

**POROUS COPOLYMERS OF METHACRYLIC ACID WITH
N-(2-HYDROXYPROPYL) METHACRYLAMIDE
AND (2-HYDROXYETHYL) METHACRYLATE.
PREPARATION, SWELLING AND MORPHOLOGY***

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Porous copolymers of methacrylic acid with N-(2-hydroxypropyl) methacrylamide or (2-hydroxyethyl) methacrylate were prepared using 1,3,5-triacryloylhexahydrotriazine as the crosslinking agent. The copolymers were characterized by their swelling, bulk weight, and morphologically by scanning electron microscopy. Data thus obtained were used in the interpretation of the formation of different porous morphology, differing in the size and ordering of globules.

In our research of the sorption of physiologically active compounds on ion-exchange materials containing methacrylic acid¹⁻³ we showed that the process of sorption was affected not only by ionic bonds between the sorbent and the compound sorbed, but also by additional interactions. The process of sorption of a given compound depends, among other things, on the chemical structure of the given gel and on its morphology. In order to verify the effect of the presence of a hydrophilic compound in ion exchange materials on the sorption of a number of compounds, we prepared new cation exchangers by copolymerizing methacrylic acid with N-(2-hydroxypropyl) methacrylamide or with (2-hydroxyethyl) methacrylate, using 1,3,5-triacryloylhexahydrotriazine as the crosslinking agent. In this work the copolymers have been characterized by swelling, bulk weight, and morphologically by scanning electron microscopy. The formation of porous structure is discussed using up-to-date views of the genesis of morphology in the precipitation copolymerization⁴. A forthcoming paper⁵ deals with the relationship between the structure of these cation exchangers and their sorption properties.

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EXPERIMENTAL

Monomers and Chemicals

Methacrylic acid (Chemical Works, Riga) was distilled twice (copper shavings as stabilizer) through a 40 cm column; b.p. 84°C/133.3 Pa. Purity was checked by gas chromatography (99.96%), n_D^{20} 1.4549.

(2-Hydroxyethyl) methacrylate⁶ was prepared by the alkaline reesterification of methyl methacrylate with ethylene glycol. The diester was removed from the reaction mixture diluted with water (1 : 1) by extraction fifteen times with hexane (volume ratio of the extractant to the aqueous monomer solution 1 : 1). The purity of distilled monomer (b.p. 79°C/133.3 Pa) was checked by gas chromatography (99.2%) and by the saponification number, n_D^{20} 1.4525.

N-(2-hydroxypropyl) methacrylamide⁷ was prepared from 1-amino-2-propanol and methacryloyl chloride in acetonitrile solution at 0°C. After removal of 1-amino-2-propanol hydrochloride by filtration, the reaction mixture was concentrated *in vacuo* and left in the freezing box at -20°C. Raw N-(2-hydroxypropyl) methacrylamide was twice recrystallized from acetone, m.p. 67–8°C.

1,3,5-Triacryloylhexahydrotriazine was prepared⁸ by gradually adding paraformaldehyde to a solution of sulphuric acid and acrylonitrile heated to 70°C. The raw product was recrystallized from ethanol. M.p. 157°C.

Preparation of Polymers

The polymerization was carried out in ampoules (50 cm³). Water and 5.15 and 30% aqueous acetic acid solutions were used as the polymerization solvent. The concentration of the monomeric mixture was 20% each time, 1,3,5-triacryloylhexahydrotriazine was the crosslinking agent (4 mol.%), and an equimolar mixture of ammonium persulphate and ascorbic acid ($2.6 \cdot 10^{-3}$ mol of both compounds per 100 g of the polymerization mixture) was the initiator. The temperature of the polymerization was maintained at 25°C for 4 h and after that at 100°C for 2 h. The isolated crosslinked polymer was crushed and covered with 0.5M-NaOH in excess for 14 h. After decantation with water repeated several times, the polymers were transformed into the H⁺ cycle by treating with 1M-HCl for 8 h. After another decantation with water until neutral reaction, the samples were predried in a desiccator over P₂O₅ for four days, and dried to constant weight in a vacuum drying box at 40°C. By sifting mechanically crushed polymers on sieves, a fraction 0.1–0.2 mm was isolated.

