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Dedicated to the memory of
Professor Ecaterina Ciorănescu-Nenitzescu (1909–2000)

SYNTHESIS AND MORPHOLOGICAL CHARACTERIZATION OF ETHYLACRYLATE : ACRYLONITRILE : DIVINYLBENZENE COPOLYMERS

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A number of ethylacrylate : acrylonitrile : divinylbenzene copolymers have been synthesized by suspension polymerization method. The use of sol or nonsol diluents such as, toluene and benzine (a mixture of aliphatic hydrocarbons with $C_5 - C_{10}$ alkyl chains) during the copolymerization led to copolymer beads having porosity in the swelling state and permanent porosity, respectively. The synthesized acrylic copolymers have been characterized from the morphological point of view by the specific and apparent densities, porosity, pore volume, surface area, mean pore radius and solvent uptake coefficients.
An additional treatment with acetone, methanol, methanol : water mixture and finally water has been applied after extraction with 1,2-dichloroethane. All the polymeric networks exhibited porous structures for those prepared both in the presence of toluene or benzine. The characterization of morphological structures showed that macroporous copolymers with a wide range of fixed pore volumes and mean pore radius were prepared.
The solubility parameter theory has been applied to explain the porous structure patterns and the swelling properties of the copolymers synthesized in the presence of different diluent systems. The additional treatment applied on the copolymers have been determined an improvement of their porosity.

INTRODUCTION

Crosslinked polymer beads have attracted attention as carrier matrices in a variety of medical, hydrometallurgical, environmental and biomedical applications due to several possibilities of modification of their chemical and physical properties. Functionalized crosslinked polymers have gained importance as well as for the preparation of a great number of ion exchangers. The most widely used crosslinked polymers are those based on the styrene : divinylbenzene (St : DVB) supports. The degree of swelling can readily be adjusted by the amount of DVB used in the gel synthesis.

Thus, the flexibility of the network chains in St : DVB copolymers has been useful for many ion exchange applications. However, there are still several limitations of St : DVB networks because of their properties, *i.e.* decreasing the degree of crosslinking of the networks in order to increase their molecular porosity resulted in a considerable volume change of the copolymers as well as in their accelerated chemical degradation.

Acrylic copolymers represent interesting macromolecular supports for the ion exchangers because of their higher physico-chemical stability and more hydrophile structure than styrene copolymers. Therefore, the acrylic matrices could have a high potential application for the synthesis of the ion exchangers with the improved ion exchange properties.

The modification of the existing acrylic matrices is a possible method of obtaining compounds with ionic or ionizable groups and high hydrophilicity of the structures. It is accepted that the presence of functional groups on the surface of the crosslinked copolymers results in an increase of hydrophilicity and this enhances the ionic exchange property. For the ion exchangers, it is

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also very important that the chemical and morphological structures of the matrix to allow them to have a long and good applicability.

Generally, the synthesis of the acrylic ion exchangers is based on the aminolysis reaction of nitrile groups contained in acrylonitrile : divinylbenzene copolymers in the bead form with N,N-dialkylaminoalkylamines in the presence of water that leads to the weak base anion exchange resins.[1] Also, macroporous acrylonitrile : divinylbenzene or ethylacrylate : divinylbenzene copolymers were quoted by literature as starting materials for the preparation of macroporous carboxylic cation exchangers having amidoxime or hydroxamic acid groups. [2-5]

The conventional method of preparation of polymeric supports in the bead form is suspension polymerization process. This method involves the addition of monomer or monomer mixture and a monomer soluble initiator to a stirred reactor containing water with a small amount of stabilizer. The stabilizer serves to prevent coalescence and agglomeration of the monomer droplets and polymer beads, respectively. This process presents some advantages such as low separation costs, possibility to synthesize porous materials and the creation of their proper internal structure. The morphological structure of the copolymers can be varied by changing the independent variables of synthesis. The sensitive dependence of the properties of the porous structure on the synthesis parameters allows one to design a tailor-made macroporous material for a specific application. The main experimental parameters are the type and amount of the diluent, the crosslinker concentration, the polymerization temperature and the type of the initiator. [6-15] Porous structures start to form when the amount of the diluent and the amount of crosslinker pass a critical value. There are three methods to prepare macroporous copolymers: (a) addition of a solvating diluent (sol) produces small average pore diameter and therefore a considerable specific surface area (50 – 500 m^2/g) and relatively low pore volume (up to 0.8 mL/g). The pore size distribution of the networks is characterized by the proportion of micro and mesopores; (b) addition of a nonsolving diluent (nonsol) results in a large pore volume (0.6 – 2.0 mL/g), a relatively large average pore diameter and a specific surface area varying from 10 – 100 m^2/g the pore size distribution of the networks is characterized by a large proportion of meso and macropores; (c) addition of a polymeric diluent produces a pore volume up to about 0.5 mL/g, a specific surface area of 0.1 – 10 m^2/g and very large pores reaching the micrometer range.

