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Polymeric cosolvents

Cooperation of polymer bound quaternary ammonium groups and *N,N*-dialkylamide groups in activation of the phenoxide anion*

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Summary

By a series of quaternization and amidoalkylation reactions a series of polymers I-IV was prepared, based on microporous poly(styrene-98-co-divinylbenzene-2), (PS-DVB). The polymers contain quaternary ammonium groups (Q) and carboxamide groups (L) imitating polar aprotic solvents, i.e. N,N-dimethylacetamide and N-methyl-2-pyrrolidone. These two types of functional groups L, Q exhibit a cooperative effect in the activation of sodium phenoxide in its reaction with 1-bromooctane. The measure of the cooperative effect depends on the type of isolation of the sites in which the functional groups L and Q are bound to the polymeric matrix. An increase in the specific rate constants by more than an order of magnitude was observed with such low-functionalized polymers IV in which both functional groups L and Q are bound in one binding site and are separated by a short spacer only.

Introduction

Synthesis of polymers containing functional groups of the new type is one of the trends in the research of polymeric catalysts applied in organic chemistry. Recently, we have described an unusually high increase in the specific rate constant of substitution reaction of sodium phenoxide catalyzed with polymers in which quaternary ammonium groups and pseudocrownether groupings are bound in a single binding site compared with polymers in which both types of functional groups are bound to the polymer separately (1). The cooperative effect has also been reported for soluble linear oligooxyethylenes with terminal quaternary ammonium groups (2).

However, in the case of polymeric pseudocrownethers based on crosslinked poly(styrene-co-divinylbenzene), in which oligooxyethylene units also are branches of

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*To Professor Pavel Kratochvíl on the occasion of his 60th birthday

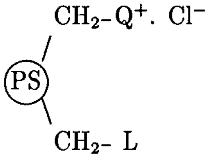
**To whom offprint requests should be sent the network, the degree of crosslinking is high and is insufficiently defined. At the same time, the type and structure of the polymeric carrier is an important factor which determines activity of the polymeric catalyst (3). Polymeric analogs of dipolar aprotic solvents of the N,N-dialkylcarbooxamide type (II) also showed high efficiency (4,5), comparable with pseudocrownethers based on PS-DVB (6). They can be readily obtained, however, by reacting the corresponding N-hydroxymethylamides with PS-DVB (4,7); the reaction of chloromethylated PS-DVB with tertiary amines also leads to polymers with well-defined structure (I) (8). In this study we describe the synthesis of polymers based on microporous poly(styrene 98-co-divinylbenzene 2) with two types of bound functional groups, i.e. quaternary ammonium groups Q and groups L having the structure of dipolar aprotic solvents, N,N-dimethylacetamide and N-methylpyrrolidone. The groups Q and L are bound to the polymeric carrier in an isolated way (III) or together in one binding site of the polymeric matrix (IV).

$\textcircled{\scriptsize PS} - CH_2Q^+ .\ Cl^-$

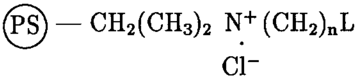
(I)

$\textcircled{\scriptsize PS} - CH_2 - L$

(II)



(III)

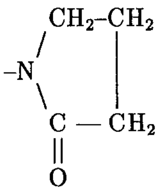


$\textcircled{\scriptsize PS} — CH_2(CH_3)_2\ \underset{Cl^-}{N^+ \cdot}(CH_2)_nL$

(IV) a: n=3
b: n=2

Q: $(CH_3)_2NCH_2CH_2CH_2CH_3$

L: a;



b; $-(CH_3)NCO-CH_3$.

The effect of these new types of functional polymers on the ionic pair was investigated in a nucleophilic substitution reaction of sodium phenoxide with 1-bromooctane carried out in anhydrous 1,4-dioxane (Eq. 1).

$$\mathrm{PhONa} + \mathrm{C_8H_{17}\,Br} \rightarrow \mathrm{PhOC_8H_{17}} + \mathrm{NaBr} \qquad \text{(Eq. 1)}$$

Experimental

Solvents (Lachema, reagent grade purity) and chemicals (Fluka) used in the syntheses were redistilled before use. Anhydrous 1,4-dioxane was prepared by repeated distillation over Na in nitrogen. Sodium phenoxide was prepared by reacting phenol with an equivalent amount of 1 M sodium ethoxide in anhydrous ethanol. After evaporation of the solvent the product was recrystallized from an ethanol-hexane mixture. Poly(styrene 98-co-divinylbenzene 2) and chloromethylated poly(styrene 98-co-divinylbenzene 2) (microporous, beads, 200-400 mesh, Fluka) were used as received. Polymers (I) and (II) were prepared by employing procedures described earlier (7,8). Temperature of the reaction mixtures was maintained with an accuracy of 0.5°C by using Term-O-Watch. GLC analyses of the reaction mixtures were performed using a CHROM 5 apparatus (Laboratory Instruments, Prague; column 0.3 × 250 cm, SP 2100, 5%, on Inerton AW-HMDS, N_2 as carrier gas, FID). IR spectra were recorded with a Perkin-Elmer 580 B apparatus.

