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REVIEW PAPER

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SYNTHESIS, PROPERTIES AND APPLICATIONS OF CROSSLINKED MACROPOROUS COPOLYMERS BASED ON METHACRYLATES

In this paper, the results obtained during extensive research on the synthesis, properties and application of crosslinked copolymers, performed at the Faculty of Technology and Metallurgy (Department of Physical Chemistry and Electrochemistry) and at the IChTM (Center for Catalysis and Chemical Engineering and Center for Chemistry) are summarized. According to the obtained results, changes in the composition of the inert component and the content, type and amount of the crosslinking agent, as well as the type of copolymerization reaction, all strongly influence the porosity parameters of the synthesized macroporous copolymers. Also, it was shown that the synthesized copolymers of glycidyl methacrylate, GMA, and ethylene glycol dimethacrylate, EGDMA, modified with ethylene diamine can be used for the selective sorption of gold and platinum from mixed solutions containing copper, cobalt and nickel ions.

Macroporous copolymers are used for the preparation of various types of ion exchange resins, as inert carriers for some types of chromatography, as adsorbents, as supports for classical catalysts or enzymes in biosynthesis, and as membranes for different purposes [1–8]. For these applications the most widely used are copolymers of styrene with divinylbenzene, whereas copolymers of vinylpyridine with divinylbenzene, and copolymers based on mono- and dimethacrylates are much less used [9–12]. There is a growing interest [13–18] in copolymers of glycidyl methacrylate (2,3-epoxypropyl methacrylate), GMA, and ethylene glycol dimethacrylate, EGDMA, since the epoxy group of GMA can be easily transformed into a hydroxy, keto, carboxy or amino group. In this way, the copolymer properties can be adjusted to the various applications. Among other factors, the applicability of these copolymers is very much influenced by their porosity. Švec et al. have shown that macroporous copolymers of glycidyl methacrylate and ethylene glycol dimethacrylate (GMA-co-EGDMA) in a shape convenient for application can be obtained by the suspension copolymerization of GMA and EGDMA when a low-molecular weight inert component is present in the mixture of monomer and initiator (monomer phase). The inert component contained cyclohexanol (solvent) and dodecanol (nonsolvent for the copolymer). According to the results of these authors, the amount of the crosslinking agent, EGDMA, in monomer mixture, the amount of inert component in the monomer phase, and the amount of dodecanol in the inert component have the largest influence on the porous structure of GMA-co-EGDMA [19–21].

In this paper, experimental results obtained during the investigation of the influence of the content of inert

component, type and amount of the crosslinking agent, and the type of the copolymerization reaction (suspension vs copolymerization in a cast) on the porosity parameters of GMA-co-EGDMA copolymers are presented. The content of the inert component (cyclohexanol+dodecanol) in the GMA-co-EGDMA synthesis was varied either by substituting dodecanol for some other aliphatic alcohols (methanol, ethanol, propanol, butanol, octanol, decanol, tetradecanol or hexadecanol) or nonionic surface active substances, PAM, with different molecular structures and HLB values or by changing the amount of aliphatic alcohols and PAM in the inert component. During this series of experiments, EGDMA was used as the crosslinking agent. In the second series of experiments, when the inert component contained cyclohexanol and hexadecanol, EGDMA, butandiol-, BDDMA, hexandiol-, HDDMA, dodecandiol-, DDDMA, and bisphenol-A-dimethacrylate, BADMA, were used as crosslinking agents. The sorption and separation ability of GMA-co-EGDMA modified with ethylene diamine towards metal ions (Cu, Ni, Co, Pt) was also investigated and the results presented in this paper.

1. EXPERIMENTAL

The suspension copolymerizations were performed in a typical reactor whose volume was 0.50 dm³. The monomer phase (80.9 g) containing monomer mixture (GMA and the crosslinking agent), initiator (1 wt.%) and inert components was suspended in 240 g of a 1 wt.% aqueous solution of poly(vinyl pyrrolidone) (Kollidon 90), PVP. Azobisisobutyronitrile was used as the initiator. The ratio of inert component to monomer mixture was 1.32 in all experiments. The copolymerization was carried out at 70°C for two hours and at 80°C for six hours with a stirring rate of 200 rpm. After completion of the reaction, the copolymer particles were washed with water and ethanol, kept in ethanol for 12 h, and then dried in a vacuum oven at 45°C.

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Copolymerization in a cast was carried out between glass plates bound a with special seal. All other experimental conditions being the same as in the corresponding synthesis by suspension copolymerization. The influence of the content of the inert component was investigated by copolymerization in the cast. Besides the copolymerization of GMA and EGDMA in the cast, copolymerization in a "tubular" reactor was performed under the same experimental conditions, using the same monomers [22].

The monomer GMA, the crosslinking agents EGDMA, BDDMA, HDMA, DDDMA, BADMA, and other chemicals used were purified by usual means [23,24].

The particle size distribution was determined by sieve analysis. The particles with diameters in the range of 150–500 μm were used for further investigations.

A commercial mercury porosimeter, Model 2000 Carlo Erba, was used for the determination of the specific pore volumes, V_s (in cm^3/g), and pore size distribution.