There are no papers in the literature dealing with the study of morphological structure of ethylacrylate : acrylonitrile : divinylbenzene (EA : AN : DVB) copolymers synthesized in the bead form. We assume that the using of polymeric support based on EA : AN : DVB copolymer leads to the improvement of the network properties due to the presence of ethylacrylate monomer which plays the role to achieve a flexible polymeric network while the presence of low amounts of acrylonitrile monomer induces a rigidity and high porosity of the matrix structure. The aim of this work is to prepare by radical suspension polymerization EA : AN : DVB copolymers with appropriate morphological characteristics which allow them to be used as precursors for ion exchangers with improved ion exchange properties. The acrylic networks were characterized by specific and apparent densities, surface area, pore volume and swelling coefficients in toluene, methanol and cyclohexane.

RESULTS AND DISCUSSION

In order to obtain acrylic matrices based on EA : AN : DVB copolymers with various morphological structures, samples with different contents of crosslinking degrees (DVB) and diluents have been prepared. Their characteristics are listed in Table 1.

As summarized in Table 1 the additional treatment of the copolymers led to changes of their morphological structures, specially for the samples synthesized in the presence of benzine as diluent. These changes are strongly dependent on dilution. Therefore, even at 10 wt. % DVB the porous structures were obtained when dilution increased. In the case of toluene used as diluent, the porosity of the copolymers appears at the crosslinking degree of 15 wt. % DVB and dilution of 0.3. For the benzine : toluene mixture, used as diluent, the highest value of the porosity is for the mixture with the highest content of benzine (Table 2). In this crosslinked network the nonsol diluent caused an increase of copolymer porosity while the sol diluent affected the gel regions. After the additional extraction all the copolymers prepared in the presence of benzine : toluene mixture exhibited changed characteristics which attested the morphological networks with enhanced porosity.

Table 1

Morphological characteristics of the synthesized EA : AN : DVB copolymers

Sample	DVB (wt.%)	Diluent	D[1]	ρ_{ap}[2],		P[3],		r_p[4],		ρ_{sp}[5], g/mL
				g/mL	*g/mL	%	*%	nm	*nm	
C1	10	benzine	0.2	1.1025	1.0064	-	8.81	-	-	1.1036
C2			0.3	1.1024	0.8765	-	20.58	-	92.00	
C3			0.4	1.1018	0.8408	-	23.81	-	88.45	
C4			0.5	1.1016	0.7154	-	35.17	-	121.50	
C5	15	benzine	0.2	1.0346	0.7730	-	28.38	-	28.86	1.0800
C6			0.3	1.0718	0.5587	-	48.24	-	50.50	
C7			0.4	1.0711	0.3959	-	63.32	-	60.40	
C8			0.5	0.5943	0.3914	45.00	63.74	41.23	55.06	
C9	20	benzine	0.2	1.0521	0.8700	-	17.10	-	10.26	1.0543
C10			0.3	0.8992	0.7190	14.71	31.80	20.00	21.00	
C11			0.4	0.7513	0.5880	28.74	44.23	29.15	27.35	
C12			0.5	0.4890	0.2845	53.62	70.00	46.17	84.00	
C13	10	toluene	0.2	1.1261	1.0798	-	4.21	-	-	1.1273
C14			0.3	1.1250	1.0730	-	4.1	-	-	
C15			0.4	1.1250	1.0730	-	4.81	-	-	
C16			0.5	1.1250	1.0730	-	4.81	-	-	
C17	15	toluene	0.2	1.0676	1.0067	-	6.58	-	-	1.0776
C18			0.3	1.0665	0.8913	-	17.30	-	-	
C19			0.4	1.0651	0.8454	-	21.55	-	-	
C20			0.5	1.0645	0.8325	-	22.74	-	51.60	
C21	20	toluene	0.2	1.0307	0.9630	-	7.90	-	3.80	1.0454
C22			0.3	1.0298	0.8394	-	19.70	-	15.36	
C23			0.4	1.0291	0.7696	-	26.40	-	15.00	
C24			0.5	1.0181	0.6789	-	35.06	-	20.00	

* Characteristics of the copolymers after additional treatment
[1] D = dilution, (mL/diluent/(mL diluent + mL monomers); [2] ρ_{ap} = apparent density, (g/mL); [3] P = porosity, (%); [4] r_p = pore radius, (nm); [5] ρ_{sp} = specific density, (g/mL)

These observations can be explained by the thermodynamic affinity of the diluent for the copolymer which is predicted by the knowledge of their solubility parameters.

