

Pseudocrown Ethers Based on Polyphosphazene as Effective Catalysts of Nucleophilic Substitution Reactions

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SUMMARY

Polymer pseudocrownethers based on polyphosphazene are active catalysts of nucleophilic substitution reactions. With respect to the catalytic activity, polyphosphazene is a more suitable carrier of oligo(oxyethylenes) than poly(styrene-co-divinylbenzene). With increasing length of oligo(oxyethylene) branches the catalytic activity of polymers increases. The favorable effect of the content of pseudocrownether structures is particularly visible in polymers having a longer oligo(oxyethylene) chain in those reactions in which the polymer acts as a solid cosolvent. The catalysts preserve their activity also if reused.

INTRODUCTION

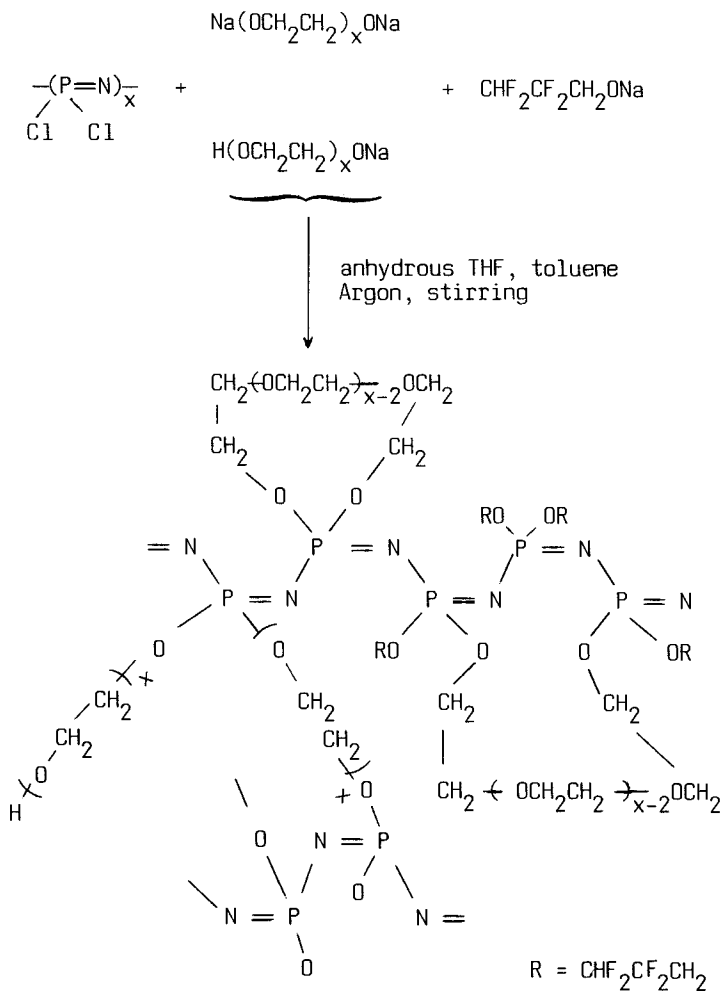
Progress in the chemistry of crownethers used as catalysts of many reactions (1) also brought about the development of polymer-bound crownethers and polymers containing bound oligo(oxyethylene) branches (2). It appears that the presence of an exactly defined cyclic structure of the crownether is not absolutely necessary if a satisfactory activity of polymer catalysts is to be achieved, but that also a polymer containing pendent and intra- or intermolecularly bound oligo(oxyethylene) chains which form pseudocrown structures possesses a catalytic activity, either satisfactorily high, or even higher than that of polymers with bound crownethers (3). The catalytic activity of these compounds in reactions involving metal ions is explained by the formation of complexes, and thus by the activation of anions. In all cases studied so far, the investigation concerned the effect of structure and of the way of binding the crownether to the polymer, of the degree of functionalization and crosslinking of the polymer matrix and of its physical factors on the catalytic activity of these polymers. A great majority of papers are devoted to polymers based on crosslinked polystyrene, and to a lesser extent also to functionalized SiO₂ (4).

Although in these papers the catalytic activity was shown to depend strongly on varying structural factors of the polymer catalyst, further heteroatomic polymer carriers of catalytically active groups have not yet been systematically investigated. This is why the idea of a favourable participation of the heteroatomic main chain of a polymer catalyst in the further development of the conception of three-phase catalysis (5) and of a solid phase cosolvent (6) seems very attractive.