Volume Swelling Measurements

The bulk volume of one gram of dry cation exchanger in the H-form (V_0 ml/g) was determined in a graduated test tube. The volume of the swollen cation exchanger in water (V_w) and in the phosphate buffer with pH 6.8 (V_b) was measured in a similar way, which approximately corresponds to a 50% ionization of carboxylic groups⁹. V_w/V_0 is regarded as the coefficient of volume swelling.

Scanning Electron Microscopy

Dried samples grain size 0.1–0.2 mm, were fixed with polybutene on a metal support and vacuum coated with carbon and gold while rotating, in order to make the surface conductive and to raise the emission of secondary electrons. Micrographs were taken with a JSM 35R JEOLCO scanning

microscope at an accelerating voltage of 25 kV. The diameter of microglobules, D , is given in Table I.

RESULTS AND DISCUSSION

A number of porous copolymers of methacrylic acid (*I*) with N-(2-hydroxypropyl) methacrylamide (*II*) or (2-hydroxyethyl) methacrylate (*III*) were prepared; their composition and properties are summarized in Table I.

The composition of the copolymerizing mixture has a decisive influence on the heterogeneity of the polymer (from here onwards, the copolymer composition always means the composition of the original mixture of monomeric components in mol.%). The opacity of dried samples shows that copolymers *I* + *III* are macroporous over the whole range of compositions studied (0–75%), while copolymers *I* + *II* are

TABLE I

Characterization of Copolymers of Methacrylic Acid (*I*)

Comonomers: N-(2-hydroxypropyl) methacrylamide (*II*), (2-hydroxyethyl) methacrylate (*III*). Concentrations expressed in mol.%.

Initial polymerization mixture ^a				Characteristics of polymers ^b			
Solvent	[<i>I</i>]	[<i>II</i>]	[<i>III</i>]	V_0	V_w	V_b	D , μm
H ₂ O	0	100	—	1.5	18.5	18.5	homog.
H ₂ O	30	70	—	1.5	14.8	22.8	0.16 ± 0.07
H ₂ O	50	50	—	4.3	15.1	26.8	1.0 ± 0.2
H ₂ O	75	25	—	3.1	7.5	15.7	1.6 ± 0.4
5% CH ₃ COOH	75	25	—	1.5	7.7	16.0	0.4 ± 0.2
15% CH ₃ COOH	75	25	—	1.5	7.5	12.6	—
30% CH ₃ COOH	75	25	—	1.4	7.1	11.5	homog.
H ₂ O	0	—	100	2.8	4.1	4.1	2.0 ± 0.6
H ₂ O	10	—	90	4.3	9.6	11.3	1.4 ± 0.3
H ₂ O	30	—	70	4.4	8.3	12.5	1.0 ± 0.3
H ₂ O	50	—	50	5.5	10.7	19.3	1.0 ± 0.2
H ₂ O	75	—	25	4.3	8.7	17.3	1.3 ± 0.7
5% CH ₃ COOH	75	—	25	4.2	9.2	16.6	—
15% CH ₃ COOH	75	—	25	1.4	4.6	10.4	—
30% CH ₃ COOH	75	—	25	1.4	5.1	14.0	—
H ₂ O	100	—	—	1.4	7.2	11.6	homog.

^a 1,3,5-Triacryloylhexahydrotriazine was the crosslinking agent (4 mol.%, calculated per the mixture of monomers). ^b Symbols defined in the Experimental.

macroporous only at 50–75% of *I*, but already at 30% no macroporosity can be seen, while microheterogeneity can be perceived. These conclusions are also corroborated by results of a comparison of the morphology of polymers and copolymers by scanning electron microscopy (Figs 1–3*).

