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MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Nanocatalytic Systems Based on Poly(ethylene glycol maleate)–Acrylamide Copolymers

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Abstract—The radical copolymerization of poly(ethylene glycol maleate) with acrylamide was performed for the first time to obtain 3D cross-linked polymers. The influence of temperature, pH of the medium, and organic solvents on the behavior of the synthesized copolymers was studied. The possibility of obtaining nickel nanoparticles in the bulk of the polymer gel for pyridine hydrogenation was demonstrated.

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Active progress of basic research in the field of radical copolymerization, allowing control of the properties, structure, and molecular mass of the copolymers and the reaction rate, makes it topical to search for new monomers for preparing polymers with a wide spectrum of valuable properties.

Unsaturated polyester resins are of much interest from this viewpoint. They readily copolymerize with vinyl monomers. Copolymerization of unsaturated polyester resins was considered for the first time by Boenig [1].

The capability of polyester resins to copolymerize with vinyl monomers, e.g., with styrene, was discovered in the middle of the XX century [2].

Unsaturated polyester resins based on maleates and fumarates, cured with vinyl monomers, exhibit specific physicochemical and physicomechanical properties [1–4]. Therefore, the production of decorative finishing materials and structural items from polyester–styrene copolymers is being actively developed today.

Copolymerization of unsaturated polyester resins with acrylates has been studied previously [5–7], but data on the related reactions with acrylamide are lacking.

The latest studies on copolymerization of unsaturated polyester resins were published in the 1980s. They mainly deal with the development of new formulations for preparing structural materials based on styrene and acrylates. On the other hand, 3D cross-linked copolymers based on unsaturated polyester resins can be highly effective polymeric supports for nanocatalysts based on transition metals. Such compounds are stable and prevent metal particles from aggregation and oxidation for a long time [8].

Here we report on a first study of the radical copolymerization of poly(ethylene glycol maleate) with acrylamide in solution to obtain 3D cross-linked polymers and consider the possibility of using these polymers as matrices for preparing catalysts based on nickel nanoparticles.

EXPERIMENTAL

Poly(ethylene glycol maleate) (*p*-EGM) was prepared by polycondensation of maleic anhydride with ethylene glycol according to the standard procedure [9]. The reaction progress was monitored by determining the acid number and the volume of the released water.

The molecular mass (MM) of *p*-EGM (2350 amu on the average) was determined by the methods of light scattering with a 2100 AN nephelometer (NACH) and of gel permeation chromatography with an Agilent 1260 Infinity device.

Репозиторий КарГУ

When determining the molecular mass by light scattering, we chose as solvent chloroform thoroughly purified to remove dust. The MM of *p*-EGM was 2342 amu, with ±2% uncertainty. The molecular mass of *p*-EGM determined by gel permeation chromatography was the same within the uncertainty: 2358 amu.

The radical copolymerization of *p*-EGM with acrylamide (AA) was performed in a dioxane solution (1 : 3) at different initial weight ratios of the components at 333 K in the presence of azobis(isobutyronitirle) (AIBN).

The synthesized copolymers were purified to remove the unchanged monomers with dioxane. The compositions of the copolymers were determined from the residual amounts of the monomers in the dioxane solution, which, in turn, were determined by gas chromatography [10] and potentiometric titration [11].

The equilibrium degree of swelling of the polymers was measured gravimetrically. The equilibrium swelling was reached within 2–3 days. The degree of swelling of the gel, α (%), was calculated as the ratio of the absolute mass of the swollen hydrogel in the equilibrium swelling point to its initial mass in the dry state:

$$\alpha = [(m - m_0)/m_0] \times 100.$$

Metal–polymer complexes (MPCs) with incorporated nickel metal were prepared from *p*-EGM–AA copolymers by reduction of a 0.01 N solution of nickel chloride. The reduction of Ni^{2+} ions to Ni^0 was performed with potassium hypophosphite in the presence of an ammonia solution of silver chloride used as catalyst:

$$2Ni^{2+} + H_2PO_2^- + 2H_2O \rightarrow 2Ni^0 + PO_4^{3-} + 6H^+.$$

The amount of nickel in the polymer matrix was determined with an AA 140 Varian atomic absorption spectrometer (the United State). The surfaces of the metal–polymer complexes were examined with an Axioscop 40 Pol microscope.

