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Crosslinking copolymerization of *N*-vinylformamide in inverse suspension

RAPID COMMUNICATION

Summary — Crosslinking copolymerization of *N*-vinylformamide (NVF) and divinylbenzene (DVB) has been carried out in reverse suspension in presence of water which serves as porosity generating feature (porogene). The continuous phase was provided by silicone oil or paraffin oil. In silicone oil the copolymer resulted in form of regular spheres what was not the case when paraffin oil was used. After base hydrolysis anion-exchangers were obtained having primary amine groups attached to the backbone. Exchange capacity, degree of swelling, water content in air conditioned resin and the specific surface were determined.
Key words: *N*-vinylformamide, polyvinylamine, anion-exchangers, suspension polymerization.

SIECIUJĄCA KOPOLIMERYZACJA *N*-WINYLOFORMAMIDU W ODWRÓCONEJ SUSPENSJI
Streszczenie — W odwróconej suspensji przeprowadzono sieciującą kopolimeryzację *N*-winyloformamidu (NVF) z diwinylobenzenem (DVB) w obecności wody jako porogenu (schemat A, tabela 1). W charakterze fazy zwartej stosowano olej parafinowy lub olej silikonowy. W oleju silikonowym otrzymano granulki sferyczne, natomiast w oleju parafinowym granulki mają kształt nieregularny (rys. 1 i 3). Po hydrolizie alkalicznej otrzymano polianionity z I-rzędowymi grupami aminowymi (rys. 2 i 4). Oznaczono pojemność jonowymienną, stopień spęcznienia, zawartość wody w żywicy kondycjonowanej na powietrzu oraz powierzchnię właściwą (tabela 2).
Słowa kluczowe: *N*-winyloformamid, poliwinyloamina, anionity, polimeryzacja suspensyjna.

Anion- and cation-exchangers are playing today significant roles in many fields of practice. They are used in large amounts for deionization of water in modern electric power stations. Most of the synthetic exchanger resins are based on styrene (S) and divinylbenzene (DVB), which copolymers form the crosslinked network. After sulfonation cation-exchangers are obtained, whereas anion-counterparts are provided by chloromethylation and subsequent amination — most often with a tertiary amine. One disadvantage results from polystyrene/DVB — crosslinked skeletons. They have by themselves high molecular weights and as a consequence the ion-exchange capacities cannot be as high as desired. In case of anion-exchangers they are in the range between 2.5—4.5 mval/g, amounting in cation-exchangers to 5 mval/g [1]. Beside that, however, the styrene/DVB copolymerization gives many benefits. First of all it can be carried out easily in suspension providing spherical beads which are preferred in column operation for hydromechanical reasons.

At present new possibilities of improving exchange capacities of anion-exchangers developed by the commercialization of *N*-vinylformamide (NVF), which polymer (PNVF) undergoes easily hydrolysis to polyvinylamine (PVAm) [2]. Detailed description of its role in the field of hydrophilic polymers is given in the work of Bortel *et al*. [3].

PNVF was found [4] to be the most suitable precursor to PVAm. Both polymers are now produced in commercial scale quantities. The monomer of PVAm does not exist because vinylamine tautomerizes readily to acetaldehyde imine.

The reason why among many other potential precursors PNVF was selected for a broad commercialization, was its readiness to hydrolyze to PVAm under mild conditions. However, syntheses of polymers and copolymers containing stable primary amine functionalities have been hitherto confined to water-soluble polyelectrolytes, exclusively, and not to crosslinked anion-exchangers, dueto difficulties in obtaining by means of reverse emulsion polymerization [5].

The aim of the present work was to work out the conditions for substituting vinylamine units for styrene ones in DVB crosslinked network. Contrary to styrene

(molecular weight of 104.07) the molecular weight of a vinylamine unit is much lower, amounting according to the formula -CH_2-$CH(NH_2)$- to 44. It should be noted that the amine group is already present in the precursor monomer. The exchange capacity of a linear PVAm polymer should be by calculation 22.7 mval/g. The built-in DVB which is regarded by far as the best crosslinking agent in ion-exchangers will somewhat reduce this value but not significantly.

The problem was how to bypass solubility incompatibilities of hydrophilic, water-soluble, NVF and of the hydrophobic DVB in a suspension polymerization aimed at yielding the copolymer in the shape of spheres.

EXPERIMENTAL

Materials

N-vinylformamide monomer (NVF) from Aldrich was distilled under vacuum over a vigreux column before use.

Divinylbenzene (DVB) used as crosslinking agent also from Aldrich (55 % technical grade mixture of isomers) was washed with sodium hydroxide solution to remove an inhibitor and dried just prior to polymerization.

2,2'-Azobisisobutyronitrile (AIBN) from Fluka AG used as free radical initiator was applied as obtained.