Within a limited composition range of opaque samples, globular morphology can be observed, which is typical of polymers prepared by the precipitation polymerization⁴. In systems with limited solubility the polymer is separated from solution in the monomeric mixture during the polymerization in the form of globular particles, which increase in size and agglomerate at higher conversions. In this way, a macroporous skeleton is formed with communicating pores between the globules. Table I shows the dependence of the globule size on composition. The crosslinked polymers of *I*, *II*, and *III* are homogeneous (Fig. 1*); the globule size of copolymers *I* + *II* increases from 0.16 to 1.60 μm in the case of samples with 30, 50 and 75% of *I*. Compared to the sample with 75% of *I*, in the case of the sample with 10% of *I* the polymer is separated from the better solvent, which makes a larger number of particles separate from the volume unit of the monomer. In the sample with 75% of *I*, the nuclei may increase to form larger globules, but *I* in excess makes them swell, which is reflected in a more pronounced collapse of the particles. The highest porosity is attained for the sample with an average composition (50%), where the globule size is average (c. 1 μm), and the globules are least agglomerated.

In the series of copolymers *I* + *III*, globular morphology can be seen within a broad range of compositions from 0 to 75% of *I*; the polymer with the highest porosity having the smallest and least sintered globules is formed at 50% of *I* (Fig. 3*). In this series too an increased agglomeration of globules is observed at 75% of *I*.

The dependence of bulk weight on composition in both series of copolymers (Fig. 4a*) is in good agreement with results of the morphological investigation. It has been confirmed that evidently macroporous samples exhibit low bulk weights (below 0.5 g/ml), the most porous being copolymers with 50% of *I*.

The relatively large size and low agglomeration of globules of the copolymer with 50% of *I* (highest porosity) indicate the smallest solubility of the copolymer having the given composition. A likely explanation may consist in a specific interaction between the components of copolymers *I* + *II* containing the amide and the carboxyl group, which is most pronounced at the 1 : 1 ratio.

The swelling properties measured for the copolymers prepared in this work and the interpretation given above are confirmed by Fig. 4b*, in which the copolymers are characterized by the coefficient of volume swelling (V_w/V_0). Obviously, for a macroporous gel to be formed, it is necessary that $V_w/V_0 < 4$. In the same figure one can

* See insert facing page 1930.

also see the dependence of V_b/V_w on the content of methacrylic acid in the polymerization mixture. This value expresses a relative change in the gel volume, if these gels are swollen in a phosphate buffer (pH 6.8) and in water. The change in swelling may be assigned to a change in the degree of ionization of methacrylic acid. Neither the effect of different morphology nor that of different chemical constitution of the polymers under study is operative in this case.

In the final part of the work we attempted to characterize qualitatively the effect of composition of the solvent on the heterogeneity of copolymers. As shown by Fig. 5*, an addition of acetic acid to the polymerization mixture improves the quality of the solvent in both systems. For copolymers *I + II* the change in the thermodynamic quality of the solvent is much more pronounced than for copolymers *I + III*. In the former case, an addition of 5% CH_3COOH to the polymerization mixture is sufficient to make the character of the polymer change from heterogeneous to homogeneous ($V_w/V_0 > 4$). In the latter case, the thermodynamic properties of the solvent are changed gradually; in the concentration range 0–30% CH_3COOH , the system changes from a heterogeneous into a homogeneous one. For copolymers *I + II*, these changes in structure are demonstrated by electron micrographs (Fig. 6*).

In the case of copolymer *I + II* (25 : 75), one can see a refinement of globular morphology with increasing concentration of acetic acid in the copolymerization mixture. This agrees well with the finding that in a better solvent the free energy of formation of polymeric nuclei decreases, and the latter are therefore separated in a larger amount⁴. In a solution containing 30% of acetic acid, a pseudohomogeneous copolymer is formed. In such case one can speak about microporosity, or swelling porosity with heterogeneities lower by two orders of magnitude than those observed with macroporous copolymers.

The results just described show that, similarly to other systems, in our case too phase separation occurs and a heterogeneous copolymer is formed, if the polymer-solvent interaction parameter attains the critical value¹⁰. Since this work had as its objective preparation of new sorption materials, the conditions of formation of a heterogeneous copolymer were determined only by the composition of the original monomeric mixture and confirmed by an electron-microscopic characterization of the polymers under study. A more detailed thermodynamic description of such systems goes beyond the scope and aims of this and forthcoming⁵ papers.