RESULTS AND DISCUSSION

It was shown previously [12] that copolymers of poly(ethylene glycol maleate) with acrylic and methacrylic acids exhibit high moisture-absorbing properties. It was interesting to synthesize copolymers of *p*-EGM with AA and to examine them as a polymeric support for nanocatalytic systems.

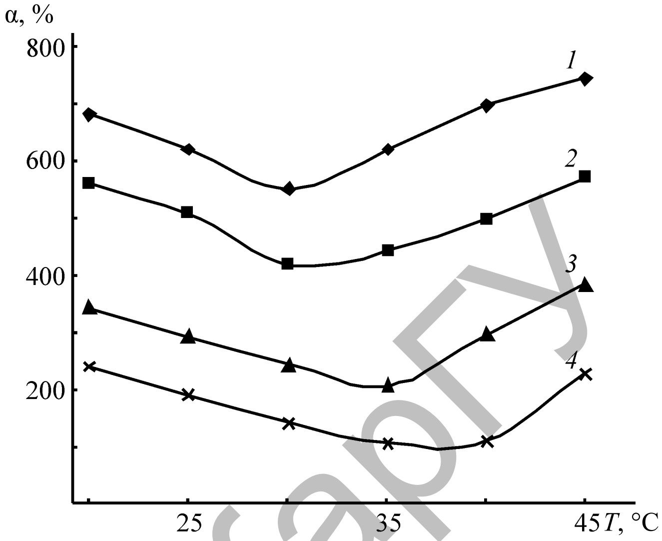

Fig. 1. Influence of temperature *T* on swelling of gels based on *p*-EGM–AA. (α) Degree of swelling; the same for Figs. 2 and 3. *p*-EGM : AA, wt %: (*1*) 11.38 : 88.62, (*2*) 19.74 : 80.26, (*3*) 34.69 : 65.31, and (*4*) 58.12 : 41.88; the same for Fig. 2.

Radical copolymerization of *p*-EGM with AA was performed in a dioxane solution at different molar ratios of components in the starting polymer–monomer mixture (see table).

As seen from the table, the copolymers are enriched in units of the vinyl monomer at any initial component ratios. The maximal degree of swelling of the products was reached for the *p*-EGM–AA copolymer of the composition 11.38 : 88.62 (wt %).

The degree of unsaturation of the copolymers, caused by the presence of the unchanged maleate groups, regularly increases with an increase in the content of the unsaturated polyester in the starting polymer–monomer mixture.

The swellability of the synthesized polymers was studied in relation to the temperature, pH of the medium, ionic strength of the solution, and composition of mixed aqueous-organic solvents.

Figure 1 shows the influence of temperature on the swelling of *p*-EGM–AA copolymers.

The *p*-EGM−AA copolymer swells when immersed in water at room temperature (20°C). As the temperature is increased up to a certain critical value, the capability of the hydrogel to take up water decreases, but further heating of the system leads to inverse temperature dependence. The complex pattern of the temperature dependence of the swellability indicates that several

Репозиторий КарГУ

Composition of the copolymers as a function of the composition of the starting mixture in copolymerization of *p*-EGM (M_1) with AA (M_2). [AIBN] = 8 mol m^{-3}, T = 333 K, [*p*-EGM–AA] : [dioxane] = 1 : 3

Initial ratio, wt %		Copolymer composition, wt %		α, %	Yield, %	Degree of unsaturation
M_1	M_2	m_1	m_2			
15.11	84.89	11.38	88.62	620.2	88.2	42.3
24.91	75.09	19.74	80.26	510.4	86.4	46.4
39.81	60.19	34.69	65.31	399.1	79.3	49.1
49.94	50.06	48.12	51.88	280.3	75.2	52.6

types of interaction are responsible for the behavior of the hydrogel. The gel collapse can be caused by interactions of hydrophobic fragments of the macrochains, accompanied by the displacement of water molecules structured at the surface of these groups. As shown in [13], phase transitions become still more pronounced on introducing a small fraction of charged units. Thus, the system under consideration is weakly charged, with the additional charges arising from hydrolysis of acrylamide groups. This capability of acrylamide groups for hydrolysis was determined by Tanaka [14, 15]. The reaction yields positively charged functional groups.