The solubility parameter theory has been applied in many papers to explain the porous structure patterns and the swelling properties of macroporous network polymers synthesized in the presence of different diluent systems. If δ_1 and δ_2 are the solubility parameters for solvent and polymer, respectively the following situations can exist: (i) when $|\delta_1 - \delta_2| \cong 0$, miscibility is favoured, the diluent is a good solvent which produces expanded network gel or small pores; (ii) when $|\delta_1 - \delta_2| > 3.0$ $(MPa)^{1/2}$, miscibility does not occur spontaneously, the diluent separates out the polymer phase producing rather large pores; (iii) when $0.1 < |\delta_1 - \delta_2| < 3.0$ $(MPa)^{1/2}$, it is an intermediary solvent. According to this theory, in this study the solvent uptake coefficients in various solvents were used to determine the solvent-polymer solubility parameter of the EA : AN : DVB copolymer (Figure 1).

As it can seen from Figure 1 the highest value of the uptake coefficient was obtained in toluene and the measured value of the solubility parameter for EA : AN : DVB network is $\delta = 19.2$ $(MPa)^{1/2}$.

Toluene with $\delta = 18.2$ $(MPa)^{1/2}$ has a very close solubility parameter value to that of the copolymer which means the toluene induces a low porosity and high nuclei swelling and accordingly, the nuclear chains were performed in a more expanded and less entangled state. When the solvating power of the diluent increases, the porous structure becomes more elastic. The nuclei are formed by cyclization reactions during the early stages of the polymerization at which the growing polymer chains are richer in divinylbenzene units and they are divided in: (a) the smaller particles called nuclei with diameter of 10^2 Aº. The nuclei are nonporous and constitute the highly crosslinked regions of the network. Micropores defined with widths of up to 20 Aº appear between the nuclei; (b) the agglomerations of nuclei are called microspheres and they are about 10^3 Aº diameter. Mesopores constitute the interstices between the microspheres; (c) microspheres are agglomerated again into larger irregular moieties of 2500 – 10,000 Aº inside the polymer material. Meso and macropores appear between the agglomerates of the microspheres. [16]

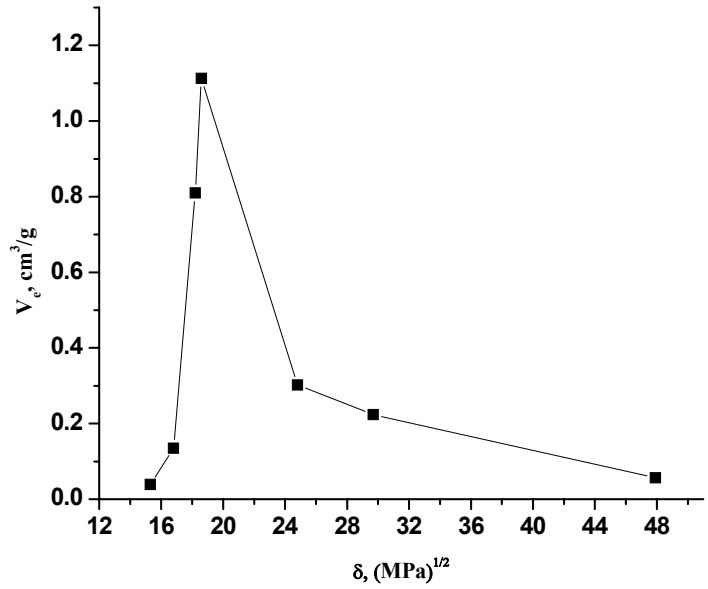


Fig. 1 – Experimental determination of solubility parameter for EA : 20% AN : 10% DVB copolymer.