The specific surface area, $S_{s,BET}$ (in m^2/g), of the copolymers was determined by the BET method from low-temperature nitrogen adsorption isotherms which were obtained at -196°C using a high-vacuum volumetric apparatus. The samples were degassed at 100°C and a pressure of 1 mPa for 3 h.

The shape of the beads, surface appearance and porous structure of the cross-section of copolymer beads were observed using a scanning electron microscopy (DSM-962, Zeiss).

The epoxy-group content was determined by the HCl-dioxane method. Modification of the synthesized copolymers with ethylene diamine was carried out in toluene at 70°C for 7h (10,0 g of copolymer+29.4 g of ethylene diamine+250 cm^3 of toluene). The modified copolymer was filtered, washed with ethanol and dried. The modified copolymers swell slightly (about 4 vol%) in aqueous solutions.

The capacities for Cu^{2+} , Co^{2+} and Ni^{2+} under non-competitive conditions were determined by contacting 0.2 g of copolymer with 50 cm^3 of the appropriate metal chloride (and sulfate for Ni^{2+}) solution (0.16M) at room temperature. After 48 h, the samples were filtered, washed with water then with ethanol and dried. The remaining solution was kept for metal analysis.

Batch metal-uptake experiments under competitive conditions were performed with metal-chloride solutions of Cu^{2+} and PtCl_6^- (0.03M). Batches of 0.2 g of copolymer were used together with a mixture of 12.5 cm^3 of each metal-chloride solution at room temperature. After 48 h, the samples were further handled as described above for the non-competitive experiments.

The metal contents were determined complexometrically or by AAS spectroscopy.

2. RESULTS AND DISCUSSION

2.1. The influence of the inert component on the porosity parameters of GMA-co-EGDMA

In order to investigate the influence of the content of the inert component on the porous structure of poly(GMA-co-EGDMA), several samples were synthesized keeping the monomer mixture content constant (42.6 mass.% of EGDMA). First, the GE-10/12 sample was synthesized with a standard content of inert component (90 mass.% of cyclohexanol and 10 mass.% of dodecanol) [13]. Under the same experimental conditions, the syntheses of five additional samples of poly(GMA-co-EGDMA) were carried out. In these syntheses, the content of the inert component was changed by substituting dodecanol with butanol (sample GE-10/4), octanol (GE-10/8), decanol (GE-10/10), tetradecanol (GE-10/14) or hexadecanol (GE-10/16).

The specific surface area, $S_{s,BET}$, was determined for all the synthesized samples; the values are presented in Table 1. The pore size distributions for all the samples were determined by mercury porosimetry; the results are given in Fig.1. The values of the specific pore volume, V_s , and pore diameter, which corresponds to half of the pore volume, $d_{v/2}$, were read from Fig.1. and are also presented in Table 1.

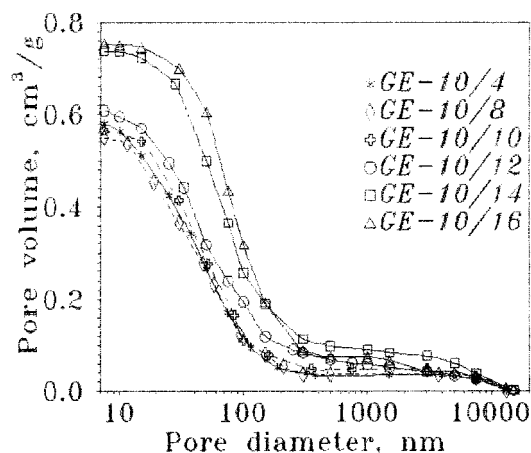


Figure 1. Cumulative pore volume distribution curves with respect to pore diameter

From the pore size distribution curves (Fig. 1.), the values of the specific surface area, $S_{s,Hg}$ (in m^2/g) were calculated using equation 1:

$$S_{s,Hg} = \sum_{i=1}^n \Delta S_i \quad (1)$$

where:

$$\Delta S_i, \text{ m}^2/\text{g} = \frac{4000(V_{i+1} - V_i)}{(d_i + d_{i+1})/2}$$

and V_i , cm^3/g ; is the value of the specific volume of pores with diameter d_i , nm [24].

Table 1. Porous structure parameters of the investigated GMA-co-EGDMA copolymers

Sample ^a	$S_{s,BET}$ (m ² /g)	$S_{s,Hg}$ (m ² /g)	V_s (cm ³ /g)	P (%)	d_p (nm)	$d_{v/2}$ (nm)
GE-10/4	68.2	70	0.580	41	34	44
GE-10/8	55.8	56	0.550	40	39	47
GE-10/10	52.0	53	0.560	40	43	48
GE-10/12	47.6	50	0.610	42	51	53
GE-10/14	46.7	47	0.740	47	63	68
GE-10/16	36.0	33	0.755	48	84	87
GE-15/10	49.6	52	0.740	47	60	60
GE-15/12	44.5	47	0.855	51	76	70
GE-15/16	35.0	34	1.020	55	117	200
GE-20/10	41.5	40	0.920	53	89	115
GE-20/12	30.0	31	0.960	54	127	120
GE-20/14	27.6	26	1.040	56	151	270
GE-20/16 ^b	13.2	12	1.125	57	341	560

^aThe first number in a sample label stands for the share of the aliphatic alcohol in the inert component and the second one for the number of C-atoms in the aliphatic alcohol.