As we found, the degree of hydrolysis of acrylamide groups, determined by titration of the formed amino groups with a 0.1 N HCl solution, varies from 0.3 to 2.4% depending on the copolymer composition.

One of the most important external factors that can strongly affect the physicochemical behavior of polymer gels is pH of the medium. Ionic polymers either swell or collapse in solution with increasing pH, and polyampholytic gels show combined behavior.

Figure 2 shows how pH of the medium influences the swelling of the *p*-EGM–AA copolymers.

As can be seen, the dependences pass through a minimum at pH 5–6. The observed trends indicate that the gel is polyampholytic, i.e., that it contains both acid and base groups in the macrochain. The minimum in the pH dependence of the degree of swelling of *p*-EGM–AA can be attributed both to a decrease in the osmotic pressure of the counterions and to Coulomb attraction of the oppositely charged units. As the content of AA units in the copolymers is increased, the pH range corresponding to the minimal sorption capacity of the hydrogel shifts toward more alkaline region. This may be due to partial hydrolysis of the acrylamide units. Because the concentration of AA units in the macrochain

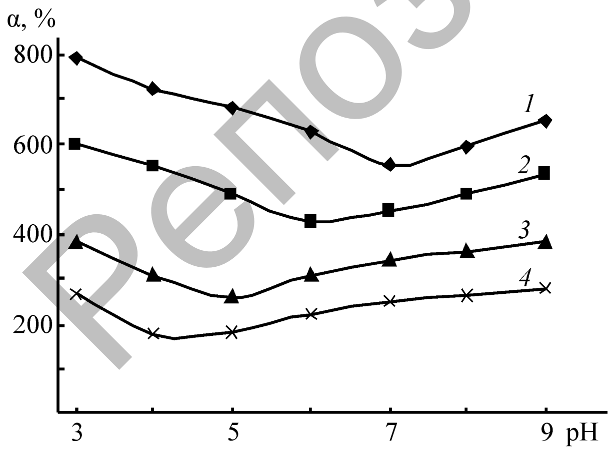

Fig. 2. Influence of pH on swelling of gels based on *p*-EGM–AA at 25°C.

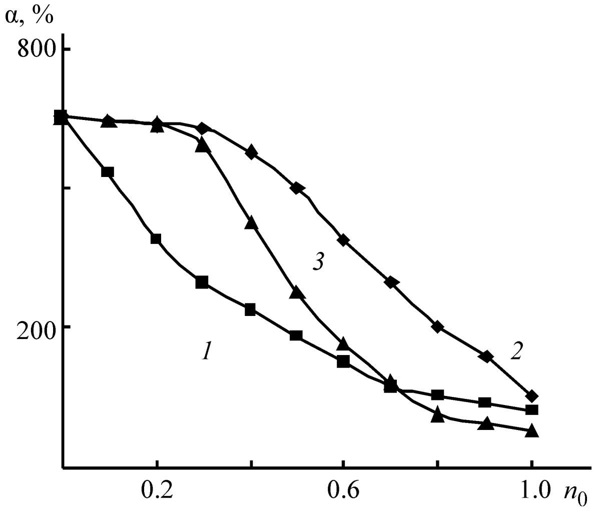

Fig. 3. Influence of the volume fraction of the organic solvent n_0 on swelling of hydrogels based on *p*-EGM–AA copolymer (11.38 : 88.62 wt %). (*1*) Water–ethanol, (*2*) water–DMF, and (*3*) water–DMSO.

