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The amine modified acrylic copolymers as catalysts in the reaction of octylbromide with sodium cyanide

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Summary

Amine-modified and alkylated (with butyl bromide or hexyl bromide) acrylonitrile-butyl acrylate-divinylbenzene terpolymers and alkyl acrylate-divinylbenzene copolymers (where alkyl= methyl, ethyl or butyl) were used as catalysts in the reaction of octyl bromide with cyanide anions. The dependence of catalytic activity as a function of the acrylate content and swelling properties was investigated. The most effective catalyst was butyl acrylate-divinylbenzene copolymer. This sample showed maximum toluene uptake from the toluene/water mixture.

Introduction

The main advantage of polymer supported phase transfer catalysis is the easy way of catalyst separation and reuse. So far cryptands (1), crown ethers (2,3), quaternary ammonium (4,5) and quarternary phosphonium salts (6,7) were attached to the crosslinked polymers. These polymers were mainly lightly crosslinked styrene-divinylbenzene, macroporous styrene-divinylbenzene (8,9) and hydrophilic polyvinylpyridine (10) and glycidyl methacrylate-ethylene dimethacrylate (11).

In the previous study (12) we described strongly polar phase transfer catalysts with quarternary ammonium groups, based on acrylonitrile-divinylbenzene copolymers. The activity of these catalysts was somewhat lower than those previously prepared (for example , glycidyl methacrylate-ethylene dimethacrylate) probably because of the presence of ordered regions in the copolymers containing numerous acrylonitrile units (13,14). Such copolymers are additionaly crosslinked by physical crosslinks.

In this work we present a series of catalysts with tributyl ammonium groups obtained from acrylonitrile-butyl acrylate-divinylbenzene terpolymers and from butyl (ethyl, methyl) acrylate-divinylbenzene copolymers. In these polymers acrylates are able to prevent formation of ordered regions (15).

Experimental

The acrylonitrile- butyl acrylate- divinylbenzene terpolymers as well as alkyl acrylate- divinylbenzene copolymers (where alkyl= methyl, ethyl or butyl) were synthesized by suspension polymerization. In order to form

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macroporous structures, polymerizations were carried out in the presence of toluene and heptane (1:9 v/v) as described (16).

These polymers, each with 10 wt.% of DVB crosslinking agent, were subjected to aminolysis with 1,3- diaminopropane. The reaction was carried out with 8 fold excess of amine in the respect to the nitrile and ester groups content for 10 hrs at 125°C.

The amino groups in N-substituted amides of acrylic acid were alkylated with butyl bromide (hexyl bromide). Thus, 3g of aminated polymer was heated in the mixture of 45 ml of butyl bromide (hexyl bromide), 7.5 ml of acetonitrile and 7.5 ml of dioxane for 8 hrs at 75°C. After the reaction the resin was washed with dioxane, acetone, acetone/water and water, and dried.

The content of strongly basic groups was determined after converting them (2g of dry mass) into the Cl^- form with 500 ml of 1M HCl following by washing with 100 ml of 0.001M HCl. Then the 500ml of 0.1M NaCl in 0.05M ammonium hydroxide and 500 ml of distilled water were passed through the column. The Cl^- ions were eluted with 4% solution of sodium sulfate and determined argentometrically. The total number of amino groups was determined as in the case of strongly basic ones except that after washing with 0.001M HCl the Cl^- ions were eluted with 4% sodium sulfate solution in 0.05M ammonium hydroxide. The content of the quarternary and remaining amino groups was also ascertained by potentiometric titration with 0.1M HCl in 1M NaCl solution using an automatic Mettler apparatus.

The apparent density was determined pycnometrically in mercury. The water and toluene regains were determined by centrifugation. To avoid errors in the case of poor solvents samples, were swollen in toluene and were washed subsequently with acetone, acetone:methanol, methanol, methanol:water and finally with a large amount of water. The simultaneous regain of water and toluene was determined as it was described (17).

The resins with strongly basic tributylammonium groups were used as catalysts for the reaction of octyl bromide with NaCN. Thus, approximately 0.1g of catalyst in Br^- form was placed in the reactor together with 0.96 ml of organic phase containing octylbromide and 1.2 ml of water phase containing NaCN according to procedure described in detail (17) in which the reaction conditions were presented as well.