^bThe particles do not have spherical shape.

The values of the total open porosity, defined as $P(\%) = (V_s/V_t)$, where V_t is the total volume of the sample (including the pore volume), were calculated using the value of 1.26 g/cm³ for the density of poly(GMA-co-EGDMA) [20]. By using the corresponding values for V_s and $S_{s,BET}$ from Table 1, the value of the average pore diameter $d_p = 4000 V_s/S_{s,BET}$ was calculated for all samples. The calculated values for $S_{s,Hg}$, P, $d_{v/2}$, and d_p are given in Table 1, in addition to other porosity parameters of the samples.

Comparing the pore size distribution curves presented in Fig.1 and the parameters of the pore structure for the corresponding copolymer samples given in Table 1, it can be concluded that there is a slight increase in the specific volume and pore diameter and a decrease in the specific surface area when the number of C-atoms in the aliphatic alcohol is increased from 4 (butanol) to 10 (decanol), keeping the amount of alcohol in the inert component constant. More significant changes in the pore structure parameters are obtained when the dodecanol in the inert component is substituted with tetradecanol or hexadecanol. Therefore, in the next two series of experiments, when the amount of aliphatic alcohol in the inert component was varied (15 and 20 mass.%), the syntheses of poly(GMA-co-EGDMA) were conducted only in the presence of either decanol, dodecanol, tetradecanol or hexadecanol together with cyclohexanol in the inert component.

Pore size distribution curves were also determined for these copolymers and the pore structure parameters obtained in the usual way are given in Table 1.

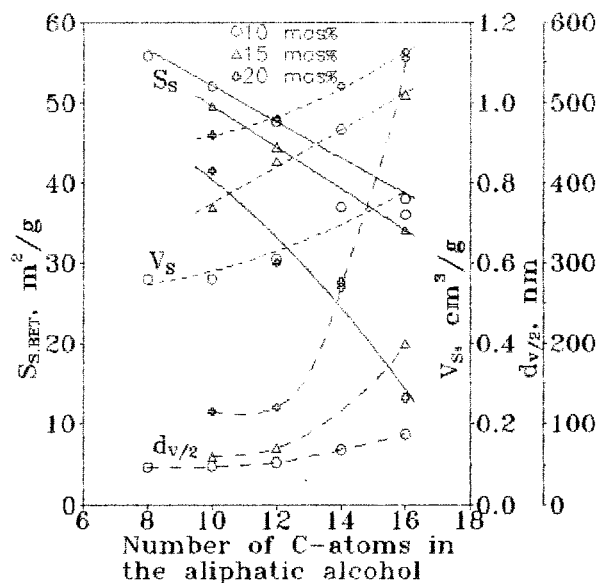


Figure 2. Dependence of the pore structure parameters poly(GMA-co-EGDMA) on the number of C-atoms in the aliphatic alcohols

The dependences of the specific pore volume, V_s , specific surface area, $S_{s,BET}$, and pore diameter, $d_{v/2}$, on the number of C-atoms in the aliphatic alcohol for different ratios of aliphatic alcohol in the inert component (10, 15 and 20 mass. %) are shown in Fig. 2.

The results given in Table 1 and Fig. 2 unambiguously show that the presence of an aliphatic alcohol in the inert component has a significant influence on the pore structure parameters of the poly(GMA-co-EGDMA) samples – with increasing number of C-atoms, i.e. with increasing molar mass of the aliphatic alcohol in the inert component, the specific volume and pore diameter increase and the specific surface area of the poly(GMA-co-EGDMA) samples decreases. Of all the aliphatic alcohols used, tetradecanol and hexadecanol have the greatest influence on the pore structure parameters, especially when their amount in the inert component is 15 or 20 mass.%. Copolymer samples GE-15/16, GE-20/14 and GE-20/16 obtained under these conditions have pore diameters larger than 200 nm values not achieved with a low-molecular weight inert component so far.

According to the commonly accepted opinion, the presence of an inert component in the monomer phase is necessary in order to obtain macroporous crosslinked copolymers during the copolymerization. The inert component should mix well with the monomers but should not dissolve the obtained copolymer. In this way it is easier to separate the copolymer particles as a new phase from the reaction mixture and form porous structures. Therefore, it is to be expected that the difference in solubility parameters of the inert component and of obtained copolymer should have a significant influence on the pore structure parameters of

the copolymers formed. However, the solubility parameters for cyclohexanol and the investigated aliphatic alcohols are very similar, their values being 23.3 for cyclohexanol and butanol, 21.7 for octanol and 20.2 (J/m^3)^{1/2} $\times 10^{-3}$ for dodecanol [25]. For tetradecanol and hexadecanol the solubility parameters were calculated [25, 26] and found to be very similar to the values for decanol and dodecanol. These facts, as well as the experimental results presented in Fig. 2 and in Table 1 indicate that the problem of pore structure formation of GMA-co-EGDMA copolymers is very complicated and it cannot be rationalized by taking into consideration only the values of the solubility parameters of the inert component.