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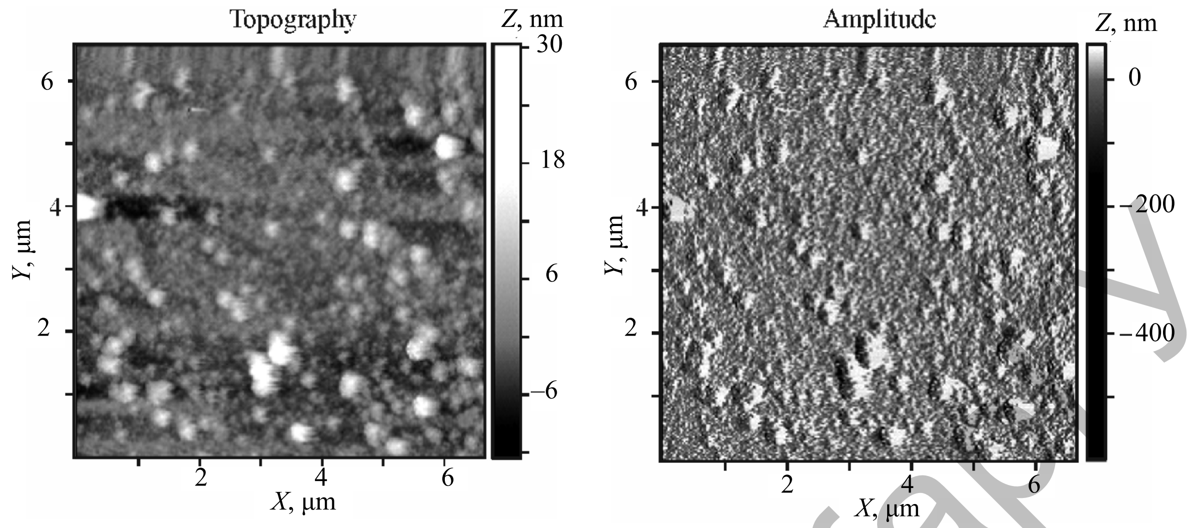

Fig. 4. Electron micrographs of the catalyst based on *p*-EGM–AA (19.74 : 80.26 wt %). Axioscop 40 Pol electron microscope.

is considerably higher than the concentration of *p*-EGM units, even a small fraction of hydrolyzed acrylamide units is capable of significantly influence the course of the process. As a result of formation of excess negative charge by the hydrolyzed acrylamide units, the compensation leading to the collapse of the polymer network of the *p*-EGM–AA gel of the composition 11.38 : 88.62 wt % occurs at higher pH values.

We examined the influence of aqueous-organic solvents on the *p*-EGM–AA copolymer of the composition 11.38 : 88.62 wt %, which appeared to be the most sensitive to the external conditions. DMSO, DMF, and ethanol were chosen as organic components.

On adding an organic solvent to the polymer swollen in water, the sample size gradually decreases (Fig. 3), which is due to worsening of the thermodynamic quality of the mixed solvent, compared to water, with an increase in the volume fraction of the organic solvent. It should be noted that the function $\alpha(n_0)$ varies gradually and not jumpwise; hence, this process cannot be considered as phase transition. It should also be noted that the shape of the plot is influenced by the kind of the organic solvent. In ethanol, the hydrogels take the more compact structure than in the DMF–water and DMSO–water systems. This trend can be attributed to the polarity and dielectric constant of the organic components.

Catalysis in the presence of effective metal–polymer nanocatalysts is being actively developed. Such metal–polymer complexes exhibit high catalytic activity, stability, and selectivity.

From the practical viewpoint, an important property of these composites is the stabilizing effect of the polymeric matrix, preventing the metal particles from aggregation and oxidation for a long time, simple separation of the catalyst from the reaction products, and possibility of controlling the catalysis by varying the swellability of the polymer base [16].

In this connection, it seemed interesting to use the synthesized *p*-EGM–AA copolymers as a polymeric matrix for preparing nanocatalysts.

The amount of free nickel in the copolymers, determined by the atomic absorption method, was 50.2, 41.6, and 35.7% in the copolymers of the compositions 11.38 : 88.62, 19.74 : 80.26, and 34.69 : 65.31 wt %, respectively. With a decrease in the swellability of the copolymers, the content of free nickel in the matrix decreases, but this difference is insignificant, which is due, most probably, to significant adsorption of nickel on the surface (Fig. 4). The nickel particle size is 350–500 nm.