Paraffin oil (Merck) characterized by boiling temperature in the range 300—500 ^oC, viscosity *ca*. 110 Pa · s was used as received.

Silicone oil DC 200 from Fluka AG with viscosity *ca*. 1000 Pa · s was used as obtained.

Sorbite monooleate (Span 80) from Aldrich, characterized by hydrophile/lipophile balance *HLB* = 4.3, was used as surfactant without further treatment.

Sodium hydroxide from POCh Gliwice (analytical grade) was used as obtained.

Deionized water was deareated before use.

Methods of preparation

Inverse suspension copolymerization of NVF and DVB in paraffin oil (PNVF/DV-I)

Into a 250 cm^3 thermostated four necked round-bottom flask, equipped with thermometer, stirrer, reflux-condenser and inert gas inlet, a mixture of 25 g of paraffin oil, and 2 cm^3 of Span 80 was placed. The mixture was deareated at 60 ^oC under a flush of argon.

A freshly prepared solution of 5 g of NVF, 1.5 g of DVB (molar ratio NVF:DVB = 10:1), 0.1197 g of AIBN [molar ratio AIBN:(DVB+NVF) = 1:100] and 2 cm^3 of H_2O was added at constant stirring (500 rpm). All ingredients were mixed and heated to 60 ^oC, at which temperature the suspended particles were polymerized for 6 h under a gentle stream of argon. Thereafter the product was filtered off, rinsed with toluene and hot water until the spheres got rid of paraffin. At the end they were vacuum dried.

Inverse suspension polymerization of NVF and DVB in silicone oil (PNVF/DVB-II)

Into a similar as previously round-bottom flask 50 g of silicone oil were put followed by additions of 5 g of NVF, 1.5 g of DVB (molar ratio NVF:DVB = 10:1), 0.1197 g of AIBN [molar ratio AIBN/(DVB+NVF) = 1:100] and 2 cm^3 of water. The mixture was polymerized for 6 h. Then it was poured into 1 dm^3 of toluene, the beads were filtered off, rinsed with toluene and water, and vacuum dried for 3 days.

Base hydrolysis of PNVF/DVB-I and PNVF/DVB-II

Into a three necked round-bottom flask (250 cm^3) equipped with thermometer, reflux-condenser and stirrer 3 g of the respective PNVF/DVB-I or PNVF/DVB-II copolymer were put and 150 cm^3 of 2M solution of NaOH was added. The content of the flask was heated to 60 ^oC at which temperature the hydrolysis lasted for 6 h under continuous stirring (300 rpm). Thereafter the suspension was neutralized by means of 2M solution of HCl and filtered off. The spherical beads were again rinsed with water and dried.

Methods of testing

Elemental analyses were performed using an EuroVector EURO EA 3000 C, H, N analyzer. The specific surface area of the dry resin was determined by the nitrogen adsorption/desorption BET technique at 77.3 K using an ASAP 2010 Micrometrics apparatus.

To determine the degree of swelling about 10 cm^3 of the air-conditioned resin was put into a volumetric cylinder (50 cm^3) and after tapping the exact volume (v_0) was established. Then the cylinder was filled with water and after 48 h again the volume of the water-soaked resin (v_s) was measured. The degree of swelling was calculated from the ratio v_s/v_0.

Determination of anion-exchange capacities and water content required proper preparation of samples. In a preliminary step a 12 g of the exchanger was treated with an axcess of 1M HCl solution. After 20 h it was thoroughly rinsed with water and subsequently again submitted to a treatment with 1M NaOH solution followed by a rinse in water until OH^- ions have been washed out. At last the beads were divided into two parts. The resin in amount *ca*. 10 g was taken for determination of the water content and 2 g were suspended for 3 days in 300 cm^3 of 0.1 M HCl solution. The exchange capacity was calculated from Cl^- uptake.

Determination of water content in air-conditioned ion-exchangers was done by weighing of vacuum dried exchange resin (*ca*. 10 g) put into an air box in which it was conditioned at 20 ^oC for 48 h. Water uptake in wt. % was calculated from difference in masses.