Higher aliphatic alcohols also behave as surface active substances. Therefore, it can be expected that this property of the higher alcohols could have an influence on the formation of the supermolecular structure during the synthesis of GMA-co-EGDMA. In order to confirm this presumption, the syntheses of three GMA-co-EGDMA samples were performed by suspension copolymerization. The only difference in the experimental conditions was in the inert component composition. Namely, the first experiment was carried out only with cyclohexanol as the inert component. In the second experiment, instead of an aliphatic alcohol, 5 wt % of a nonionic surface active substance, Arcopal N-040 (HLB=8,9) was added to the cyclohexanol. Finally, in the third experiment, 10 wt % of Arcopal N-300 (HLB=17,1) was added to the cyclohexanol. The synthesized samples were labeled as SGE-0, SGE-A-5/9 and SGE-A2-94 (10/17), respectively. The inert component content in the monomer phase was the same in all three of these experiments.

The pore size distribution curves for the synthesized samples were determined by mercury porosimetry and the results presented in Fig. 3.

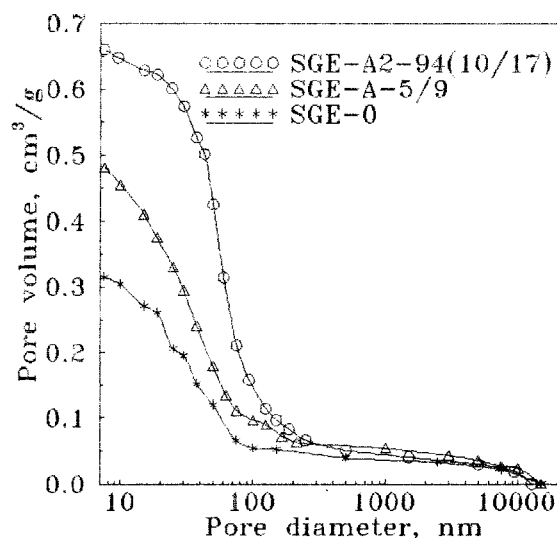


Figure 3. Cumulative pore volume distribution curves with respect to pore diameter

As can be seen in Fig. 3., the addition of a surface active substance to the inert component has a significant influence on the porosity parameters (V_s , $S_{s,Hg}$ and $d_{V/2}$). Moreover, this influence increases with increasing HLB value of the used surface active substance. Comparison of the results given in Figs. 2. and 3. suggests that the presence of aliphatic alcohols or a surface active substances in the inert component has the same influence on the porosity parameters of the synthesized GMA-co-EGDMA.

These experiments show for the first time that the influence of the inert component on the porosity parameters of the synthesized copolymers is the result of the surface activity of the substances that constitute the inert component, besides their solubility parameters.

The shape of the SGE-A2-94 (10/17) beads, their surface and cross section were determined by scanning electron microscopy (SEM) and the micrographs are presented on Fig. 4.

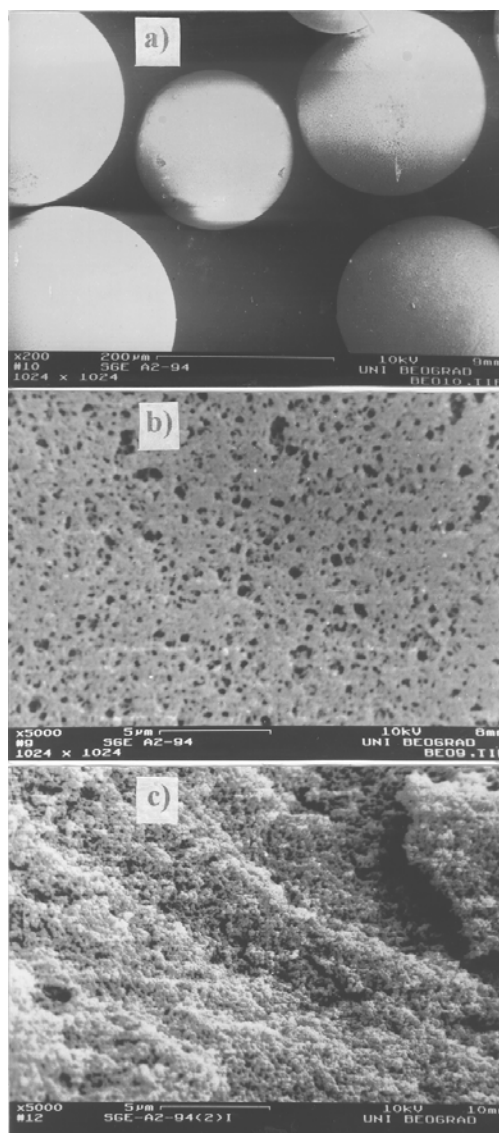


Figure 4. Scanning electron micrographs of copolymer SGE-A2-94: a) shape of the beads; b) surface; c) cross-section

It can be seen from Fig. 4. that sample SGE-A2-94 has regular shaped spherical beads of uniform size (fraction 150–500 (μm)). Also, the pores with diameters from 0.1 to 2 μm (Fig. 4b.) are randomly distributed on the surface of the copolymer beads. It should be emphasized that the surface pore size is of major importance for a variety of preparative and analytical applications, because of its role in promoting rapid mass transfer through copolymer beads.