Benzine with solubility parameter value of 13.5 - 15.8 $(MPa)^{1/2}$ has a lower value of solubility parameter than that of the copolymer. In the presence of nonsolvent the precipitated polymer tends to agglomerate rapidly to form large microspheres, consequently, the diluent distributes preferentially among the microsphere agglomerates to form big pores. The microspheres are rather small when they are formed in the presence of solvating diluent which distributes inside and outside of the microspheres. During the polymerization, the entanglement degree of the nuclear and internuclear chains is particularly affected by the diluent solvating power of benzine. In the presence of a nonsolvent diluent, the precipitated polymer extracts unreacted monomer from the monomer/diluent solution, and the nuclear chains become more entangled as the extracted monomer polymerizes. Due to the tendency of the precipitated polymer to agglomerate, there is a lack of diluent between the nuclei so that the internuclear chains are rather short and entangled.

One of the most important parameter of the porous structure is specific surface (S). In Figure 2 is illustrated S dependence on diluent content and additional treatment by the copolymers prepared with benzine is given in.

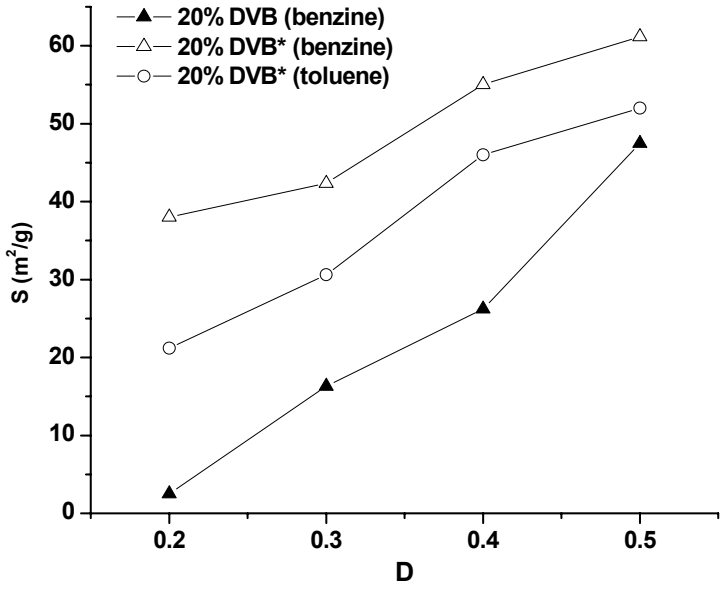


Fig. 2 – Effect of the dilution and additional treatment (*) on specific surface (S) for EA : AN : DVB copolymers synthesized in the presence of toluene and benzine as diluents.

The values of specific surface increase with the increase of diluent content. It was also observed that the additional treatment of the samples has an important role in the formation of porous structures. The treatment with acetone determines the relaxation of the polymeric chains whereas methanol which a bad solvent for the matrix leads to the contraction of them. This treatment with acetone, methanol, methanol : water and water induces a higher porosity of the structures and the copolymers with higher specific surface values have been formed. The explanation of this result is based on the solvating power of the solvents for the macromolecular matrix. When a solvent with the increased solvating power is used, *i.e.* acetone the morphological structure of the copolymer become more expanded and therefore, an extension of the polymer chains between crosslinks are occurred. As the solvating power of solvent is reduced, *i.e.* methanol, it occurs the contraction of polymer chains and the polymer structure become more heterogeneous. The light passage through these beads provokes intense light reflection that is the cause of the opaque appearance of these beads. A comparison of the copolymers with the same crosslinking degree (20% DVB) showed that those prepared in the presence of benzine have higher specific surface values than those synthesized in the presence of toluene.

The dependence of pore volume (V_p, mL/g) on the content of diluent and additional treatment of the studied acrylic copolymers is represented in Figure 3.

