

## The amine modified acrylonitrile-divinylbenzene copolymers in the phase transfer catalysis\*

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### Summary

Amine modified, macroporous acrylonitrile-divinylbenzene copolymers of various crosslinking degree were used as catalysts in the reaction of octylbromide with cyano anions. The dependence of their catalytic activity upon swelling and strongly basic amino groups content were discussed. The reaction rate constants were somewhat lower than those for the reactions catalysed by other polymers containing tributylammonium groups. It was probably due to the presence of ordered regions in copolymers containing large amounts of acrylonitrile units.

### Introduction

In the phase transfer catalysis (PTC) mainly low molecular weight compounds like crown ethers, tetraalkylammonium salts and cryptands (1,2,3) were used although application of macroporous and gel-type copolymers of styrene-divinylbenzene (4) and glycidylmethacrylate-ethylenedimethacrylate (5) was reported as well. The copolymers served as carriers for the substances mentioned above.

There are several factors such as crosslinking degree, swelling of polymeric matrix in the reaction mixture, specific surface area and presence and nature of spacers that influence catalytic activity of polymer supported catalysts. All these factors determine the accessibility of active sites.

The aim of this work is to report an application of macroporous and gel-type acrylonitrile (AN)-divinylbenzene (DVB) copolymers as carriers in PTC. AN-DVB copolymers were previously aminated then alkylated to obtain strongly basic amino groups on their surface.

### Experimental

Four types of AN-DVB copolymers were synthesized using the suspension technique: three were prepared in the presence of toluene and hexadecane (9:1 v/v) as inert diluents with 5, 10 and 20 wt.-% of DVB as the crosslinking agent and one with 10 wt.-% of DVB without any diluent. In each case the ratio of monomers to the sum of inert diluents was 1:1. After polymerization the copolymers were washed with hot water and methanol, dried, pre-swelled in benzene and extracted with this solvent in Soxhlet apparatus. The polymerization procedure was described in (6).

The next step was the aminolysis, which was carried out using 1,3-diaminopropane (DAP) or 1,6-diaminohexane (DAH) with 8 fold excess of amine in respect to the content of nitrile groups in each copolymer. The reaction was carried out in the presence of good solvent - toluene (1:1 v/v) at 100°C for 15 hrs. Aminolysis of nitrile groups with diamines lead to N-substituted

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amides of acrylic acid with terminal  $\text{NH}_2$  groups. These amino groups were subjected to alkylation with butylbromide in polar solvents, using 10g samples, 50ml of a solvent and 150ml of butylbromide. Reaction time: 6 hrs for samples with 5 and 10 wt.-% of DVB and 9 hrs for that with 20 wt.-%. The thus obtained ionosorbents with strongly basic amino groups were used as catalysts in the reaction of octylbromide with cyano anions.

The apparent and true densities were determined pycnometrically (in mercury and methanol, respectively) and used to calculate porosity. The water and toluene regains were determined by centrifugation off the excess of liquid. The contents of strongly and weakly basic amino groups in the modified copolymers were determined by Hecker's method (7) or by direct titration with HCl solution. These strongly basic groups were used to catalyse the reaction of octylbromide with NaCN. Thus, into 5ml glass reactor equipped with a propeller stirrer 0.1g of dry copolymer in  $\text{Br}^-$  form were placed, 0.96 ml of solution of octylbromide and o-dichlorobenzene (as internal standard in GC) in toluene and 1.2ml of NaCN aqueous solution. The reaction mixture was kept at 363K while stirring (560rpm). After each 15 min a 0.5 $\mu\text{l}$  sample of organic phase was taken away and concentration of octylbromide was determined chromatographically using Perkin Elmer apparatus F-11B.

### Results

The copolymers obtained by suspension polymerization were modified in a reaction with diamines: 1,3-diaminopropane and 1,6-diaminohexane. In order to increase capacity the reaction with diamines was carried out in good solvent - toluene. At the conditions applied only about 20% of nitrile groups in macroporous resins were converted into N-substituted acrylamide. Not more than 6% of substitution was reached in the case of the gel-type copolymers. The effectivity of aminolysis measured in terms of amino groups content was somewhat smaller in the case of diaminohexane although basicity of this amine was higher than that of diaminopropane ( 2.15-3.50 mmol/g for DAP modified samples and 1.55-2.10 mmol/g for DAH modified samples, depended on the crosslinking degree). Probably the amine with the higher distance between  $\text{NH}_2$  groups reacted more easily with its two groups than it was in the case of 1,3-diaminopropane. After aminolysis the copolymers were washed with acetone and water. Several solvents, such as ethanol, dioxane and acetonitrile were used in the alkylation of aminated copolymers with butylbromide. The higher was polarity of the solvent the higher amount of strongly basic groups was introduced. As in the alkylation of the methacrylate copolymers, the increasing of alkylation time was found not to yield a higher, strongly basic capacity of ionosorbents but even to decrease due to decomposition of quaternary groups (8). The strongly basic capacities obtained in various solvents at various time are presented in table 1.