Results and Discussion

Characteristics of catalysts obtained by the aminolysis of acrylonitrile-butyl acrylate- divinylbenzene terpolymers and butyl (ethyl, methyl) acrylate- divinylbenzene copolymers are summarized in Table 1. Modification was carried out with 1,3-diaminopropane followed by alkylation of the free primary amino groups with butyl or hexyl bromide. These reactions lead to polymers with high apparent density, and porosity in the range of a few percent, and specific surface area approximately equal to zero. This means that the modification of acrylonitrile- butyl acrylate- divinylbenzene terpolymers results in greater changes in supermolecular structure than the modification of acrylonitrile - divinylbenzene copolymers of the same degree of crosslinking (12).

Table 1. Properties of phase transfer catalysts containing tributylammonium groups

Sample1 Properties	2	3	4	5	6	7*	8**	9	10
Ratio AN/BA 4:1	2:1	1:1	1:2	1:3	BA	BA	BA	MA	EA

Properties	1	2	3	4	5	6	7*	8**	9	10
Ratio AN/BA	4:1	2:1	1:1	1:2	1:3	BA	BA	BA	MA	EA
Apparent density g/cm^3	1.18	1.24	1.23	1.21	1.25	1.21	1.15	1.06	1.31	1.29
Ion-exchange capacity mmol/g,total	1.76	1.86	1.96	1.32	2.62	2.24	2.20	0.00	2.99	3.17
strong-base	0.34	0.44	0.32	0.06	0.34	0.12	0.40	0.00	0.49	0.56
Regains, g/g from water	2.01	2.23	2.30	1.84	2.26	1.45	0.33	0.05	1.66	1.60
from toluene	0.04	0.03	0.05	0.09	0.04	0.05	0.27	1.25	0.04	0.03
from water/toluene mixture 1:1										
water	1.12	1.05	1.23	0.98	1.38	0.45	0.18	0.00	0.92	0.95
toluene	0.28	0.32	0.26	0.20	0.17	0.52	0.26	1.10	0.09	0.11

AN - acrylonitrile, BA - butyl acrylate, EA - ethyl acrylate, MA - methyl acrylate

*sample alkylated twice **non-modified butyl acrylate-divinylbenzene resin

ALL copolymers with 10 wt.-% of DVB as the crosslinking agent

Modification makes these polymers more hydrophilic: their water regains increase as compared to the starting samples. It should be noted that after modification, which is almost of the same extend for all samples, hydrophilicity depends mainly on the content of amino groups despite of the different number of nitrile and ester groups in the resins. Samples 6 and 7 were obtained from the same starting material. Comparing their water and toluene regains one can see that hydrophilicity is sensitive to alkylation. Thus, an increase in the content of the strong-base groups with butyl chains from 0.12 to 0.40 mmol/g results in a decrease in toluene regain. Total ion-exchange capacity of these two resins is the same.

The hydrophilicity-hydrophobicity balance is important for the mechanism of phase transfer catalysis in triphase system proposed by Montanari (18). It requires that the polymer bonded cation should be able to contact with both organic and water phases. This can be achieved when the spacer arm with cation moves from the water to organic phase, depending on the counterion or by the motions of polymer chains between water and organic phases as a result of the changes of hydrophilicity in the surroundings of the chains. Both types of motions could be facilitated when the swelling of polymer matrix in water and organic solvent is improved.

The content of organic solvent and water in polymer can be estimated by measuring the solvents regains. But this method is not good because of different swelling conditions in pure solvent and in the reaction mixture, which consists of both organic solvent and water. In the previous work (17) it was shown that the difference between toluene uptake from pure solvent and from its mixture with water (1:1 v/v) were quite large. Now, we have the same situation. Toluene regain from pure solvent is equal to only few percent of polymer mass, except sample 7. Toluene regain from the mixture is few times greater, and it seems that these differences are the function of the number of the strong-base groups with hydrophobic butyl chains and of the number of butyl acrylate units in the main polymer chain. Since toluene is a good solvent for divinylbenzene and for butyl acrylate and poor one for acrylonitrile one should expect greater toluene uptake for polymers with a large number of butyl acrylate units and/or with a high content of strongly basic groups.

Moreover, molecular motions should improve when the glass temperature of polymer decreases. In our polymers we have this because the increase in the butyl acrylate content decreases the glass temperature. The T_g of polyacrylonitrile is in the range 60-125°C, whereas that of poly(butyl acrylate) is -45°C.