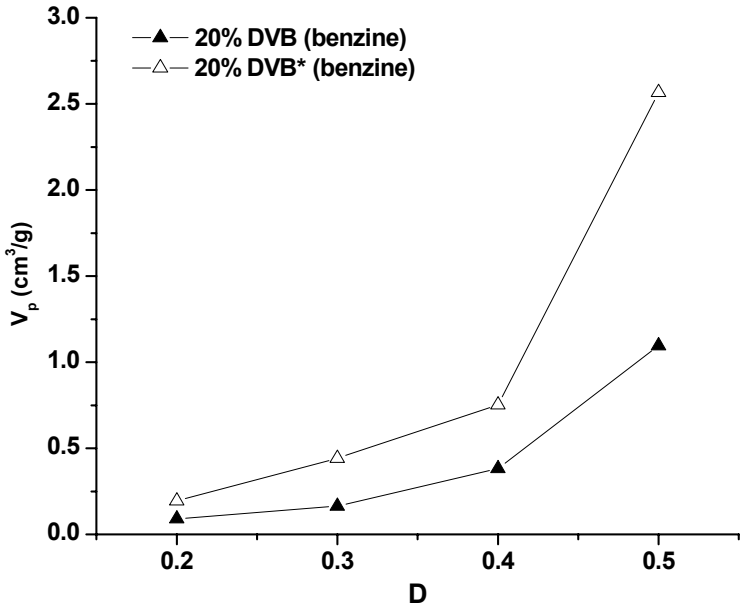
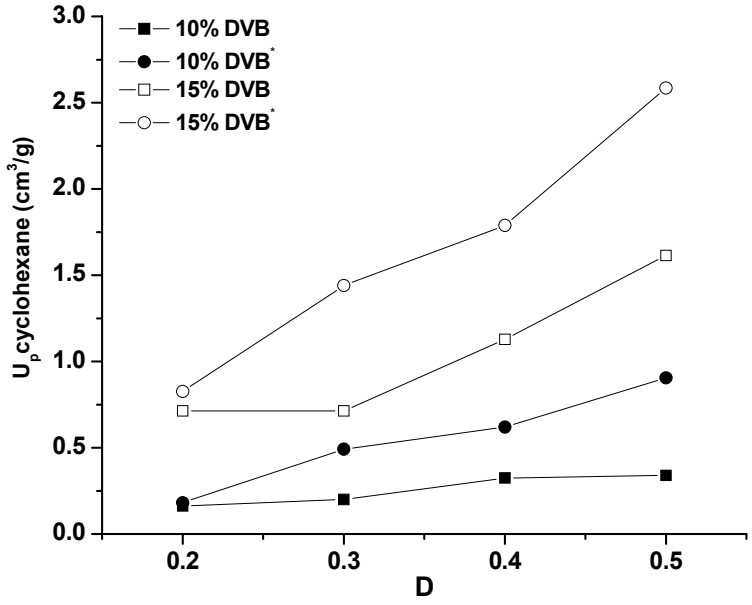


Fig. 3 – Effect of the dilution and additional treatment (*) on the pore volume (V_p) for EA : AN : DVB copolymers synthesized in the presence of benzine as diluent.

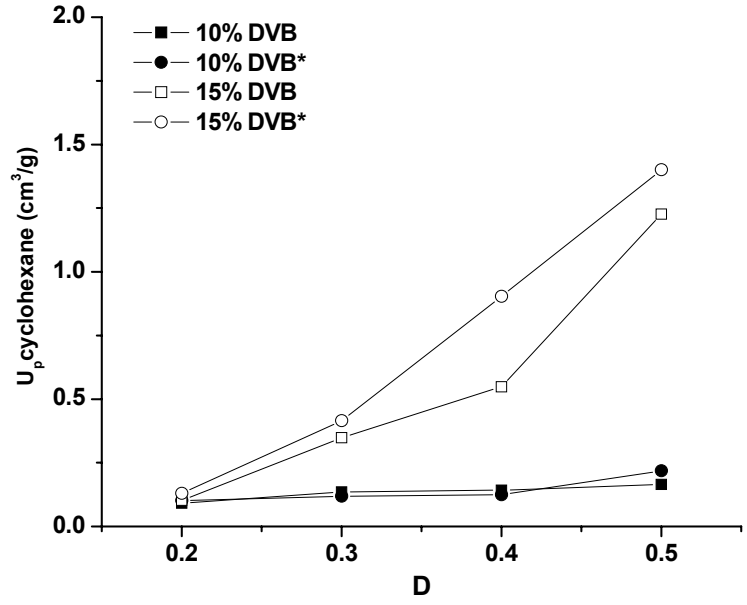
An analysis of this figure led to the following remarks: (i) V_p increase with the increase of dilution (D), the most remarkable increase being for the dilution range of 0.4 – 0.5; (ii) at the same crosslinking degree (20%) the values of V_p for the samples prepared in the presence of benzine with and without supplemental extraction are different.

The acrylic copolymers performed in the presence of nonsol diluent have pore volume values higher than those performed in the presence of sol diluent.

The porous structure characterization showed that macroporous copolymers can be obtained with a wide range of fixed pore volumes and average pore diameters by modification of the synthesis conditions. It is clear that these copolymers as polymeric supports for ion exchangers will display varied accessibility and selectivity. However, the choice of a suitable copolymer for a given application is complex due to the variation of the swelling properties, specially as the copolymers show different porous structures. For a macroporous copolymer the accessibility can depend on the nuclei swelling and an eventual expansion of fixed pores.[16] We have tried to separate the swelling effects of the copolymers in various solvents since they are “good” or “poor” solvents for the polymer networks (Figs. 4 and 5).