Preparation of Polymer IIIa

To 0.125 g of polymer I (33% r.s., 3.20% N) preswollen in 1.5 ml $CHCl_3$ for 30 min. 0.200 g (2.02 mmol) N-hydroxymethyl-2-pyrrolidone and a mixture of 0.60 ml acetanhydride and 2.00 ml CF_3COOH were gradually added. The mixture was maintained with stirring in a closed flask at the bath temperature 70°C for 96 h. After that the polymer was successively washed on the glass filter with 20 ml chloroform, acetone, ethanol, dichloromethane and n-hexane. The polymer was dried at 40°C and 133 Pa for 24 h. The yield was 0.147 g. IR spectra (KBr,cm^{-1}): 1680, 1610, 1590.Elemental analysis: %C 68.61, %H 7.49, %N 3.72, %Cl 7.52, corresponding to 0.61 mmol/g pyrrolidone units and 2.02 mmol/g quaternary ammonium groups.

Preparation of Polymer IVa

To 0.250 g of chloromethylated poly(styrene 98-co-divinylbenzene 2) (0.95 mmol Cl/g) preswollen in 2.00 ml of anhydrous 1,4-dioxane 0.403 g (2.37 mmol) of 1-(3-dimethylaminopropyl)-2-pyrrolidone was added at 80°C. The reaction mixture was kept with stirring at 80°C for 192 h. After that the polymer was washed on the glass filter successively with 20 ml methanol, acetone and n-hexane. The polymer was dried at 40°C, 133 Pa for 24 h. IR spectra (KBr, cm^{-1}): 1670, 1600, 1490, 1450. Elemental analysis: %C 84.26; %H 8.13; %N 2.47; %Cl 2.99. Composition of the copolymer corresponds to an equimolar content of pyrrolidone and quaternary ammonium units 0.885 mmol/g. The polymer with a higher content of functional groups was prepared using similar reaction conditions. The starting polymers contained 1.52 mmol Cl/g and 4.42 mmol Cl/g and were refunctionalized using 3.80 mmol or 11.05 mmol 1-(3-dimethylaminopropyl)-2-pyrrolidone. Composition of the copolymers thus obtained corresponds to an equimolar content of pyrrolidone and quaternary ammonium units 0.984 mmol/g and 2.40 mmol/g, respectively.

Preparation of Polymer IVb

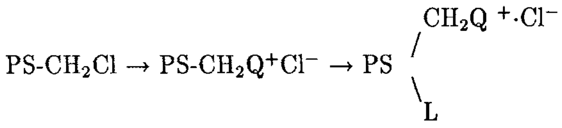
To 0.500 g of chloromethylated poly(styrene 98-co-divinylbenzene 2) swollen in 3.0 ml of anhydrous 1,4-dioxane at 80° C for 30 min., 0.152 g (1.06 mmol) of 1-(2-dimethylaminoethyl)-N-methylacetamide was added. The reaction mixture was maintained with stirring at 80°C for 92 h. After that, the polymer was successively washed on the glass filter with 20 ml ethanol, dichloromethane, acetone and n-hexane, and dried at 40°C, 133 Pa for 24 h. 0.581 g of the product was obtained. IR spectra (KBr,cm^{-1}): 1640, 1600, 1490, 1450. Elemental analysis: %C 86.54; %H 8.48; %N 1.46; %Cl 2.07. Composition of the copolymer corresponds to an equimolar content of acetamide and quaternary ammonium units 0.52 mmol/g.

Reaction of Sodium Phenoxide with 1-Bromooctane in the Presence of Polymer (I)-(IV)

To a solution of 1-bromooctane in anhydrous 1,4-dioxane (0.50 ml, concentration 2.0 mol/l) the polymer (20-25 mg) was added and the mixture was equilibrated at 75°C for 30 min. After that a solution of sodium phenoxide in anhydrous 1,4-dioxane (0.50 ml, concentration 0.50 mol/l) was added, and the reaction mixture was magnetically stirred (600 r.p.m.) for 22 h. Samples (0.5 μl) were taken from the reaction mixture in regular intervals and were analyzed by gas chromatography using dodecane and tetradecane as internal standards. The observed rate constants k_o were calculated according to the second-order kinetics using the concentration of the reaction product — 1-phenoxyoctane determined at five conversions with an accuracy of 3%.