By comparing the data of water regain, we can say that these polymers, except samples 6 and 7, are more hydrophilic than styrene-divinylbenzene catalysts and or even glycidyl dimethacrylate copolymers whereas the water regains are similar. At the same time the reaction rate constants are a few times higher for polymers tested in this work (Table 2). Very sharp increase in the reaction rate constant was obtained for sample 6, which consists of butyl acrylate and divinylbenzene. With this sample we made two additional experiments: First, a second alkylation led to a greater number of active strong-base groups. Sample 7 has strong- base capacity 0.40 mmol/g but both reaction rate constants k_1 and k_2 are smaller than that of sample 6. It indicates that the more active are the catalytic groups deposited on the bead surface whereas those located

Table 2. Catalytic activity of acrylate polymers containing tributylammonium groups

Sample a	Activity $k_1 \times 10^5$ (s^{-1})	$k_2 \times 10^3$ $(dm^3 s^{-1} mol^{-1})$
1	3.20	2.21
2	2.28	1.16
3	2.85	1.78
4	1.88	5.64
5	2.66	1.76
6	3.75	6.73
7	1.02	0.56
8[b]	0.14	-
9	0.82	0.31
10	0.95	0.35
AN-DVB resin 20% of DVB		0.94 (ref.12)
GMA-EGDMA resin 40% of EGDMA		1.42 (ref.18)
Tributylammonium bromide		18.06 (ref.18)

a particle size 150-250 mm,
b non-modified resin.

inside the polymeric material are less active or non-active, but they contribute to the total solvent regain and to the recalculated reaction rate constant - k_2. Second, an experiment in which we used unmodified butyl acrylate-divinylbenzene copolymer should answer the question if these polymers with strongly polar carbonyl groups and nonpolar aliphatic chains show any co-solvent effect. The reaction rate constant for the unmodified sample 8 is 0.14 s^{-1} (Table 2) which is about 4.5% of the rate constant for sample 6; hence we can say that co-solvent effect does not influence the reaction between octyl bromide and NaCN.

Samples 11 to 15 were obtained from the same starting polymers as samples 6, 9 and 10, but hexyl bromide was used for their preparation. Samples alkylated with hexyl bromide posses similar water and toluene regains, except for sample 15 (BA-DVB) (Table 3). For the latter water regain is much smaller when compared with water regain for sample 6, alkylated with butyl bromide. But solvents uptake from the mixture of water and toluene shows affinity to organic solvent. At the same time the rate constants for catalysts with trihexylammonium groups are higher than those with tributylammonium groups. This dependence is easily observable for copolymers of methyl or ethyl acrylate with divinylbenzene (samples 9 and 12, 10 and 14, see Table 4). The introduction of hexyl chains into butyl acrylate-divinylbenzene copolymer results in only a slight increase of rate constant. It seems that relatively high rate constants can be achieved when the amount of imbibed toluene and water is similar.

The influence of the number of strongly basic groups can be also observed in samples 11-13. These samples were alkylated

Table 3. Properties of phase-transfer catalysts containing trihexylammonium groups

Sample[a] Properties	11[b]	12[b]	13[b]	14	15
Monomer	MA	MA	MA	EA	BA
Apparent density,g/cm3	1.30	1.31	1.31	1.29	1.23
Ion-exchange capacity, mmol/g					
total	3.00	3.04	3.05	3.17	1.70
strong-base	0.35	0.43	0.52	0.48	0.24
Regains, g/g					
from water	1.97	1.78	1.53	1.54	0.35
from toluene	0.01	0.03	0.03	0.02	0.39
from water/toluene mixture 1:1					
water	0.98	0.90	0.78	0.65	0.20
toluene	0.09	0.13	0.20	0.25	0.24

[a] copolymers crosslinked with 10 wt.-% of DVB,

[b] samples with the same matrices but different strong-base groups content

Table 4. Catalytic activity of acrylic copolymers with trihexylammonium groups

Sample a	Activity	
	$k_1 x10^5$ (s^{-1})	$k_2 x10^3$ $(dm^3 s^{-1} mol^{-1})$
11	2.01	1.11
12	2.32	1.02
13	2.47	0.89
14	2.40	0.99
15	3.91	3.07

a particle size 150-250 mm.

to different extents. We can observe an increase of toluene uptake under triphase conditions and an increase of the rate constant. However, the recalculated rate constant k_2 gets smaller with increasing number of the strongly basic groups. It means that the groups inside the beads are less active, like in the case of butyl acrylate-divinylbenzene copolymer i.e., samples 6 and 7.

Conclusions

The highest catalytic activity are displayed by polymers with large toluene/water uptake under triphase conditions. Increase of the number of strongly basic groups led to a decrease of catalytic activity, hence high toluene regain must be obtained by using more hydrophobic matrix (e.g., with butyl acrylate).

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