As a continuation of the studies, it seemed interesting to evaluate the catalytic activity of the prepared catalysts based on *p*-EGM–AA copolymers in electrocatalytic reduction of pyridine in comparison with the activity of the known Raney catalysts. Because the hydrogels under consideration are sensitive to temperature variations, hydrogenation of pyridine was performed under different temperature conditions. Hydrogenation was performed without catalyst, in the presence of Raney catalyst, and in the presence of MPC based on *p*-EGM–AA. The ex-

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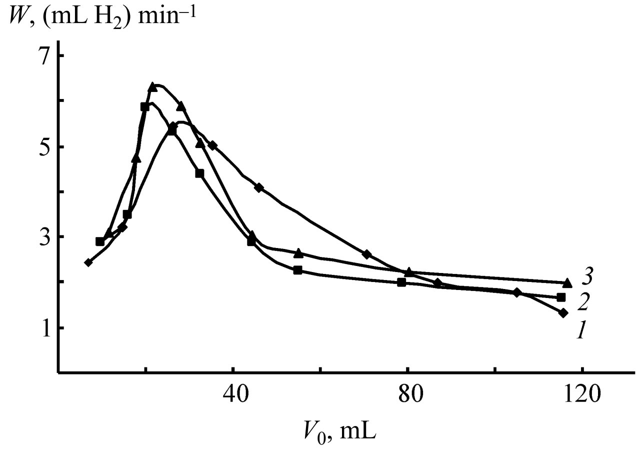

Fig. 5. Uptake rate W of hydrogen as a function of its volume V_0. p-EGM–AA 11.38 : 88.62 wt %, $I = 2$ A, $V_{\text{pyridine}} = 1$ mL, stirring at 400 rpm. T, °C: (*1*) 20, (*2*) 30, and (*3*) 40.

periments were carried out in an electrolytic cell made of Pyrex glass, equipped with a temperature-control jacket, and separated with a 3MK-40 diaphragm at a current of 2 A and temperatures of 20, 30, and 40°C, with 0.05 g of the catalyst. "Posts" arranged on spurs were mounted in the cathodic and anodic compartments of the electrolyzer, making the cell hermetic. The released gases were removed through a connecting tube, and their volume was measured from the amount of the displaced water.

The results of electrocatalytic hydrogenation of pyridine in the presence of metal–polymer complexes of different compositions indicate that the pyridine hydrogenation rate increases with temperature (Fig. 5).

An increase in the temperature leads to an increase in the copolymer swelling, increasing the frequency of contacts of nickel with pyridine. In particular, the catalytic hydrogenation of pyridine in the presence of MPC based on p-EGM–AA occurs with high efficiency at 40°C (Figs. 6–8).

As seen from these plots, the pyridine hydrogenation curve consists of three portions. The first portion is characterized by intense uptake of hydrogen molecules; correspondingly, the major fraction of piperidine is synthesized specifically in this step. The second portion is characterized by a decrease in the pyridine hydrogenation rate due to partial consumption of pyridine in the previous step. In the third portion, the hydrogenation rate remains practically unchanged, which is caused by the reaction completion.

Our results show that, in the first step, the hydrogenation rate and the hydrogen uptake in the presence of MPC based on p-EGM–AA and Raney nickel are comparable. Then, the rate of the piperidine synthesis in the presence of the catalyst based on p-EGM–AA copolymers becomes higher.

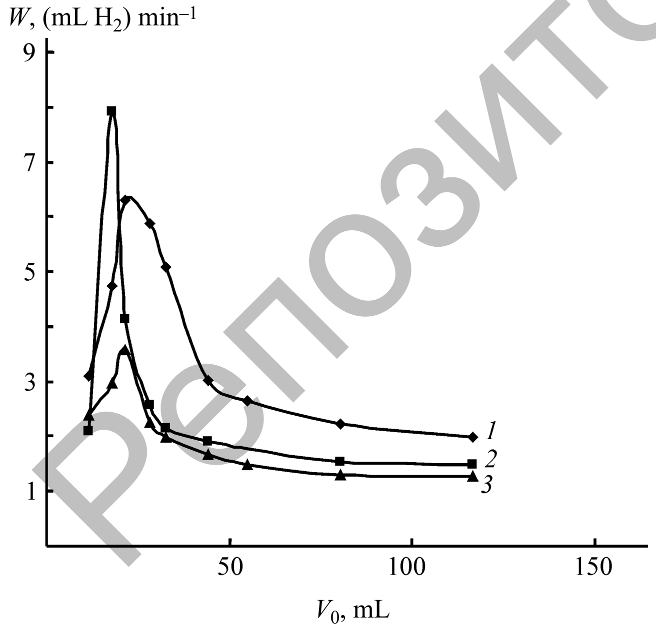

Fig. 6. Uptake rate W of hydrogen as a function of its volume V_0. p-EGM–AA 11.38 : 88.62 wt %, $I = 2$ A, $T = 40$°C, $V_{\text{pyridine}} = 1$ mL, stirring at 400 rpm. (*1*) PMC, (*2*) Raney nickel, and (*3*) no catalyst; the same for Figs. 7 and 8.