Results and Discussion

Polymers I and IV were prepared by employing the usual routine procedures. The procedure of preparation of polymer IIa,b by a reaction between the corresponding N-hydroxymethylamides and poly(styrene-co-divinylbenzene) has been reported in preceding papers (4,7). Polymer IIIa was obtained by employing a procedure according to Eq. 2:



$$\text{PS-CH}_2\text{Cl} \rightarrow \text{PS-CH}_2\text{Q}^+\text{Cl}^- \rightarrow \text{PS}\begin{matrix} /\,\text{CH}_2\text{Q}^{+}\cdot\text{Cl}^- \\ \backslash\,\text{L} \end{matrix} \qquad \text{(Eq. 2)}$$

It was found that an alternative synthesis involving in the first step amidoalkylation of chloromethylated PS-DVB and in the second step quaternization leads to a product the total composition of which (elemental analysis) is very close to that of the product obtained according to Eq. 2.

The effect of mutual cooperation of functional groups of different type and variously bound to the polymeric carrier on the activation of the anion was investigated using the reaction between sodium phenoxide and 1-bromooctane. The reaction was carried out in anhydrous 1,4-dioxane at 75°C. Under these conditions both the cation and the anion form a close ionic pair, as indicated by the fact that in the absence of the activator the reaction proceeds at a negligible rate (Table). The activation effect of the polymer on the reaction course was followed by means of the specific reaction constants k calculated from the observed rate constants k_o so that $k = k_o/c$, where c is concentration of all functional groups L,Q present in the reaction mixture. In this way the specific rate constants k allow us to compare the activation effect of polymers with various contents of functional groups.

Results summarized in the Table show that quaternary ammonium groups bound on polymer I have an activation effect of the same order of magnitude as functional groups of polymer IIa, IIb. On the other hand, however, polymer IIIa which contains both pyrrolidone and quaternary ammonium groups bound separately in the polymeric

Table. Reactions of sodium phenoxide with 1-bromooctane carried out in the presence of polymers (I)-(IV). Reaction conditions: concentration of bromooctane 2.0 mol/l,PhONa 0.5 mol/l, 75°C, stirring 600 r.p.m., c is the concentration of functional groups of the polymer in the reaction mixture, solvent 1,4-dioxane, $k = k_o/c$ is the specific rate constant, k_o is the observed rate constant [l, mol^{-1} s^{-1}]

Polymer	Content, mmol/g		10^2c, mol/l		10^5k
	L	Q	L	Q	$\mathrm{l}^2/\mathrm{mol}^2{\cdot}\mathrm{s}$
I	–	2.29	–	5.73	14[a]
IIa	2.69	–	6.7	–	28.9
	1.50	–	3.7	–	15.8
IIIa	0.61	2.01	1.53	5.09	198
IVa	0.885	0.885	2.21	2.21	497
	0.984	0.984	2.42	2.42	386
	2.40	2.40	6.00	6.00	68
IIb	2.42	–	6.05	–	13
IVb	0.52	0.52	1.3	1.3	143

[a] In the absence of polymers the conversion after 22 h is 9%, with polymers as catalysts it is 45-100%.

matrix has an activation effect which is higher by an order of magnitude. This activation effect is related to all functional groups present in polymer IIIa. Recalculation of the observed rate constant to such specific rate constant k which expresses the contribution of pyrrolidone units alone makes this effect even more distinct ($k = 862 \times 10^{-5}$ $\mathrm{l}^2/\mathrm{mol}^2$ s). This finding supports the view regarding mutual cooperation of both functional groups in the activation of the phenoxide anion as observed also with other polyfunctional polymers (1-2). The cooperative effect becomes even more pronounced with polymer IVa, where the proximity of pyrrolidone and quaternary ammonium units is given by the short spacer between them, where in the case of the polymer with the lowest degree of functionalization the effect is 2.5 times higher compared with polymer IIIa, and 17 to 31 times higher than with polymer IIa. Similarly, polymer IVb compared with the polymeric analog of N,N-dimethylacetamide IIb also has an activation effect higher by an order of magnitude, indicating cooperation between both types of functional groups. However, the assumed favourable effect of structural proximity of both types of functional groups L,Q in polymer IV can be seen only with the polymer having a low degree of functionalization. With increasing degree of functionalization the activating effect of polymer IVa distinctly decreases. This trend is just opposite to that observed with the polymeric analog of N-methylpyrrolidone IIa. From this, it can be deduced that the structural aspect which in the polymeric matrix guarantees mutual proximity of both types of functional groups, thus making possible an favourable interaction with both ions of the ionic pair without reorganization of the polymeric matrix (which can be assumed for polymer IIIa), will be weaker than the other structural factors, possible interactions and diffusion phenomena. Also, in the simple catalytic system selected by us all these factors may be operative in a different way and even counteract each other. It is known, namely, that also in the investigation of the degree of functionalization of PS-DVB by using dimethylacetamide units the increase in functionalization up to a definite degree brings about a rise in the catalytic activity followed by a decrease as low as to zero value (9). In the case of our system whose structure is even more complicated one should bear in mind also strong electrostatic interactions of groups Q and dipole-dipole interactions of groups L which in polymers III and IV may be reflected in a different way, and thus have different catalytic effects.

The cooperative effect of various types of functional groups and the subsequent increased activation of the reactants renders polymers of this type promising objects of research in the catalysis of organic reactions with polymers.

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