, the strong dipolar character of the bond in groups attached to the polymeric carrier also is one of the important factors affecting activity of the catalysts. This may also be inferred from results presented in other papers[2,7] dealing with the investigation of the activity of polymers containing phosphortriamide units. In all these cases it may be assumed that the favourable catalytic activity is due to interactions between dipolar groups and cations of alkali metals.

Unlike the effect of catalysts containing the quaternary ammonium group observed by Regen and coworkers[14], in the case of catalyst *IV* which also contains a large number of groups with the quaternized nitrogen atom a comparatively high catalytic activity was observed, which persists, though to a reduced extent, also after regeneration. This does not generally hold for all functional groups, *e.g.*, with catalysts *II* and *V* (*cf.* experiments in Table I). The nonregenerable activity of catalyst *V* containing phosphonium groups, though somewhat surprising after opposite findings reported by other authors[8,14] for analogous polymers, nevertheless completes the lower catalytic activity of catalyst *V* containing triphenylphosphonium groups compared with the catalyst containing trimethylphosphonium groups[14] under comparable conditions.

With respect to yields, chlorobenzene usually appears to be a more suitable component of the three-phase system than toluene (*cf.*[14], Table I). The importance of the nature of the organic solvent for the result of the reaction can however be evidenced using experiments with a different supermolecular structure of catalysts and various amounts of the latter. The effective size of the catalytically active domains strongly affects the extent of the reaction. With the polymer used in the pulverized form, the catalytic activity is higher than that of a polymeric catalyst in the granulated form (spherical). In the more active of the systems under investigation, *i.e.* in the system water–chlorobenzene, such a decrease in the surface of catalysts *II* and *V*

TABLE I

Effect of the type of the catalyst (C) and medium on the extent of the nucleophilic substitution reaction (ξ) of 1-bromobutane with potassium cyanide at 80°C: 2 ml of 0·13 C_4H_9Br (toluene or chlorobenzene), 2 ml of aqueous 8 mmol KCN, pulverized catalyst, 50—200 mg C/g KCN (3·3—12·7 mg C per mmol KCN)

Catalyst C	Water–toluene		Water–chlorobenzene	
	mg C	ξ, %	mg C	ξ, %
Without C	—	0	—	0
I	51	0	49	0
II	31	21·6	26	28·6
	50	22·4[a]	50	29·6
	74	23·2	76	29·8
	104	36·0	101	36·6
III	52	0	51	0
IV	47	36·8[a,b]	48	71·4[c]
V	26	10·8[a]	—	—
	50	28·5[b]	50	37·7[c]
	99	31·6	100	38·1
VI	56	28·0	53	45·9
VII	50	29·0	52	29·8
VIII	49	59·5	50	65·0
IX	53	44·8	53	60·2

[a] With regenerated catalyst re-used: *II* (49 mg) 0, *IV* (56 mg) 19·2, *V* (36 mg) 0. [b,c] Granulated catalyst: [b] *IV* (51 mg), 0, *V* (49 mg) 0; [c] *IV* (50 mg) 52·1, *V* (52 mg) 25·5.

reduces conversion relatively by some 30%, while in the system water–toluene the effect is still more pronounced, and the polymeric carriers appear to be catalytically inactive (Table I). The dependence of the extent of the reaction on the amount of the pulverized catalyst is not a continuous one. While only a three- or fourfold increase in the amount of catalyst *II* from the level 50 mg/g KCN resulted in a steep rise in conversion relatively by 67% (water–toluene) or 28% (water–chlorobenzene), in the case of catalyst *V* in the system water–toluene a twofold amount already caused a sudden rise in conversion relatively by 164% (but only an insignificant rise in the system water–chlorobenzene). This means that for each catalyst or functional group on the carrier in the given system of solvents there exists a specific optimal ratio to reactants in the meaning of the catalyzed reaction. Owing to the complexity of mutual effects of the individual factors in a multicomponent three-phase system (ions in the aqueous phase, organic phase with a weakly polar coreactant, adsorption interactions between reacting components and the polymer, swelling of the polymeric catalyst, number and nature of reaction domains), this finding cannot yet be described unequivocally. The results obtained in this study show, of course, that the chemical nature of the polymer and its supermolecular structure, as well as the nature of the organic solvent, pronouncedly affect the catalytic activity in the nucleophilic substitution reaction carried out under conditions of three-phase catalysis.

EXPERIMENTAL

The IR spectra were recorded with a Perkin–Elmer 580 B spectrometer. The gas chromatographic measurements were performed with a Perkin–Elmer F 30 apparatus (FID; column length 1·8 m, diameter 2 mm; packed with 2-cyanomethylethylsilicone (15%) on Chromosorb W, 80—100 mesh; carrier gas nitrogen, 30 cm^3/min). A Haake FS thermostat was used for reactions at constant temperature (temperature adjusted with accuracy ±0·1°C).