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RESULTS AND DISCUSSION

Recently, we have reported preparation of a number of polymer pseudocrown-ethers based on polyphosphazene (7). The preparation starts from high-molecular weight poly(dichlorophosphazene) and alkoxides of the respective oligo(oxyethylenes) (Fig.1). Poly(dichlorophosphazene) is an example of a highly-reactive polymer, offering the possibility of preparation of a crosslinked polymer catalyst by using refunctionalization reactions. This polymer catalyst



- has a heteroatomic main chain,
- contains both pendent oligo(oxyethylene) branches (1) and oligo(oxyethylene) chains (2) joined with the main chain both intra- and intermolecularly and forming pseudocrownether structures, the amount of (1) and (2) being controlled by the preparation procedure,
- contains fluoroalkoxy groups as components which contribute by their hydrophobicity to the properties of the polymer catalyst, the extent of this contribution being optional.

Hence, properties of the polymer catalysts may be modified in a wide range by varying the procedure used. Indeed, preliminary results showed that crosslinked pseudocrownethers based on polyphosphazene are active catalysts of substitution reactions carried out under the conditions of the L-S-L three-phase catalysis (7).

In this study we also investigated in greater detail the effect of the structure of polymer pseudocrownethers I-IV based on polyphosphazene (Fig.1, Table 1) and polyphosphazene with bound 18-crown-6 rings (V) on the catalytic activity of these polymer catalysts in nucleophilic substitution reactions carried out in two-phase conditions L-S (solid-phase cosolvent) and in the conditions of the three-phase L-S-L catalysis. The activity was compared with that of analogous polymers VI-IX based on crosslinked polystyrene (Table 1):

Table 1. Structural characteristics of polymer catalysts based on polyphosphazene (I-V) and crosslinked polystyrene (VI-IX). Symbols: x is the number of oxyethylene units in the oligo(oxyethylene) chain, f is the molar degree of functionalization with oligo(oxyethylene) chains, n_U/m_P is the content of oxyethylene units, n_B/m_P is the content of pendent oligo(oxyethylene) branches, n_S/m_P is the content of pseudocrownether sequences

Polymer catalyst	x	f	n_U/m_P	n_B/m_P	n_S/m_P
Ia	3	0.59	8.01	1.66	1.01
Ib	3	0.64	9.06	0.69	2.33
IIa	4	0.30	6.68	1.57	0.10
IIb	4	0.51	8.28	0.71	1.36
IIIa	5	0.45	8.30	1.06	0.60
IIIb	5	0.64	9.50	0.66	1.24
IVa	7	0.42	10.78	1.21	0.33
IVb	7	0.69	15.40	0.96	1.24
V	6 ^a	0.07	2.52	-	0.42 ^b
VI	3	0.64	9.24	2.71	0.19
VII	4	0.64	10.08	2.50	0.11
VIII	5	0.64	12.10	2.30	0.06
IX	7	0.64	14.00	1.78	0.06

^a 18-Crown-6. ^b Regular crownether ring.

The two-phase S-L arrangement is a typical example in which the polymer acts as a solid cosolvent, and its activation influence on the reaction course is assigned to its effect on the cation-anion bond. In this case the reaction between sodium phenoxide and 1-bromooctane was investigated in anhydrous 1,4-dioxan at 75° C in the presence of polymers containing, on the one hand, side oligo(oxyethylene) chains, and on the other, free oligo(oxyethylenes). The results are summarized in Table 2. The observed rate constants k were calculated from kinetic curves for a second-order reactions conducted to the conversion of 1-bromooctane to 1-phenoxyoctane.

The specific rate constants k_s are given by k/c_U , where c_U

Table 2. Reaction of 1-bromooctane ($c_H = 1.0 \text{ mol l}^{-1}$) with sodium phenoxide ($c_F = 0.25 \text{ mol l}^{-1}$) in 1,4-dioxan (volume of mixture 1 ml) in the presence of polymer catalysts ($m_p = 25 \text{ mg}$) at 75°C.

Symbols: n_U is the mass amount of oxyethylene units in the weighed amount of the catalyst, n_S is the mass amount of pseudo-crownether sequences in the weighed amount of catalyst, k and k_s respectively are the observed and specific rate constants, ξ is the extent of reaction after 22 h.