In the Fig. 4., which represents a cross-section of the beads, it can be seen that GMA-co-EGDMA macroporous copolymers have globular structure with interconnected pores. By comparing the SEM photographs of the cross-section of the beads for numerous GMA-co-EGDMA samples it was concluded that all the synthesized samples have a globular structure. Furthermore, it was also observed that the influence of the inert component on the porosity parameters of GMA-co-EGDMA manifests itself on the size of the primary globules, their association into aggregates, and internal organization of the aggregates within the copolymer beads.

2.2. Influence of the crosslinking agent

In order to investigate the influence of the crosslink density on the porosity parameters of copolymers of glycidyl methacrylate and ethylene glycol dimethacrylate, poly(GMA-co-EGDMA), four copolymer samples were synthesized. The content of the inert component was kept constant (90 mass.% of cyclohexanol and 10 mass.% of hexadecanol) but the amount of the crosslinking agent, EGDMA, in the monomer mixture was varied from 10 to 40 mass.%. The samples obtained were labeled as GE-90/10, GE-80/20, GE-70/30 and GE-60/40.

The influence of the length and rigidity of the molecular chain between two double bonds in a molecule of the crosslinking agent on the porosity parameters was investigated by synthesizing five copolymers of GMA with different crosslinking agents. As crosslinking agents, EGDMA, BDDMA, HDDMA, DDDMA and BADMA were used. The amount of crosslinking agent in the monomer mixture was 45 mass.% for all samples. The samples obtained were labeled as GE-55/45, GB-55/45, GH-55/45, GD-55/45 and GBA-55/45, respectively.

The specific pore volumes, V_s , and the pore size distribution curves for all the samples were determined by mercury porosimetry and the results are presented in Figs. 5 and 6. From the pore volume distribution curve, the specific surface area, $S_{s,Hg}$, was calculated. The values obtained are presented in Table 2 together with the values of the average pore diameter, d_p , and the total porosity, P which were calculated in the same way as in the previous section.

From the pore size distribution curves for the samples GE-60/40, GE-70/30, GE-80/20 and GE-90/10,

Table 2. Characteristic parameters of the investigated crosslinked polymers

Sample ^a	b	$S_{s,BET}$ (m^2/g)	$S_{s,Hg}$ (m^2/g)	V_s (cm^3/g)	P (%)	d_p (nm)
GE-60/40	1.05	62	63	0.845	49.2	54
GE-70/30	1.62	49	50	0.760	46.6	61
GE-80/20	2.79	29	31	0.530	38.0	74
GE-90/10	6.27	1.8	3	0.135	13.3	300
GE-55/45	0.85	77	76	0.810	48.1	42
GB-55/45	0.97	47	47	0.435	32.2	37
GH-55/45	1.09	1	2	0.077	8.2	210
GD-55/45	1.45	1	2	0.062	6.5	240
GBA-55/45	1.56	50	45	0.795	47.1	64

which are shown in Fig. 5, it can be seen that with decreasing amount of the crosslinking agent, EGDMA, in the monomer mixture, i.e. with decreasing crosslinking density, the specific pore volume decreases from 0.845 to 0.135 cm^3/g . These results imply that when the ratio of the number of moles of double bonds, b, from GMA and crosslinking agent, is equal or larger than 6, the GMA-co-EGDMA copolymers obtained have very low porosity in spite of the fact that 57 mass.% of inert component was present in the monomer phase. With increasing amount of EGDMA in the GMA/EGDMA mixture from 20 to 40 mass.%, the specific surface area of the samples increases from 30 to 62 m^2/g while the average pore diameter changes only a little. Since it was shown that the porosity is a consequence of the globular structure of the copolymers obtained and that the pore size is determined by the size of globule [23], the obtained results indicate that, in this case, an increase of the amount of the crosslinking agent in the monomer mixture has little effect on the size of the globule.

The pore size distribution curves for copolymers crosslinked with crosslinking agents having different lengths of the molecular chain between the double bonds are shown in Fig. 6. The results from Table 2 and Fig. 6 show that with increasing molar mass of the crosslinking agent, the specific pore volume and specific surface area of the copolymer samples decrease considerably. Copolymers with very small porosity are obtained already with HDDMA and DDDMA as crosslinkers. Practically, these copolymers cannot be considered as macroporous. The increasing molar mass of the crosslinking agent is a consequence of the increasing average number of $-\text{CH}_2-$ groups between the double bonds. This means that when the number of $-\text{CH}_2-$ groups is equal or larger than six, the molecular chain between the points of crosslinking is so flexible that under the employed conditions of synthesis and copolymer separation from the reaction mixture, a

collapse of the porous structure occurs and the resulting copolymer is almost transparent, i.e. has very small porosity ($V_s = 0.13 \text{ cm}^3/\text{g}$).