(a)



(b)

Fig. 4 – Effect of the crosslinking degree and additional treatment on the cyclohexane uptake coefficients for EA : AN : DVB copolymers synthesized in the presence of benzine (a) and toluene (b).

These figures showed that the uptake solvent coefficients for a given DVB content tend to increase with the increase of dilution, specially for the crosslinking degree of 15% DVB.

As it shown in Figures 4a and 4b all the resulted copolymers exhibited cyclohexane uptake coefficients higher than 0.1 ml/g. According to Millar's rule, the macroporosity exists only when cyclohexane uptake coefficients are higher than 0.1 ml/g and therefore, the synthesized networks have the macroporous structures. For the low content of DVB, *i.e.* 10% the cyclohexane uptake coefficients are not strongly influenced by the dilution for the copolymers performed in the presence of toluene as diluent. An additional proof of the positive effect of the supplemental treatment and DVB content on the porosity is evidenced by the cyclohexane uptake coefficients. The major differences have been observed for the cyclohexane uptake coefficients of the copolymers synthesized in the presence of toluene (Figure 4b).

It is also observed that the copolymers obtained in the presence of toluene exhibit a higher toluene uptake coefficients for a 10% DVB content than those for 20% DVB content. These results can be explained by the difference of the two types of

structures. The copolymers synthesized in the presence of toluene have porosity in the swelling state, the network is more flexible and can swell more at a lower percent of DVB. Therefore, toluene uptake coefficient is a measure of the flexibility for EA : AN : DVB copolymers. The increase of crosslinking degree enhances the phase separation which, in the case of solvating diluents, is characterized by the formation of micropores which can collapse totally or not after removal of the diluent. Also, the above-mentioned figures showed that all the synthesized acrylic polymeric supports with supplemental treatment exhibit higher values of the solvent uptake coefficient than those for copolymers of which the supplemental treatment was not applied.

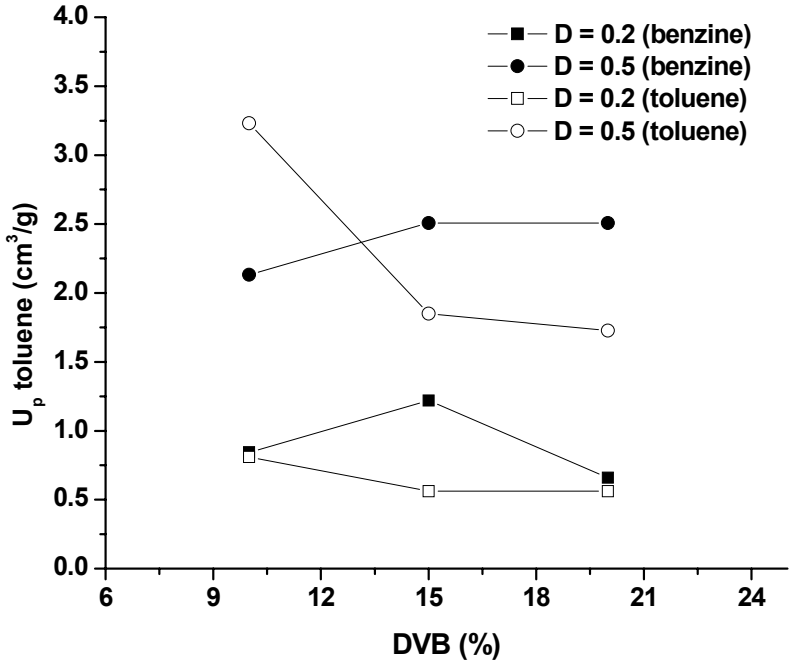


Fig. 5 – Effect of the DVB content and dilution on the toluene uptake coefficients for EA : AN : DVB copolymers synthesized in the presence of benzine (■, •) and toluene (□,○) without additional treatment.

Characteristics of the copolymers synthesized in the presence of the mixtures of good and poor solvents in different ratios are listed in Tables 2 and 3.