Polymer catalyst	n_U mmol	$n_S \cdot 10^2$ mmol	$k \cdot 10^5$ $l \text{ mol}^{-1} s^{-1}$	$k_s \cdot 10^5$ $l^2 \text{ mol}^{-2} s^{-1}$	ξ %
PTFEP ^a	-	-	-	-	9
Ia	0.20	2.5	0.24	1.2	18
Ib	0.23	5.8	0.29	1.3	26
IIa	0.17	0.25	0.60	3.5	40
IIb	0.21	3.4	0.75 ^b	3.6	48
IIIa	0.21	1.5	1.7	8.2	76
IIIb	0.24	3.1	3.7	15	93
IVa	0.27	0.82	3.7 ^c	14	93
IVb	0.39	3.1	8.0	21	97
V	0.13	1.0 ^d	1.3	10	70
PS ^e	-	-	0.11	-	10
VII	0.20	-	0.38	1.9	40
IX	0.28	-	1.5	5.5	68
H(OCH ₂ CH ₂) ₄ OH	0.34	0	12	34	100
H(OCH ₂ CH ₂) ₇ OH	0.33	0	17	52	99
18-Crown-6	0.30	5 ^d	9	30	98

^a Poly[bis(2,2,2-trifluoroethoxy)phosphazene] ^{b,c} In the third reuse of catalyst: ^b 0.76, ^c 3.7. ^d Regular crownether ring.

^e Poly [styrene(98)-co-divinylbenzene(2)].

is the mass concentration of oxyethylene units in the reaction mixture. Thus, the rate constant k_s describes the specific activity of one constitutional unit of the oligo(oxyethylene) chain. The results prove that the reaction is considerably accelerated by the presence of oxyethylene units; in the presence of a polymer with bound oligo(oxyethylene) chains I-IV, VII and IX the acceleration is the greater, the longer the oligo(oxyethylene) chain. The polyphosphazene carrier is more advantageous than the polystyrene one. In the case of polymer pseudocrowns based on polyphosphazene I-IV one can also notice the favourable effect of the higher content of pseudocrown sequences. This phenomenon is extraordinary, because the higher the content of pseudocrown sequences, the higher the expected degree of crosslinking of the polymer (7). In the catalysis with polymers the higher degree of crosslinking is a factor acting very strongly in just the opposite sense (2). According to k_s , polyphosphazene with bound 18-crown-6-rings (V) shows a specific activity comparable with polyphosphazenes containing bound penta(oxyethylene) and hepta(oxyethylene) chains; its disadvantage, however, consists in its difficult preparation by a time-consuming and little effective synthesis. Even though the reactions in the presence of free oligo(oxyethylenes), including 18-crown-6, proceed almost twice as quickly as in the presence of polymers most effective with respect to activation, a great advantage of crosslinked polymers containing bound oligo(oxyethylene) chains is their easy separability and the possibility of reuse. Polymer catalysts are stable under such conditions.

Results of the reactions occurring under the conditions of the L-S-L three-phase catalysis are summarized in Table 3. In the absence of the

Table 3. Reaction of 1-bromooctane (1 ml 0.6 M, toluene) with NaI or KSCN (1 ml 6 M, water) in the presence of polymer catalysts ($m_p = 50$ mg) at 100°C (48 h).

Symbols: n_U is the mass amount of oxyethylene units in the weighed amount of catalysts (2 ml of reaction mixture), ξ is extent of the reaction, A is activity ($\xi/100c_U$, $l\ mol^{-1}$)

Polymer catalyst	n_U mmol	1-Iodoctane		octyl thiocyanate	
		ξ , %	A, $l\ mol^{-1}$	ξ , %	A, $l\ mol^{-1}$
-	-	0	-	1	-
PTFEP ^a	-	12	-	12	-
PBPP ^b	-	8	-	10	-
Ia	0.40	14	0.70	76 ^f	3.80
Ib	0.45	20	0.88	82	3.64
IIIb	0.48	79 ^d	3.30 ^d	95	3.96
IVa	0.54	83	3.08	99 [,]	74 ^d 2.74 ^d
IVb	0.77	86 ^{d,e}	2.24 ^d	98 ^g ,	80 ^d 2.08 ^d
PS ^c	-	-	-	1	-
VI	0.46	7	0.30	12	0.52
VIII	0.65	76 ^d	2.34 ^d	85 [,]	60 ^d 1.85 ^d
IX	0.70	90 ^d	2.58 ^d	98 [,]	78 ^d 2.22 ^d

^a Poly[bis(2,2,2-trifluoroethoxy)phosphazene]. ^b Poly(bisphenoxyphosphazene). ^c Poly[styrene(98)-co-divinylbenzene(2)]. ^d After 24 h. ^{e-g} In the second use of catalyst the following values were reached: ^e 0.83 (24 h), ^f 0.73 (48 h), ^g 0.99 (48 h).