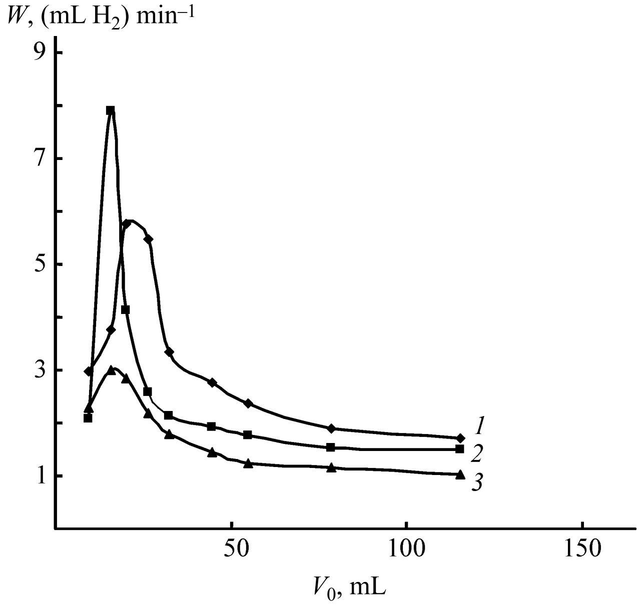

Fig. 7. Uptake rate W of hydrogen as a function of its volume V_0. p-EGM–AA 19.74 : 80.26 wt %, $I = 2$ A, $T = 40$°C, $V_{\text{pyridine}} = 1$ mL, stirring at 400 rpm.

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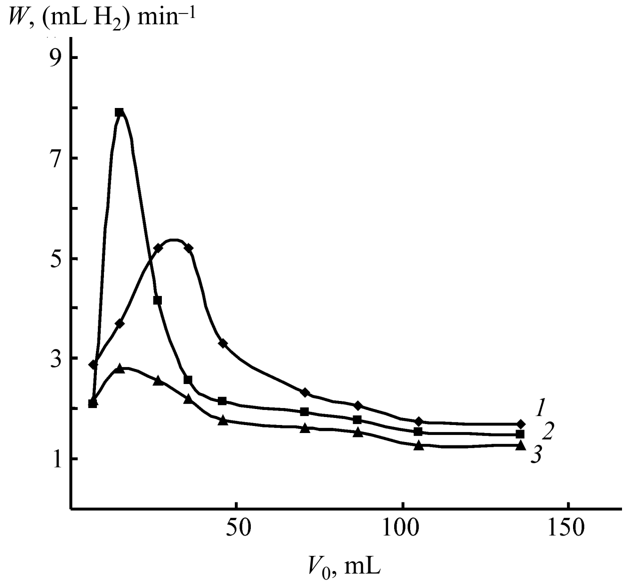

Fig. 8. Uptake rate W of hydrogen as a function of its volume V_0. p-EGM–AA 34.69 : 65.31 wt %, $I = 2$ A, $T = 40$°C, $V_{\text{pyridine}} =$ 1 mL, stirring at 400 rpm.

Thus, we demonstrated the possibility of using p-EGM–AA copolymers as a matrix for preparing effective nanocatalysts for pyridine hydrogenation, based on metal–polymer complexes.

CONCLUSIONS

(1) New 3D cross-linked copolymers of poly(ethylene glycol maleate) with acrylamide were prepared for the first time by radical copolymerization.

(2) The influence of pH, temperature, and organic solvents on the swelling and collapse of the copolymers was studied.

(3) The possibility of using poly(ethylene glycol maleate)–acrylamide copolymers for preparing metal–polymer complexes for pyridine hydrogenation was demonstrated.

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