REFERENCES

1. Samsonov G. V.: Pure Appl. Chem. 38, 151 (1974).
2. Kuznetzova N. N., Genender K. I., Samsonov G. V., Selezneva A. A., Kozlova T. A., Babenko G. A., Vitols O. A., Shtrausa A. A.: U.S.S.R. 332322.
3. Shataeva L. K., Samsonov G. V.: Pharm. Zh. 1977, (4) 78.

* See insert facing page 1930.

4. Pelzbauer Z.: *2nd International Microsymposium on Polymer Morphology*, Kiev, March 1974; Proceedings *Physicochemical Properties and Synthesis of High-Molecular Weight Compounds*, p. 76. Naukova Dumka, Kiev 1976.
5. Vacík J., Shataeva L. K., Samsonov G. V., Kálal J., Kopeček J.: This Journal, in press.
6. Kopeček J., Jokl J., Lim D.: *J. Polym. Sci. C 16*, 3877 (1968).
7. Strohalm J., Kopeček J.: *Angew. Makromol. Chem.* **70**, 109 (1978).
8. Gradsten M. A., Pollock M. W.: *J. Amer. Chem. Soc.* **70**, 3079 (1948).
9. Shataeva L. K., Chernova I. A., Vacík J., Samsonov G. V.: *Izv. Akad. Nauk SSSR, Ser. Khim.* **1977**, 353.
10. Dušek K.: *J. Polym. Sci. B 3*, 209 (1965).

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Porous Copolymers of Methacrylic Acid

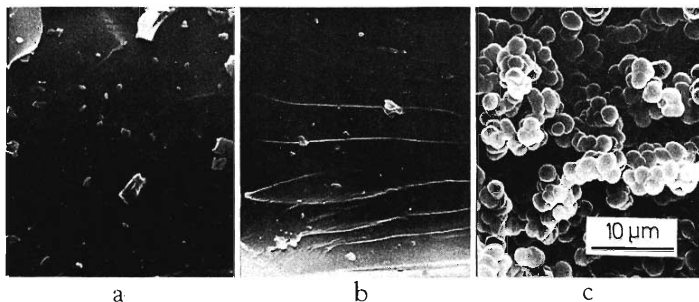


FIG. 1

The Morphology of Crosslinked Poly[N-(2-Hydroxypropyl) Methacrylamide] (a), Poly-methacrylic Acid (b), Poly[(2-Hydroxyethyl) Methacrylate] (c)

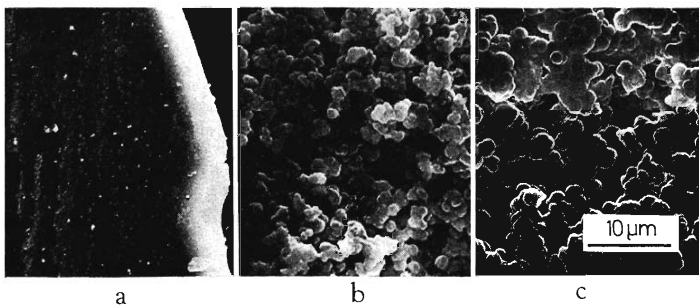


FIG. 2

The Morphology of Crosslinked Copolymers of Methacrylic Acid (I) with N-(2-Hydroxypropyl) Methacrylamide

The concentration of I in the initial mixture of monomers, mol.%, a 30, b 50, c 75. Polymerization solvent: water.