The ratio of the number of moles of double bonds from GMA and crosslinking agent, b , for the GH-55/45 copolymer is equal to 1.09 and for the GBA-55/45 copolymer 1.56, which means that the latter has a lower crosslink density than the former. Since the molecular chain between the double bonds in the BADMA molecule is longer than in the HDDMA molecule, it should be expected that the GBA-55/45 copolymer would have a low porosity, just like the GH-55/45 copolymer. However, on the basis of the values of the porosity parameters given in Table 2 it can be concluded that the GBA-55/45 copolymer is macroporous and that it has a specific pore volume equal to the value for the GE-55/45 copolymer (Fig. 6), although the latter has a much higher crosslink density and a shorter molecular chain between the double bonds. This means that the porous structure of copolymers of GMA is determined not only by the crosslink density but also by the length and rigidity of the molecular chain between the double bonds in the crosslinking agent. It is interesting to note that these two copolymers have very different values of the specific surface area and average pore diameter (Table 2) although their pore volumes are similar.

2.3. Copolymerization of GMA and EGDMA in a cast and in the tubular reactor

Copolymerization of GMA and EGDMA in a cast in which only the monomer phase was present, made possible the investigation of the influence of lower aliphatic alcohol in the inert component on the porous structure parameters of the poly(GMA-co-EGDMA) samples obtained. Seven samples of poly(GMA-co-EGDMA), which were in the shape of a plate 2.0 mm thick, were synthesized by copolymerization in a cast. In these experiments only the type of aliphatic alcohol was changed, while its amount in inert component was 10 mass.%. As aliphatic alcohols methanol (1), ethanol (2), propanol (3), butanol (4), hexanol (6), octanol (8), and hexadecanol (16) were used and the copolymers obtained were labeled as: PGE-10/1, PGE-10/2, PGE-10/3, PGE-10/4, PGE-10/6, PGE-10/8 and PGE-10/16, respectively. The pore size distributions for all the samples were determined by mercury porosimetry and the results obtained are presented in Fig. 7 as dependences $100V/V_s$ vs d . The values for $S_{s,Hg}$, V_s , P and $d_{V/2}$ are presented in Table 3. Comparing these results with the results shown in Fig. 1 and Table 1, which were obtained for samples synthesized by suspension copolymerization, it can be concluded that in the case of copolymerization in the cast the influence of the type of aliphatic alcohol on the pore diameter, $d_{V/2}$, is much more pronounced. So, it is possible by copolymerization in the cast to obtain with hexadecanol, for example, poly(GMA-co-EGDMA)

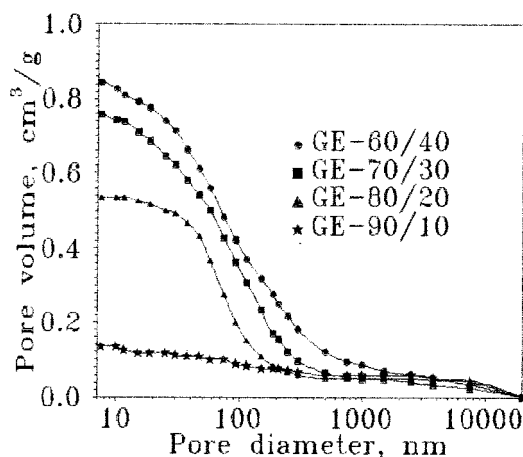


Figure 5. Cumulative pore volume distribution curves with respect to pore diameter

Table 3. Parameters of pore structure of copolymers obtained by copolymerization in a cast

Sample	$S_{s,Hg}$ (m^2/g)	V_s (cm^3/g)	P (%)	$d_{V/2}$ (nm)
PGE-10/1	64	0.89	53	83
PGE-10/2	68	0.85	52	82
PGE-10/3	44	0.99	56	107
PGE-10/4	30	0.86	52	180
PGE-10/6	28	1.05	57	230
PGE-10/8	27	1.08	58	290
PGE-10/16	19	1.03	57	560

samples with five to six times larger pore diameter, $d_{V/2}$, than for the corresponding samples obtained by suspension copolymerization. The reason for this is probably the partial miscibility of monomer, inert component and water in suspension polymerization and the influence of this on the separation of the new phase during the copolymerization reaction.

Macroporous GMA-co-EGDMA copolymer in the shape of spherical beads, synthesized by suspension copolymerization, can be used as column packing for gas or gel chromatography. However, GMA-co-EGDMA has a globular structure, i.e. flow-through the pores even when the copolymerization is performed in a tubular reactor. Švec et al. replaced conventional column packing (crosslinked polymers in the shape of spherical beads) with suitable copolymers obtained by performing the copolymerization directly within a chromatographic column-tubular reactor. In this case, the column packing is obtained as a single "molded" polymer monolith which is practically incompressible [27, 28].

