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Studies on N-vinylformamide cross-linked copolymers

Joanna Świder [a], Agnieszka Tąta [b], Katarzyna Sokołowska [a], Ewa Witek [a],
Edyta Proniewicz [b], *

[a] *Faculty of Chemistry, Jagiellonian University, ul. Ingardena 3, 30-060 Krakow, Poland*
[b] *Faculty of Foundry Engineering, AGH University of Science and Technology, ul. Reymonta 23, 30-059 Krakow, Poland*

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ABSTRACT

Copolymers of N-vinylformamide (NVF) cross-linked with three multifunctional monomers, including divinylbenzene (DVB), ethylene glycol dimethacrylate (EGDMA), and N,N′-methylenebisacrylamide (MBA) were synthetized by a three-dimensional free radical polymerization in inverse suspension using 2,2′-azobis(2-methylpropionamide) dihydrochloride (AIBA) as an initiator. Methyl silicon oil was used as the continuous phase during the polymerization processes. Fourier-transform adsorption infrared (FT-IR) spectra revealed the presence of silicone oil traces and suggested that silicone oil strongly interacted with the copolymers surface. Purification procedure allowed to completely remove the silicon oil traces from P(NVF-*co*-DVB) only. The morphology and the structure of the investigated copolymers were examined by optical microscopy, FT-IR, and FT-Raman (Fourier-transform Raman spectroscopy) methods.

1. Introduction

The hydrophilic water-insoluble three-dimensional polymer networks are known as superabsorbent polymers (SAP) and ion-exchange resins. The low-density cross-linked polymer network is characteristic of superabsorbents, also known as hydrogels. On the other hand, the ion-exchange resins are composed of the high-density cross-linked polymer networks and show low degree of swelling in water. Ranging from the 60s of the last century, both the hydrogels and ion-exchange resins are commercially available [1]. They are extensively used in power industry, food industry, agriculture, medicine, pharmacy, and in the production of personal care products [2]. Other opportunities for application of ion-exchange resins concern the heterogenization of homogeneous chemical catalysts [3] and biocatalysts [4,5]. By developing new methods for the synthesis of selective ion-exchange resins new possibilities for they application in recovering precious metals [6], selective removing heavy metals from drinking water, and purification of surface water and industrial effluents were created [7–10]. Our research also tends to develop method of synthesis of three-dimensional networks of hydrophilic polymers, which are useful for enzyme immobilization. The free-radical cross-linking copolymerization of water-soluble mono-vinyl monomers with multi-vinyl monomers is the preferred method for the synthesis of covalently cross-linked stable hydrogels [11,12]. In this method, non-ionic acrylamide (AAm) is commonly used [13–18]. However, in some cases, the application of the AAm polymers is limited due to the fact that AAm is a potential carcinogen [14]. An alternative solution is to use N-vinylformamide (NVF) that is non-toxic water-soluble isomer of AAm [19–21]. The NVF monomer readily undergoes free-radical homo- and copolymerization with a variety of the commercially important vinyl monomers [22]. In addition, under acidic and basic conditions homo- and copolymers of NVF easily hydrolyze to polymers containing vinylamine units having great application potential [23–25]. The most of processes involving superabsorbents and ion-exchange resins run in a continuous manner on columns; thus, the polymers showing spherical grains are preferred. The spherically grained polymeric material, with the size allowing separation on a metal sieves, can be obtained in the suspension polymerization process. The suspension of free-radical crosslinking polymerizations water-soluble

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* Corresponding author.
E-mail address: proniewi@agh.edu.pl (E. Proniewicz).

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monomers occurs as a water-in-oil (w/o) process called the inverse-suspension. The conditions of this process cause difficulties with the stabilization of the system and the solubility of hydrophobic monomers in many organic solvents [25,26].

We developed the method of synthesis of spherically grained cross-linked N-vinylformamide via polymerization in the inverse-suspension using silicone oil as the continuous phase. We received the anion-exchangers that contain the vinylamine units with high ion exchange capacities [24], polymeric carriers for α-amylase [27], and polymeric adsorbents for the removal of microcystin-LR from water [28]. The morphology and microstructure of the copolymers grains obtained from of N-vinylformamide with three different cross-linking monomers: divinylbenzene (DVB), ethylene glycol dimethacrylate (EGDMA), and *N,N′*-methylenebisacrylamide (MBA), by the developed free-radical cross-linking polymerization in inverse suspension, were examined.

Fourier-transform absorption infrared (FT-IR) and Fourier-transform Raman (FT-Raman) spectroscopies are the most comprehensive molecular spectroscopy methods for polymer characterization. They allow to identify structure, chain conformation, stereo chemical configuration, and chemical functionalities of polymers. This is possible thanks to the analysis of infrared spectra that give mainly information about the chemical groups commonly found in the polymer side-chins showing a significant dipole moment; i.e., C–H and C═O (this groups are commonly found in polymers structures) [29]. However, the Raman spectroscopy is more sensitive to highly polarizable groups; for example, C–C and C═C, that are generally found in the polymer chain backbone [30]. Using both vibrational methods the structural changes during crosslinking polymerization of NVF with three different crosslinkers were investigated.