RESULTS AND DISCUSSION

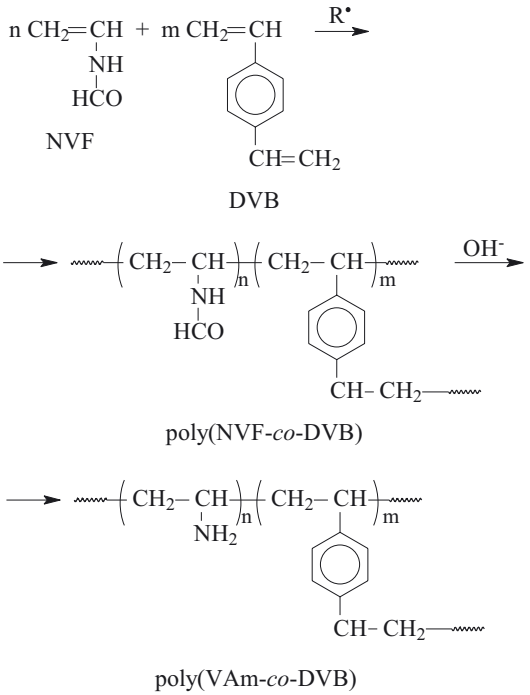
There are numerous obstacles in getting spherical beads from hydrophilic NVF crosslinked with divinylbezene, which is regarded by far as the best crosslinking agent for ion-exchange resins. First of all, the copolymerization of NVF and DVB has to be carried out in reverse emulsion in which the organic continuous phase should be a non-solvent for both comonomers. To satisfy that demand a problem arises. During polymerization the resulting beads should sediment, not collapse. The velocity of spheres sedimentation (w_s) is given by the Stockes formula:

$$w_s = \frac{d^2(\rho_s - \rho)g}{18\eta}$$

where: *d — diameter of spheres*, (ρ_s-ρ) *— density difference of the dispersed and continuous phase, respectively*, *g — gravity acceleration constant*, η *— dynamic viscosity*.

Here the density difference appears to be unfavorable because the only non-solvents for DVB are aliphatic hydrocarbons which densities are obviously < 1 g/cm^3. Chloroderivatives, other polar solvents and aromatic ones must be excluded due to solubility effects. In case of ion-exchangers the beads diameters should not be too small, and as a consequence the only parameter capable to stabilize the feed was viscosity of the continuous phase.

In the present investigations two kinds of continuous phases were tried. In one case the continuous phase was set up by paraffin oil. In the second one the continuous



where n >> m

Scheme A. Design of copolymerization in reverse (water/oil) suspension aimed at the preparation of high capacity ion-exchange resins

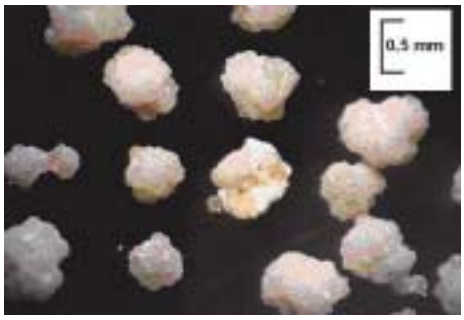


Fig. 1. Optical microscopic image of PNVF/DVB-I particles obtained in paraffin oil as continuous phase (before hydrolysis)

Fig. 2. Optical microscopic image of PVAm/DVB-I particles obtained in paraffin oil as continuous phase (after hydrolysis)

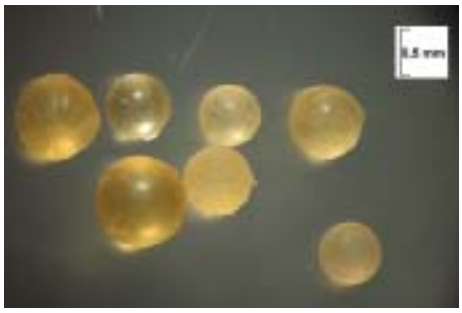


Fig. 3. Optical microscopic image of PNVF/DVB-II beads obtained in silicone oil as continuous phase (before hydrolysis)

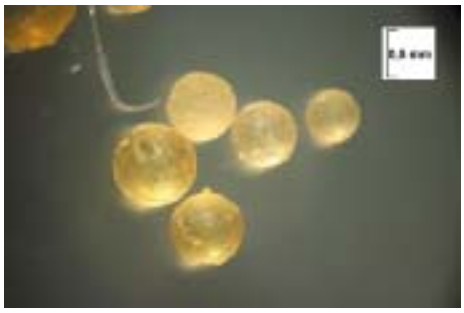


Fig. 4. Optical microscopic image of PVAm/DVB-II beads obtained in silicone oil as continuous phase (after hydrolysis)

phase was provided by a silicone oil of higher viscosity. Using the paraffin oil it was necessary to admit a non-ionic surfactant (Span 80) in order to prevent formation of clusters. In case of silicone oil the addition of surfactant was superfluous. All remaining parameters were in both cases identical. The route providing the anion-ex-

changers was comprised of two steps according to Scheme A. In the first step poly(NVF-*co*-DVB) beads were obtained in reverse suspension and in the second one the hydrolysis took place, yielding the poly(VAm-*co*--DVB) anion-exchange resin.