Copolymerization of GMA and EGDMA under the mentioned experimental conditions is, in fact, a precipitation copolymerization. Practically, this means that the GMA-co-EGDMA formed during the copoly-

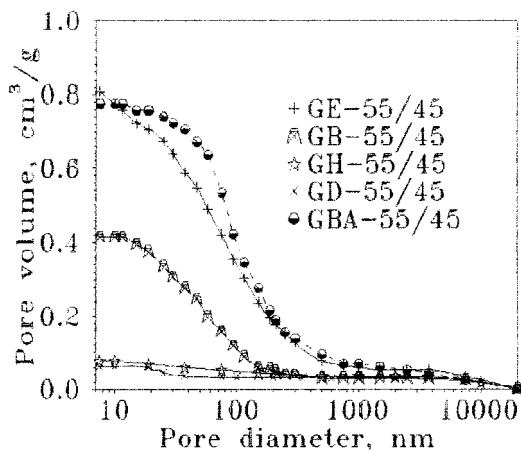


Figure 6. Cumulative pore volume distribution curves with respect to pore diameter

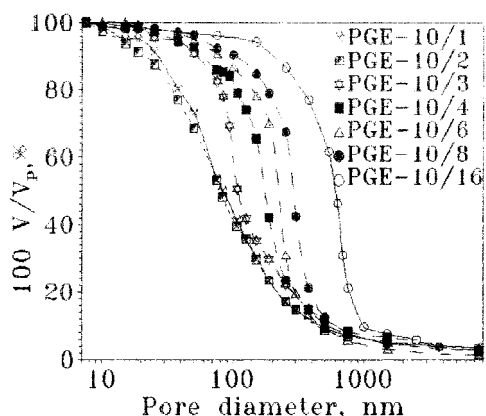


Figure 7. Cumulative pore volume distribution curves with respect to pore diameter

merization is insoluble in the mixture of unreacted monomers and inert component. All the results presented so far show that the composition of the inert component pays a decisive role on the porosity

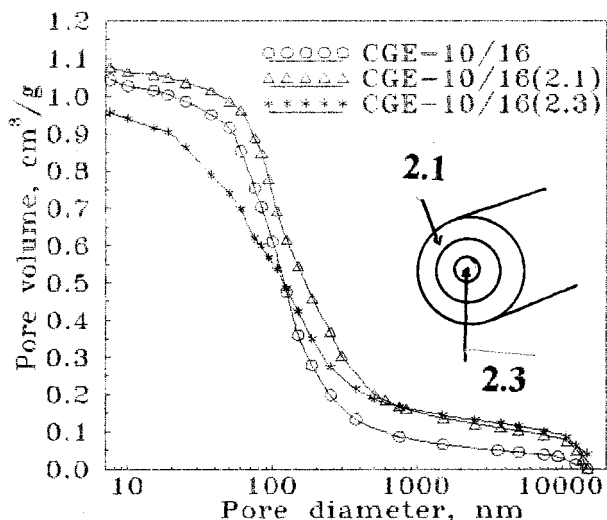


Figure 8. Cumulative pore volume distribution curves with respect to pore diameter

parameters of the synthesized copolymers, i.e. on the size of the primary globules, their aggregation and their spatial arrangement.

It is a well known fact that during the reaction, copolymer separates as a new phase, causing variations in the inert component/monomers ratio. Considering this, it is not to be expected that the size of the globules and aggregates, as well as their spatial arrangement, would be the same for copolymer formed in the first and in the final stage of copolymerization. To verify this, a number of GMA and EGDMA copolymerization experiments was performed in tubular reactors of different diameter (7, 15 and 21 mm). As an illustration, Fig. 8. shows only the results of the determination of the pore size distribution curves for two layers of the CGM-10/16 sample with additional labels 2.1 and 2.3 (see Fig. 8.) and for the whole sample. As expected, the porosity parameters vary with the diameter of the monolith. In the Fig. 9., SEM photographs of cross-section of the first (2.1) and the third (2.3) monolith layer of the sample CGM-10/16 are presented. These micrographs confirm the results presented on Fig. 8.

The fact that the porosity parameters vary with the diameter of the monolith will surely affect the flow-rate distribution of solvent and solution through the column; homogeneity of the investigated substance fractions and also on the reliability of the fractionation results obtained in this manner.



Figure 9. Scanning electron micrographs of CGE-10/16 (2.1) and CGE-10/16 (2.3)

2.4. Metal sorption on the macroporous GMA-co-EGDMA copolymer modified with ethylene diamine

Macromolecules with different functional groups have been widely used directly as a solution or crosslinked in a shape of classical or macroporous ion-exchange resins and membranes. These polymers have found application in industrial waste-water treatment, selective sorption of metals, in the food and pharmaceutical industry, as stationary phase carriers for some types of chromatography, etc [27, 28].

This section is concerned with sorption and separation ability of macroporous crosslinked glycidyl methacrylate, GMA, and ethylene glycol dimethacrylate, EGDMA copolymers with different porosity parameters towards platinum, nickel, cobalt and copper ions.

The content of epoxy groups on the surface of chosen macroporous SGE-10/12 and SGE-15/16 samples was determined and presented in Table 4., together with their porosity parameters. The total epoxy-group content was 4.22 mmol/g.