2. Experimental

2.1. Materials

All high grade chemicals were used. Immediately before use, N–vinylformamide (NVF) (Sigma–Aldrich) was distilled in vacuum over a Vigreoux column. 2,2′-Azobis(2-methylpropionamidine) dihydrohloride (AIBA), divinylbenzene (DVB), *N,N′*-methylenebisacrylamide (MBA), ethylene glycol dimethylacrylate (EGDMA) were used without further treatment. POLSIL OM® 2000 and POLSIL OM® 3000 oils (Silikony Polskie Sp. z o. o.) were used as continuous phase.

2.2. Preparation of copolymers

Cross-linked copolymers of *N*-vinylformamide P(NVF–*co*–DVB), P(NVF–*co*–MBA), and P(NVF–*co*–EGDMA) were obtained by free-radical polymerization in inverse-suspension under an inert atmosphere as shown in Fig. 1. Divinylbenzene (DVB), *N,N′*-methylenebisacrylamide (MBA), or ethylene glycol dimethylacrylate (EGDMA) were used as cross-linkers. The reaction was carried out in a thermostated round-bottom reactor (250 cm^3) equipped with a reflux condenser, mechanical stirrer and stirring element with 2-bladed propeller (diam. 50 mm), thermometer, and inert gas inlet. The reaction parameters (Table 1), such as methyl silicone oil viscosity and stirring speed, which affect the diameter of copolymer particle, were chosen based on our previous studies [31,32]. Silicone oil was placed inside the reactor, vigorously stirred, and heated to 60 °C or 80 °C (see Table 1). Then, the freshly prepared solution of monomers (NVF and cross-linker) and free radical initiator (AIBA, 1 mol-% with respect to the total monomer) was bubbled with argon for 10 min and added dropwise to oil at constant stirring (500 rpm or 250 rpm). The concentrations of cross-linkers were 11 mol-% of MBA and EGDMA and 27 mol-% of DVB. All ingredients were mixed and heated to 60 °C or 80 °C, at which temperature the suspended particles were polymerized for 4 h under a gentle stream of argon. The polymerization products were filtered and washed with toluene on Buchner funnel. In addition, in order to remove the trace amounts of silicone oil, washing in toluene (oils used in the present studies dissolve without limitation only in toluene) in a flask with stirring at room temperature for 24 h was done. Also, the use of toluene in the purification process of the copolymers beads allowed to remove the trace amounts of N-vinylformamide (NVF) because toluene is a good solvent for NFV. The details of polymerization conditions are summarized in Table 1.

2.3. Swelling degree

Swelling degree (S_w) of P(NVF–*co*–DVB), P(NVF–*co*–MBA), and P(NVF–*co*–EGDMA) (Table 1) was determined by the gravimetric method. The sample of copolymer was weighed (W_0) then soaked in a deionized water at room temperature for 72 h and weighed again (W_t). S_w was calculated according to the Eq. (1) [33]:

$$S_w = \frac{W_t - W_o}{W_o} \cdot 100\% \tag{1}$$

where: W_t is the weight of copolymer after soaking and hydration and Wo is the weight of the dried product.

2.4. Measurements

2.4.1. Fourier-transform infrared spectroscopy

Thin disks containing 1 mg of copolymer dispersed in 200 mg of KBr were used for infrared measurements. The spectra were recorded at room temperature as an average of 30 scans using a Bruker infrared spectrometer (model EQUINOX 55) equipped with a Nernst rod as the excitation source and a DT-GS detector in the 400–4000 cm^{-1} range with a spectral resolution of 4 cm^{-1}.

2.4.2. Fourier-transform Raman spectroscopy

FT-Raman measurements were performed on samples placed on a glass plate. FT-Raman spectra were recorded on a Nicolet spectrometer (model NXR 9650) equipped with a liquid-nitrogen-cooled germanium detector. Typically, 2000 scans were collected with a resolution of 4 cm^{-1}. The 1064 nm line from a continuum-wave Nd^{+3}:YAG laser was used as an excitation source. The laser output power was maintained at 500 mW.

2.4.3. The morphology of the copolymer supports

The morphology of the polymer supports was determined using an Optical Genetic Pro Bino microscope with the 1000 times magnification.

3. Results and discussion

The separated spherical grains of P(NVF–*co*–DVB) were obtained with the silicon oil viscosity of 2000 cSt and stirring speed of 250 rpm for the reaction proceeding in the round-bottom flask (250 cm^3) equipped with mechanical stirrer and stirring element with 2-bladed propeller (diam. 50 mm) [31]. Using the same reaction set, the P(NVF-co-EGDMA) copolymer was synthetized in silicone oil with the viscosity of 3000 cSt and the stirrer speed of 500 rpm. The optimization of the polymerization parameters for NVF/MBA in silicone oil failed, so that the copolymer has the form of the aggregated spherical grains [32]. This fact shows that not only the oil viscosity and rate of stirring, but also the type of cross-linker determine the morphology of the copolymer grains.