Compounds

1-Bromobutane was prepared from 1-butanol by the usual procedure. Chloromethylated copolymer was prepared from poly[styrene(99)-co-divinylbenzene(1)], 500—710 mesh, by boiling two hours with chlorodimethyl ether (after preceding preswelling at room temperature (for 30 min and at boil for 10 min) with zinc chloride as catalyst; the chlorine content in the product was 24·05% (6·7 mequiv./g). Catalyst *IV* was prepared as described[14]; elemental analysis confirmed the total substitution of the chlorine atom in the chloromethylated copolymer based on polystyrene with N-triethylammonium groups. The other chemicals were commercial samples and were used without further treatment, the solvents were repurified by usual methods before use.

Polymer Thiol

A mixture of 2·977 g of chloromethylated poly(styrene-co-divinylbenzene) (19·5 mgequiv.) and 30 ml of dimethylformamide was heated to 80°C for one hour. To the swollen polymer, 2·468 g of thiourea (32 mmol) dissolved in 7·5 ml of dimethylformamide was added, and the mixture was heated to 80°C for 8 h. A small amount of the sample was taken, washed by stirring with dimethylformamide three times with 20 ml ethanol at 50°C (3 h on the whole), and finally, with ether. On drying (50°C, 130 Pa, 24 h) the salt was analyzed; for $C_{10}H_{13}ClN_2S$ (228·5), calculated: 52·52% C, 5·69% H, 15·54% Cl, 12·25% N, 14·00% S; found: 52·32% C, 6·03% H, 12·01% N, 16·02% Cl, 13·85% S. The raw salt was washed by stirring with 20 ml of dimethylformamide and then by stirring with 20 ml water at 50–60°C (30 min). After hydrolysis with 5M NaOH (7·5 ml) at 90°C in nitrogen atmosphere (10 h), the mixture was acidified with 20 ml 1·5M-H_2SO_4 and left to stand at room temperature for 10 h; the polymer was filtered off in nitrogen, washed five times by stirring with 50 ml water, three times with 50 ml methanol (in nitrogen), and eventually, dried (40°C, 130 Pa, 24 h); the yield was 2·83 g of polymeric thiol. For $C_9H_{10}S$ (150·1), calculated: 71·95% C, 6·66% H, 21·31% S; found: 71·62% C, 6·57% H, 21·25% S. IR spectrum (KBr): 670, 860, 1 020, 2 560 cm^{-1}.

Thioether *I*

To a mixture of 2·7 g of polymeric thiol (18 mgequiv.) and 10 ml methanol, a solution of 0·511 g sodium (22 mgatom) in 40 ml methanol was added, the mixture was left to stand for 3 h under nitrogen and after the addition of 2·646 g (2·5 ml) dimethyl sulphate (26 mmol) stirred at 40°C under nitrogen for 45 h. The polymer was sucked off on a glass filter, washed with water, stirred five times with 30 ml of water at 50°C (5 h on the whole), washed on the glass filter three times with 50 ml of methanol and dried at 40°C/130 PA (24 h); 3·05 g of the product. For $C_{10}H_{12}S$ (164·3), calculated: 73·12% C, 7·36% H, 19·52% S; found: 72·80% C, 6·87% H, 19·61% S. IR spectrum (KBr): 670, 750, 1 430, 2 915, 2 990, 3 020, 3 050 cm^{-1}.

Sulphoxide *II*

A mixture of 0·765 g thioether *I* (4·7 mgequiv.), 1·15 ml 30%H_2O_2 and 5 ml of acetic acid was left to stand at –10°C for 5 h, and after that, 50 ml of water was added. The polymer was separated on a glass filter, washed by stirring three times with 50 ml of water, three times with 50 ml of methanol, and eventually with 50 ml of ether at room temperature under nitrogen. On drying (40°C, 130 Pa, 24 h) 0·81 g of the product was obtained. For $C_{10}H_{12}SO$ (180·3), calculated: 66·61% C, 6·71% H, 17·79% S, found: 66·55% C, 6·87% H, 17·48% S. IR spectrum (KBr): 360, 1 030, 1 110, 1 425, 2 920, 2 990, 3 010 cm^{-1}.

Sulphone *III*

Thioether *I* (0·770 g, 4·8 mgequiv.) was oxidized similarly to the preparation of sulphoxide *II*, with the only difference that the reaction was conducted at 5°C for 44 h; 0·85 g of the product was obtained. For $C_{10}H_{12}O_2S$ (196·3), calculated: 61·19% C, 6·16% H, 16·33% S; found: 61·05% C, 6·16% H, 16·05% S. IR spectrum (KBr): 1 130, 1 300, 1 420, 1 510, 2 850, 2 920, 2 970, 3 020, 3 050 cm^{-1}.