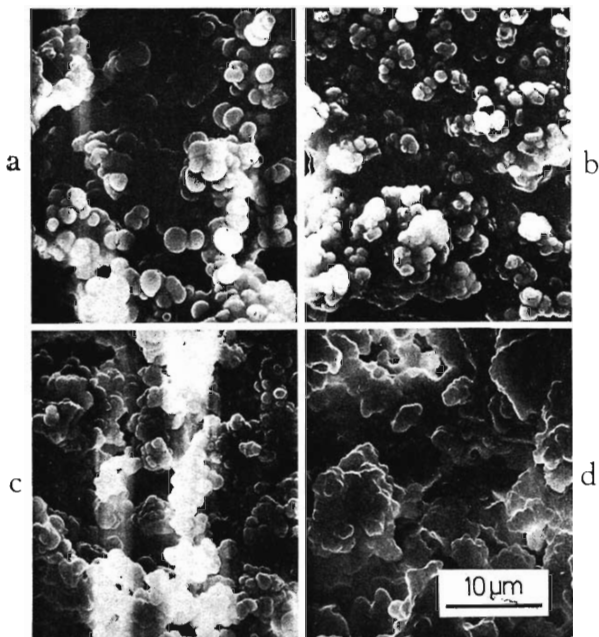
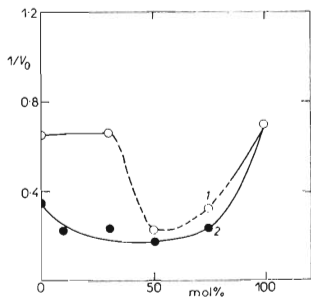


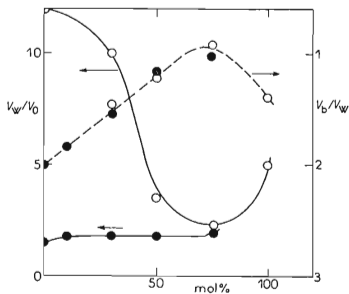
FIG. 3

The Morphology of Crosslinked Copolymers of Methacrylic Acid (*I*) with (2-Hydroxyethyl) Methacrylate

The concentration of *I* in the initial mixture of monomers, mol. %: *a* 10, *b* 30, *c* 50, *d* 75. Polymerization solvent: water.



a



b

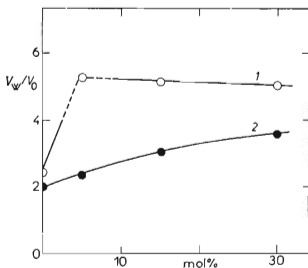
FIG. 4

The Dependence of Bulk Weight in the Dry State ($1/V_0$, g/ml) and of the Coefficient of Volume Swelling (V_w/V_0), or V_b/V_0 on the Content of Methacrylic Acid (I) in Copolymers with (2-Hydroxyethyl) Methacrylate (●) or N-(2-Hydroxypropyl) Methacrylamide (○)

a) $1/V_0$ vs I ; b) V_w/V_0 vs I . V_b/V_w vs I .

FIG. 5

The Dependence of the Coefficient of Volume Swelling (V_w/V_0) on the Content of Acetic Acid in the Polymerization Mixture in the Copolymerization of Methacrylic Acid (75 mol.%) with (2-Hydroxyethyl) Methacrylate (2), or N-(2-Hydroxypropyl) Methacrylamide (1)



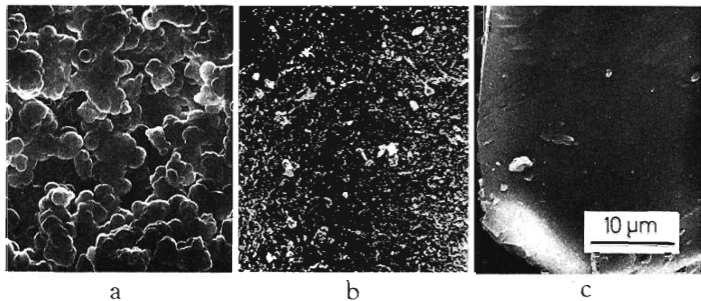


FIG. 6

The Effect of the Concentration of Acetic Acid as the Polymerization Solvent on the Morphology of the Crosslinked Copolymer Methacrylic Acid (*I*) — N-(2-Hydroxypropyl) Methacrylamide (*II*)

The concentration of components in the mixture of monomers: 75 mol.% *I*, 25 mol.% *II*. Solvent: *a* H₂O, *b* 5% CH₃COOH, *c* 30% CH₃COOH.