catalyst the reactions do not proceed. In the presence of polyphosphazenes with bound 2,2,2-trifluoroethoxy- or phenoxy groups inactive from the catalytic point of view, a small but perceptible extent of the reaction was recorded. Introduction of the side chain $\text{H}(\text{OCH}_2\text{CH}_2)_3\text{O}$ into the crosslinked polystyrene (catalyst IV) has a weaker effect with respect to the increase in the catalytic activity than introduction of the same chain into the polyphosphazene carrier chain (catalyst I). Introduction of longer residues of oligo(oxyethylenes) into both polymer carriers brings about a rise in activity (becoming optimal when the number of oxyethylene units is five), and differences in the activities of the corresponding polymer catalysts are wiped out. This is probably caused by the predominance of the hydrophilic character of the polymer containing longer oligo(oxyethylene) side chains. There are no pronounced differences in the activities of polyphosphazenes with bound oligo(oxyethylenes) containing various amounts of pseudocrown sequences. Hence, it may be inferred that in the mechanism of the three-phase catalysis the easiness of complex formation need not be the decisive factor affecting the kinetics of nucleophilic substitution reactions. This was also demonstrated for the polymer analog of dimethylsulfoxide (8). Under the conditions of the L-S-L three-phase catalysis catalysts based on polyphosphazene had also a good chemical stability when reused.

Experimental Part

Anhydrous 1,4-dioxan and toluene were distilled from sodium in the nitrogen atmosphere in the presence of benzophenone. 1-Bromooctane was redistilled before use. Sodium phenoxide was prepared by reacting equivalent amounts of phenol and sodium ethoxide in ethanol and recrystallized from ethanol. Polymer catalysts containing bound oligo(oxyethylenes) on the polystyrene carrier were prepared from chloromethylated poly [styrene(98)-co-divinylbenzene(2)] (64% r.s., particle size 200-400 nm) by employing a procedure described by Regen (3). Poly [bis(2,2,2-trifluoroethoxy)phosphazene] and poly(bisphenoxyphosphazene) were prepared by the described procedures (9). Polymer catalysts based on polyphosphazene were prepared from poly(dichlorophosphazene) (7). The content of oxyethylene units in the polymers was calculated from an elemental analysis of the samples. The content of pendent oligo(oxyethylene) branches on polymer carriers was determined by determining hydroxyl groups by the acetylation method; that of pseudocrown sequences was calculated as the difference between the contents of oligo(oxyethylene) chains and pendent branches. Constant temperature of the reaction mixtures was maintained by means of a Term-O-Watch, LS-1000 apparatus with an accuracy of $\pm 0.1^\circ\text{C}$. The reaction mixtures were analyzed by gas chromatography using a Chrom 5 apparatus (steel column 0.3 x 100 cm, packing SP-2100 on Inerton AW DMCS, carrier gas N_2 , FID) and internal standards.

Reaction between 1-bromooctane and sodium phenoxide

To a mixture of 0.5 ml of 2M 1-bromooctane in anhydrous 1,4-dioxane and 25 mg of polymer, 0.5 ml of 0.5 M sodium phenoxide was introduced at 75°C after 30 min. of stirring (anhydrous 1,4-dioxane containing dodecane as the internal standard). The mixture, vigorously stirred (600 r.p.m.), was maintained at 75°C , and its composition was continuously checked (samples 0.05 μl were taken for the GLC analysis). The rate constants were determined from concentration changes of 1-phenoxyoctane determined with an accuracy of 5%. After the chosen time the solution above the

polymer was sucked off, the polymer was washed three times with 3 ml of anhydrous dioxan and the experiment was repeated.

Reaction of 1-bromooctane with sodium iodide and potassium thiocyanate

To 50 mg of polymer, 1 ml of 0.6 M 1-bromooctane (toluene) was added and the mixture was stirred at 100°C (magnetically with a teflon stirrer 2.5 x 10 mm) for 30 min. After that, 1 ml of a 6 M salt (H₂O) was introduced and the mixture was maintained with intensive stirring (600 r.p.m.) at 100°C for 48 h (or 24 h), after which it was analyzed by GLC (sample 0.05 ul). The extent of the reaction was determined as the average from values calculated from the concentrations of 1-bromooctane and octyl thiocyanate (deviation of the averaged value 2% at most). In selected cases the liquid mixture was separated from the polymer by filtration, the polymer was washed three times by mixing with 3 ml of toluene at 100°C and after the last separation reused in a further experiment.

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