Table 2

Morphological characteristics of the EA : AN : DVB copolymers prepared in the presence of toluene : benzine mixture

Sample[1]	ρ_{ap}[5],		P[6],		V_p[7],		S[8],		r_p[9],	
	g/mL	*g/mL	%	*%	mL/g	*mL/g	m^2/g	*m^2/g	nm	*nm
C25[2]	0.9153	0.6372	13.16	39.55	0.144	0.620	39.27	78.22	7.33	15.85
C26[3]	0.9985	0.7531	5.27	28.55	0.053	0.380	16.82	69.48	6.30	11.00
C27[4]	0.9883	0.7542	6.24	28.45	0.063	0.377	-	35.14	-	21.45

[1] The copolymer samples were obtained with 20% DVB and D = 0.4 and ρ_{sp} = 1.051 g/mL
[2] Mixture of 25 wt. % toluene and 75 wt.% benzine; [3] Mixture of 50 wt.% toluene, 50 wt.% benzine; [4] Mixture of 75 wt. % toluene, 25 wt. % benzine; [5] ρ_{ap} = apparent density, (g/mL); [6] P = porosity, (%); [7] V_p = pore volume, (mL/g); [8] S = surface area, (m^2/g); r_p – pore radius, (nm)
* Characteristics of the copolymers after additional treatment

Table 3

Solvent uptake coefficients of synthesized copolymers in the presence of toluene : benzine mixture

Sample	U_p[1] water, mL/g		U_p[2] toluene, mL/g		U_p[3] methanol, mL/g		U_p[4] cyclohexane, mL/g	
C25	0.078	0.148*	1.635	1.470*	1.358	1.325*	1.254	1.231*
C26	0.065	0.281*	1.486	1.514*	1.400	1.402*	1.275	1.800*
C27	0.088	0.132*	1.405	2.084*	1.285	1.326*	0.500	0.984*

* Characteristics of the copolymers after additional treatment; [1]U_p = uptake coefficient in water, (mL/g); [2]U_p = uptake coefficient in toluene, (mL/g); [3]U_p = uptake coefficient in methanol, (mL/g); [4]U_p = uptake coefficient in cyclohexane, (mL/g)

Analysis of the data presented in this table led to the conclusion that the copolymers obtained in the presence of a mixture enriched with the sol diluent should have a different structure than those obtained in a poorly solvating environment. The later displays lower porosity, low values of the cyclohexane uptake coefficients and higher gel homogeneity than copolymers obtained in the presence of a mixture of diluent enriched with nonsol diluent because their supramolecular structure was formed in the well-swollen state. The increase of concentration of the nonsol component increases the copolymer inhomogeneities that induces the formation of a macroporous structure (high values of the cyclohexane regain coefficients). The phase separation processes, chain cycling and entanglement are mostly responsible for this phenomenon. The copolymer obtained in the presence of equimolecular amounts of benzine and toluene (sample C26) has a morphological structure with better swelling properties than that when nonsol diluent predominates in the mixture of diluents (sample C25).

EXPERIMENTAL

Materials

Commercial divinylbenzene (DVB) (containing 80 wt. % pure divinylbenzene, Merck) was used as received. Commercial acrylonitrile with a concentration of 99.50 % (Fluka) and ethylacrylate with the concentration of 99 % (Fluka) were freshly distilled prior to use. Benzoyl peroxide purum moistened with 25.0 % water and the solvents were used as received; toluene and a fraction of benzine (a mixture of aliphatic hydrocarbons with C_5 – C_{10}) with boiling point in the temperature range of 100 – 130 ºC were used as diluent.

Methods

Synthesis of acrylic copolymers

The acrylic (EA : 20 wt. % AN : DVB) crosslinked copolymers were obtained through the aqueous suspension copolymerization of the ethylacrylate (EA), 20 wt. % acrylonitrile (AN) and divinylbenzene (DVB) in the presence of toluene, benzine and mixture of them using 1.0 wt. % benzoyl peroxide as initiator. DVB content of the copolymers was considered to be equal with those of the monomer mixtures. The amounts of AN and DVB were calculated versus entire amount of the monomers. Aqueous phase consisted of ammonium salt of styrene : maleic anhydride copolymer (0.5 wt. %), gelatine (1.5 wt. %) and NaCl (2.0 wt. %). The mixture of monomers, diluent and initiator was added to a flask reactor fitted with a mechanical stirrer, thermometer and condenser and containing the aqueous phase under continuous stirring. The polymerization reaction was left to proceed at 65°C for 4 h and then at 85°C for 8 h. The contents of toluene and benzine used in this study is calculated as follows: D, dilution = (mL diluent/mL diluent + mL monomers)x100. An organic to aqueous phase ratio of 1 : 2 (v/v) was kept constant for all copolymerizations. After copolymerization, the copolymer beads were washed with warm water, then extracted in a Soxhlet apparatus with 1,2-dichloroethane in order to remove the diluent and oligomers. After extraction, part of beads were additionally treated with various solvents in the following order, acetone, methanol, methanol : water mixture and finally, water. All the purified beads were separated into fractions in the range of 0.35 – 1.00 mm by sieving. After separation, the samples were dried to constant weight.