For such obtained beads the optical microscopie images, presented in Figure 1—4, were made. Comparing the microphotographies obtained in paraffin oil with those of beads prepared in silicone oil continuous phase (cf. Fig. 1 and 2 with Fig. 3 and 4) it is clear that only the silicone oil phase guarantees the formation of regular spheres.

Taking into account the preferences given for ion-exchangers with round particles [1], silicone oil phase appears to be superior to paraffin phases in the investigated reverse suspension copolymerization. Further advantages are provided by greater bead diameters required in column operations, and by the lack of surfactant in the feed.

The ion-exchange capacities depend on the degree of conversion of –NH–CHO groups into -NH_2 groups in accordance with Scheme A. It is difficult, however, to determine this conversion directly from *N*-content in the precursor and in the derived PVAm because both resins are strongly hydrophilic [6]. More relevant appear to be the ratio of C/N in the polymer before and after hydrolysis. Theoretically the calculated value C/N for linear PNVF should be 2.57 and that for PVAm 1.71, respectively. Relations determined by elemental analyses are listed in Table 1. Results relating to anion exchange capacities, degrees of swelling, water contents of air-conditioned resins, and specific surfaces are displayed in Table 2.

T a b l e 1. Results of elemental analyses of crosslinked polymers before and after hydrolysis

Anion-exchanger	Concentration of elements, wt. %			C/N
	C	H	N	
PNVF/DVB-I	46.748	7.410	15.439	3.03
PVAm/DVB-I	42.303	8.505	17.310	2.44
PNVF/DVB-II	52.142	10.245	13.278	3.93
PVAm/DVB-II	50.431	9.945	17.420	2.90

T a b l e 2. Exchange capacity, degree of swelling, water content in air conditioned resin, and the specific surface determined for anion-exchangers

Anion-exchanger	Exchange capacity mval/g	Degree of swelling cm^3/cm^3	Water in air--conditioned state, wt. %	Specific surface m^2/g
PVAm/DVB-I	10.15	2.44	31.0	1.88
PVAm/DVB-II	11.23	2.17	19.7	1.91

Taking into account the fact that the obtained anion-exchangers are derived from a vinyl monomer, their exchange capacities leveling to 10.5 and 11.25 mval/g, respectively, should be regarded as extraordinary high. The small specific surface (see Table 2) indicate the lack of macroreticular structure.

It is clear that crosslinked polyvinylamines should offer unique opportunities for the derivatizations which may provide a novel class of ion-exchangers. Up to now, however, no paper has been published on synthesis and exploration of ion-exchange resin with vinyl chains having primary amine functionalities attached to the backbone. Hitherto the focus in literature was directed mainly on linear homo- and copolymers possessing -NH_2 groups within the backbone. These linear cationic polyelectrolytes have found broad applications in areas such as waste water treatment, sludge dewatering and paper making [7]. Independently, the proof was provided that linear polyvinylamines are very effective in complexation of cations of transition metals [8]. This capacity would be of great value in vinylamine based exchange resin, in which the selectivity of complexation could be enhanced by facile derivatization with selected chelating molecules. Similar attempts were reported, till now, by modification of poly(styrene-*co*-DVB) matrices or crosslinked polyacrylates [9].

The poly(VAm-*co*-DVB) exchangers described in the present paper were found to be effective carriers for immobilization of enzymes [10] what will be the subject of a separate paper.

Obviously, enzymes are the best catalysts concerning selectivity. Hence, it is understandable that efforts are undertaken to develop the synthetic enzyme-like catalysts.

A convenient route for doing it involves derivatization of ion-exchange resins with chelating molecules. In that respect Kolarz and Owsik [11] published a worthy report of their own achievements and of other authors working in that field.

REFERENCES

1. Kunin R.: *"Ion Exchange Resin"*, J. Wiley&Sons, New York 1958, p. 33.
2. Krömer M., Depois J., Winter M.: *J. Pract. Chem.* 2000, **342**, 115.
3. Bortel E., Witek E., Izak P., Kochanowski A., Puzdro M.: *Polimery* 2005, **50**, 491.
4. Steve R.: *Sci. Technol.* 2005, **85**, 38.
5. Bortel E., Witek E., Pazdro M., Kochanowski A.: *Polimery* 2007, **52**, 19.
6. Mandl A., Spange S.: *Macromol. Symp.* 2000, **161**, 149.
7. Gu L., Zhu S., Hrymac A. N.: *Colloid Polym.* 2000, **342**, 115.
8. Kobayashi S., Suh K-D., Shirokura Y.: *Macromolecules* 1989, **22**, 2363.
9. Trochimczuk A. W., Jezierski J.: *Polymer* 2000, **41**, 3463.
10. Witek E., Kochanowski A., Puzdro M., Fortel E.: *Polimery* 2006, **51**, 507.
11. Kolarz B., Owsik J.: *Polimery* 2003, **48**, 490.

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