Table 4. Porosity parameters and epoxy-group content on the surface of samples SGE-10/12 and SGE-15/16 (total epoxy-group content was 4.22 mmol/g).

Sample	V_s , cm ³ /g	S_{H_2O} , m ² /g	$d_{V/2}$, nm	Epoxy-group content, mmol/g
SGE-10/12	0.610	50	53	2.08 (49,2%)
SGE-15/16	1.020	34	200	2.48 (59,8%)

The maximum Cu²⁺, Co²⁺ and Ni²⁺ uptake capacities of SGE-10/12 and SGE-15/16 from aqueous solutions are presented in Table 5. The capacity of the same copolymer samples towards H₂PtCl₆ was determined and is also shown in Table 5.

Table 5. Capacity of the copolymers SGE-10/12 and SGE-15/16 for different ionic species of Cu²⁺, Co²⁺, Ni²⁺ and PtCl₆²⁻

Copolymer	Capacity, mmol/g of copolymer				
	CuCl ₂	CoCl ₂	NiCl ₂	NiSO ₄	H ₂ PtCl ₆
SGE-10/12	1.109	0.280	0.256	0.192	2.597
SGE-15/16	1.236	0.237	0.207	0.439	1.045

From the results in Table 5 it can be seen that the uptake of Cu²⁺ is four times higher compared with Ni²⁺ and Co²⁺, for both copolymer samples. Also, it appears that besides the type of anion, the porosity parameters of used copolymers have a significant influence on the metal uptake capacities. It is particularly interesting that used macroporous copolymers can bind five to eight times more platinum than copper and nickel. This fact suggests that SGE-10/12 and SGE-15/16 can be used for selective sorption of

platinum from mixed solution with Cu²⁺, Ni²⁺ or Co²⁺. For this reason, batch metal-uptake experiments under competitive conditions were performed with 0,03M metal-chloride solutions of Cu²⁺ and PtCl₆⁻, and results presented in Table 6.

Table 6. Capacity of the copolymers SGE-10/12 and SGE-15/16 for platinum and copper.

Copolymer	Capacity, mmol/g of copolymer (mg/g of copolymer)	
	Cu ²⁺	PtCl ₆ ⁻
SGE-10/12	1.048 (66.5)	1.675 (327)
SGE-15/16	0.972 (61.8)	1.799 (351)

The results presented in Table 6 indicate that macroporous GMA-co-EGDMA copolymers can sorb five times more platinum than copper, even from their mixed chloride solutions. So, it is obvious that SGE-10/12 and SGE-15/16 show a selectivity for platinum over copper, nickel and cobalt.

It can be expected that optimization of the porosity parameters or changing the substituents in the used macroporous copolymers can increase their capacity and adjust them to different ionic species.

3. CONCLUSIONS

The results presented in this paper show for the first time that the porous structure parameters of macroporous poly(GMA-co-EGDMA) samples can be influenced by changing the type of the aliphatic alcohol in the inert component and by changing not only the crosslink density, but also the length and rigidity of the molecular chain between the double bonds in a molecule of the crosslinking agent. For example, the pore diameter, $d_{V/2}$, of a macroporous samples increases from 44 to 560 nm if the number of C-atoms of the aliphatic alcohol in the inert component increases from 4 to 16.

It is also shown that by performing copolymerization in a cast it is possible to obtain samples with pore diameter five to six times larger than in the case of the corresponding samples obtained by suspension copolymerization.

Copolymerization experiments carried out with non-ionic surface active substances in the inert component instead of aliphatic alcohols, indicate that the HLB value of the used PAM have a significant influence on the porosity parameters of synthesized macroporous copolymers.

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IZVOD

SINTEZA, SVOJSTVA I PRIMENA UMREŽENIH MAKROPOROZNIH KOPOLIMERA NA BAZI METAKRILATA

(Pregledni rad)

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U okviru ovoga rada prikazani su rezultati dobijeni u toku višegodišnjeg izučavanja sinteze, svojstava i primene makroporoznih umreženih kopolimera na bazi metakrilata, koja su obavljena pri Katedri za fizičku hemiju i elektrohemiju Tehnološko–metalurškog fakulteta u Beogradu, Centra za katalizu i hemijsko inženjerstvo i Centra za hemiju Instituta za hemiju, tehnologiju i metalurgiju u Beogradu. Pokazano je da se izmenom sastava i udela inertne komponente, vrste i udela umreživača, kao i načina izvođenja reakcije kopolimerizacije može bitno uticati na parametre porozne strukture sintetizovanih umreženih makroporoznih kopolimera i na taj način njihova svojstva prilagoditi različitim potrebama. Pokazano je takođe da se sintetizovani kopolimeri glicidimetakrilata i etilenglikoldimetakrilata obrađeni sa etilendiaminom mogu uspešno koristiti za selektivno izdvajanje platine iz mešanih rastvora sa jonima bakra, kobalta i nikla.

Ključne reči: makroporozni kopolimeri • GMA–dimetakrilati • porozna struktura • vezivanje metala •
Key words: Macroporous copolymers • Copolymerization • GMA–dimethacrylates • Porous structure •