Characterization of acrylic copolymers

The copolymer samples were characterized by specific and apparent densities, surface areas and solvent uptake coefficients.

Apparent density (ρ_{ap}) was measured by a pycnometric method in mercury (dry state) at 13 mPa. The specific density (ρ_{sp}) was measured in n-heptane for established crosslinked degrees and diluent (D = 0.3).

The pore volume determined by mercury porosimetry is conducted in the non-swollen state and therefore measures only the fixed pores. Total porosity (P) and pore volume (V_p) were calculated according to the following equations:

$$P = (1 - \rho_{ap}/\rho_{sp})\cdot 100 \quad (1)$$

$$V_p = 1/\rho_{ap} - 1/\rho_{sp} \quad (2)$$

The surface area S_{BET} was determined by nitrogen adsorption at the boiling temperature of liquid nitrogen on a Ströhlein Area Meter apparatus following the BET method.

The mean pore radius of samples was calculated according to equation (3):

$$r_p = (2V_p/S_{BET}) \cdot 10^3 \text{ (nm)} \quad (3)$$

The solvent uptake coefficients (U_{solv}) were determined by equilibrium swelling in solvents with various solubility parameters using the centrifugation method according to equation (4):

$$U_{solv} = \frac{W_s}{W_p} \quad (4)$$

where, W_s and W_p represent the weights of dried and swollen polymers, respectively.

The solvent uptake coefficients were determined by immersing of a dry sample in water, toluene, methanol or cyclohexane for 24 h and then centrifuging at 2000 rpm for 20 min.

The solubility parameters (δ) were experimentally determined by plotting the solvent regained by copolymer samples at equilibrium (V_e), as measured according to Pepper's method vs. the solubility parameters of several solvents. [19] The δ values were also calculated by the method of Small. [20]

CONCLUSIONS

By the copolymerization reaction of EA, AN and DVB monomers in the presence of solvating or nonsolvating diluents copolymers with various morphological characteristics have been prepared. Several parameters which influence the morphological structures of the synthesized networks were the type and amount of diluent, the crosslinking degree as well as the additional treatment with different solvents after extraction of the copolymers with 1,2-dichloroethane.

All the copolymers which have been additionally treated exhibit higher porosities for those prepared in the presence of both toluene and benzine as diluents.

Toluene, considered a good solvent, benzene, a "poor" solvent and their mixture in various ratios have been used as diluents to modify the internal structure of the acrylic copolymers.

Copolymers obtained in the presence of a nonsol diluent exhibited the enhanced porosity after the supplemental treatment.

The thermodynamic affinity of the diluent for the synthesized copolymer was predicted by the knowledge of its solubility parameters. Therefore, the solvent uptake coefficients in different solvents were used to determine the solvent-polymer solubility parameter for the EA : AN : 10% DVB, gel type.

The benzine : toluene (1:1, v/v) mixture used to modify the acrylic copolymers and the supplemental extraction of performed copolymer led to the improvement of their morphological characteristics. The nonsolvating diluent caused an increase of copolymer porosity, while the sol diluent affected the gel regions.

The porous structure characterization showed that macroporous copolymers were obtained with a wide range of fixed pore volumes and mean pore radius. Use of these copolymers as polymeric supports for the ion exchangers depends on their swelling property.

Morphological characteristics of the polymeric matrix play an important role for an ion exchanger. The accessibility of the specific reagents inside of the copolymer beads depends on the nuclei swelling and eventual expansion of fixed pores. The solvent uptake coefficients for the performed acrylic copolymers increase with the increase of the dilution for a given DVB content.

All the presented networks have cyclohexane uptake coefficients higher than 0.1 mL/g which means that the synthesized copolymers have macroporous structures with fixed pores, when benzine was used as diluent and swelling pores when toluene was used to modify the morphological structure of the copolymers.

Using a mixture of benzine : toluene (1:1, v/v) as diluent (sample C 26) the swelling property of the copolymer in the studied solvents was improved as compared to sample C 27.

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