Table 1. The influence of the solvent and reaction time on the strongly basic capacity of the resin 10/DAH. (strongly basic capacity in mmol/g)

| Solvent      | Reaction time, hrs | 2    | 4    | 6    | 12   |
|--------------|--------------------|------|------|------|------|
| Ethanol      |                    | ~0   | 0.08 | 0.10 | 0.05 |
| Dioxane      |                    | 0.10 | 0.19 | 0.28 | 0.20 |
| Acetonitrile |                    | 0.25 | 0.34 | 0.56 | 0.40 |

Reaction conditions: see Experimental Part

The characteristics of all modified AN-DVB copolymers (alkylated in acetonitrile) tested as catalysts are presented in table 2. As one can see, the alkylation took place in to a small extent only. Not more than 30% of amino groups were

Table 2. Characteristics of modified copolymers (aminated than alkylated)

| DVB/amine | Density                       |                           | Porosity<br>% | Regain       |                | Ion-exchange capacity    |                 |
|-----------|-------------------------------|---------------------------|---------------|--------------|----------------|--------------------------|-----------------|
|           | Apparent<br>g/cm <sup>3</sup> | True<br>g/cm <sup>3</sup> |               | Water<br>g/g | Toluene<br>g/g | Strongly basic<br>mmol/g | Total<br>mmol/g |
| 20/DAP    | 1.235                         | 0.723                     | 41.5          | 1.20         | 0.61           | 0.34                     | 2.33            |
| 20/DAH    | 1.291                         | 0.630                     | 51.2          | 1.03         | 0.73           | 0.47                     | 1.54            |
| 10/DAP    | 1.275                         | 0.821                     | 35.6          | 1.10         | 0.41           | 0.48                     | 3.39            |
| 10/DAH    | 1.262                         | 0.593                     | 53.0          | 1.25         | 0.78           | 0.56                     | 1.97            |
| 5/DAP     | 1.286                         | 0.574                     | 55.3          | 4.16         | 0.53           | 0.52                     | 3.08            |
| 5/DAH     | 1.143                         | 0.595                     | 48.0          | 1.39         | 0.64           | 0.38                     | 2.04            |
| 10gel/DAP | 1.192                         | 1.176                     | 1.4           | 0.90         | 0.07           | 0.15                     | 0.86            |
| 10gel/DAH | 1.140                         | 1.065                     | 6.6           | 1.24         | 0.15           | 0.16                     | 0.95            |

converted and in the case of gel-type copolymers with 10 wt.-% of DVB, yield of alkylation was even smaller.

The results of PTC experiments are presented in table 3. The values  $k_1$  and  $k_2$  are the first order reaction rate constant and the normalized reaction rate constant, respectively.

$$k_2 = \frac{k_1}{wa/V} \quad /dm^3 \text{ mol}^{-1} \text{ s}^{-1}/,$$

where:  $w$  is the weight of polymer (g),  
 $a$  is the amount of strongly basic groups (mmol/g),  
 $V$  is the volume of the liquid phase.

$k_2$  is a convenient measure of the catalytic activity of copolymers with different amounts of strongly basic amino groups. As can be seen the activities of these copolymers are not so good as for another polymeric matrices. For catalysts based on glycidyl methacrylate-ethylene dimethacrylate the reaction rate constant

$k_2$  was  $0.91 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  in the case of the sample with 40% of the crosslinking agent and particle size and active groups content similar to that in the present study (9). This  $k_2$  value can be compared with that obtained for sample 20/DAP. For all other samples the values of  $k_2$  were smaller (table 2). It is probably due to ordered structure which becomes poorly accessible (10). Because acrylonitrile is able to form ordered structures, which can act as the additional, physical crosslinks the accessibility of active sites decreases with increasing AN content. This seems to explain the lowest activity of the samples

Table 3. Phase Transfer Catalysis by acrylonitrile-divinylbenzene copolymers with tributylammonium groups

| DVB content/amine | Ion-exchange capacity    |                 | $k_1 \times 10^5$<br>s <sup>-1</sup> | $k_2 \times 10^3$<br>dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> |
|-------------------|--------------------------|-----------------|--------------------------------------|--|
|                   | Strongly basic<br>mmol/g | Total<br>mmol/g |                                      |  |
| 20/DAP            | 0.34                     | 2.33            | 1.628                                | 0.938  |
| 20/DAH            | 0.47                     | 1.54            | 0.655                                | 0.262  |
| 10/DAP            | 0.48                     | 3.39            | 0.898                                | 0.356  |
| 10/DAH            | 0.56                     | 1.97            | 1.449                                | 0.532  |
| 5/DAP             | 0.52                     | 3.08            | 0.474                                | 0.266  |
| 5/DAH             | 0.38                     | 2.04            | 0.620                                | 0.327  |
| 10gel/DAP         | 0.15                     | 0.86            | 0.730                                | 0.744  |
| 10gel/DAH         | 0.16                     | 0.95            | 0.576                                | 0.638  |

5/DAP and 5/DAH. The more crosslinked copolymers, the greater values of the reaction rate constant are observed. Probably, the increase in DVB content results in less ordered structure of the supports.

One should also notice the fact that the nonporous polymers (10gel/DAP and 10gel/DAH) are more effective as catalysts than those of the same crosslinking degree but having porous structure (10/DAP and 10/DAH). It means that catalytically active are only the groups on the surface beads. The external surfaces of the macroporous copolymers are lower, in comparison with gel-type ones, of the entering of the pores, which are filled with water, as observed earlier (11).

Because the mechanism of the catalytic action involves the extraction of reagent from water to the organic phase, we determined the water and toluene regains for all copolymer tested (table 2). Results indicate that these copolymers are hydrophilic. Water regain depended mainly on the crosslinking degree while toluene regain is similar for all copolymers but in each case larger for copolymer modified with DAH. For copolymers having the same porosity an improved toluene regain results in increasing activity.

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