Polymeric Catalyst with Triphenylphosphonium Groups *V*

To 0·258 g of chloromethylated polymer (1·67 mgequiv.) swollen at 40°C in 10 ml of dimethylformamide (30 min), a solution of 0·441 g of triphenylphosphine (1·68 mmol) in 5 ml of dimethylformamide was added, and the mixture was left to stand at 70–80°C for 48 h. After that, the solvent was separated, the polymer was washed by stirring five times with 30 ml of ethanol at 50°C (4 h) and dried (50°C, 130 Pa, 48 g). For $C_{27}H_{24}$ ClP (414·9), calculated: 78·16% C, 5·83% H, 7·47% P, 8·54% Cl; found: 77·93% 5·92% H, 7·04% P, 8·58% Cl. IR spectrum (KBr): 570, 690, 730, 760, 840, 1 000, 1 020, 1 110, 1 160, 1 190, 1 320, 1 435, 1 480, 1 500, 1 580, 1 610, 2 780, 2 850, 2 910, 2 960, 2 990, 3 010, 3 020 $^{-1}$.

Catalyst *VI*

Preparation proceeded similarly to that of catalyst *V*: 0·544 g (1·68 mmol) quinine was used, reaction time 22 h. The product was dried, and 0·79 g of the polymer was obtained with fixed quinine units (98·0%). For $C_{29}H_{33}Cl\ N_2O_2$ (477·0), calculated: 73·02%, 6·97% H, 7·43% Cl, 5·87% N; found: 72·70% C, 6·84% H, 8·41% Cl 5·7, 5%N. IR spectrum (KBr): 720, 780, 830, 860, 930, 1 030, 1 090, 1 170, 1 225, 1 240, 1 260, 1 320, 1 360, 1 430, 1 450, 1 510. 1 620, 3 400, 3 600 cm^{-1}.

Thioether *VII*

To 2·00 g of chloromethylated polymer (13·1 mgequiv.) swollen by stirring with 10 ml of dimethylformamide at 50°C (1 h), a mixture of 4·00 g $Na_2S.9\ H_2O$ (16·7 mmol) in 20 ml of dimethylformamide was added and after that 10 ml of water was added to dissolve the salts; the mixture was heated to 90—100°C for 32 h; the solvent was separated, 30 ml of water was added, and the mixture was boiled. The polymer was separated, washed by stirring three times with 50 ml of water at 50°C and three times with 50 ml of ethanol at 70°C, and dried (40°C, 130 Pa, 24 h); 1·52 g of the product was obtained. For $C_{18}H_{18}S$ (266·4), calculated: 81·15% C, 6·82% H, 12·01% S; found: 79·85% C, 7·03% H, 9·94% S; assuming that thioether has not been oxidized, analysis gives its content as 83—92%, along with the initial polymer. IR spectrum (KBr): 620, 710, 1 415, 2 840, 2 860, 2 920, 3 000 cm^{-1}.

Sulphoxide *VIII* and Sulphone *IX*

The compounds were prepared by oxidizing thioether *VII* with hydrogen peroxide, similarly to the preparations of *II* and *III*. Sulphoxide *VIII* — for $C_{18}H_{18}OS$ (282·4), calculated: 76·55% C, 6·44% H, 11·33% S; found: 75·91% C, 6·97% H, 8·88% S. IR spectrum: (KBr): 1 020, 1 110 cm^{-1}. Sulphone *IX* — for $C_{18}H_{18}O_2S$ (298·4), calculated: 72·45% C, 6·09% H, 10·72% S; found: 71·96% C, 6·22% H, 8·48% S. spectrum (KBr): 1 170, 1 360 cm^{-1}. Thc analyscs are adequate to the composition of the initial thioether *VII* at the extent of oxidation reactions 0·95 with respect to sulphur.

Reaction of Bromobutane with KCN

The reactions were performed in a closed test tube. To 2 ml of a solution of 1-bromobutane (0·13 mol l^{-1}) in an organic solvent (toluene, chlorobenzene), a chosen amount of the polymeric catalyst was added (usually pulverized), and a solution of 0·52 g KCN (8 mmol) in 2 ml of water was added to the mixture. After heating the mixture to 80°C for 10 h, the upper organic layer was separated, filtered through a small glass filter and analyzed by gas chromatography; the extent of the reaction was determined by determining the concentration of the valeronitrile formed, with an accuracy of ±2%. The catalyst was regenerated by washing with water, stirring three times with 30 ml of a 5% aqueous NaCl solution and with 30 ml of water at 40°C, washing on the glass filter with 50 ml of ethanol, and drying (40°C, 120 Pa, 24 h).

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