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Pentaerythritol triacrylate-homopolymer and its copolymers with butyl acrylate

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The swelling and porosity change of the pentaerythritol triacrylate (PENTA) homopolymer and PENTA–butyl acrylate (BA) copolymers were investigated as a function of PENTA content (80, 60, 40 and 20 wt%). Polymers were synthesized by the suspension polymerization method using cyclohexanol and 2-ethylhexanol as inert diluents. The solubility parameter of poly(PENTA) (18.2 $MPa^{1/2}$) was estimated by swelling in the heptane and tetraline mixture. From the swelling of copolymers in the solvents toluene, THF, benzene and dioxane, one may conclude that the swelling of copolymers is not only a function of the solubility parameter of the solvent. The presence of hydroxyl groups in PENTA results in the highest sorption of dioxane. The porosity of copolymers in the swollen state is similar in all solvents. The porosity in the swollen state was characterized by inverse size exclusion chromatography (ISEC) using THF (polystyrene standards) and water (dextrane standards). Swelling in good solvents proceeds with an enlargement of the bead volume, hence the pore volume after swelling in THF is greater than in water in which the influence of hydroxyl groups leads to swelling of triacrylate segments at the cost of the pore volume. Copolymers synthesized with the higher diluents:monomer ratio are hydrogels with the ability to change their porosity, pore diameter and volume of beads. During drying, their pores collapse. © 1997 Elsevier Science Ltd.

(Keywords: Hydrogel; Pentaerythritol triacrylate homopolymer; Pentaerythritol triacrylate–butyl acrylate copolymer)

INTRODUCTION

Triacrylate monomers with ester groups, chemically similar to ethyleneglycol dimethacrylates, have expanded the possibilities of obtaining not only porous polymers intended for filling in chromatographic columns, but carriers for immobilization of metals and biologically active substances as well. One of the most frequently applied monomers, trimethylolpropane trimethacrylate (TMPMA), was examined by Flodin[1–7] and Reinholdsson[8,9]. They analysed the influence of such factors as conditions of polymerization, type of diluents and addition of a comonomer on the structure of poly(TMPMA). It was found that poly(TMPMA) was characterized by a regular structure with a narrow pore diameter distribution as the result of a tetraedric structure of the monomer. It is also noteworthy that, due to steric reasons, TMPMA tends to create a linear chain at first. On the other hand, a considerable concentration of double bonds leads to the formation of monocyclic forms, which, according to Matsumoto[10], constitute as much as 82% of the primary chains in methyl methacrylate and TMPMA copolymers.

The networks of trimethylolpropane triacrylate (TMPA) homopolymers and copolymers are more flexible and less porous than all the groups of acrylates compared with the networks formed by TMPMA under the same conditions[11–13]. Moreover, the presence of a hydroxyl group in the pentaerythlite triacrylate (PENTA) molecule should provide the desired hydrophilicity of the copolymers surface. We found by experiment that modified PENTA–BA copolymers were very good carriers for the immobilization of enzymes because they 'preferred' hydrophilic and hydrophobic fragments in a matrix[14]. In the present work, we report the synthesis and some properties of poly(PENTA) and PENTA–butyl acrylate (BA) copolymers (*Figure 1*).

EXPERIMENTAL SECTION

Copolymers

Poly(PENTA) (100 PENTA) and PENTA–BA copolymers were obtained by suspension polymerization in the presence of 0.5 wt% benzoyl peroxide. The monomer mixture diluted with solvents (cyclohexanol and 2-ethylhexanol, volume ratio 9:1) was suspended in 10 wt% sodium chloride solution containing 1 wt% of a poly(vinyl alcohol). (The sodium chloride decreases pentaerythritol triacrylate solubility in the water phase during suspension polymerization.) All reactants were purchased from Aldrich Chemical Co., St Louis, MO. Polymerization was carried out at 70–95°C for 8 h. After this time, copolymers with beads 0.1–0.5 mm in diameter were washed with hot water and methanol, dried and finally extracted with hot toluene in Soxhlet apparatus. Copolymers were coded with symbols describing the volume composition of pentaerythritol triacrylate in monomer mixtures (80 PENTA, 6O PENTA, 4O PENTA and 2O PENTA) (*Table 1*).

Porosity determination

The true density (*d*) was measured pycnometrically in cyclohexane. The apparent density of the samples in the dry state was determined pycnometrically in mercury after treating them with solvents (toluene, acetone, methanol) and water. The above data enabled us to calculate the porosity (*P*) and the pore volume (V_d) in the dry state[15].

The water (or other solvent) regain (W, $g\,g^{-1}$) was determined by the weight method. Copolymer swollen in a solvent to equilibrium was centrifuged and dried to a

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Table 1 Characteristics of pentaerythritol triacrylate and butyl acrylate copolymers in the dry state

Symbol	BA:PENTA (mol:mol)	V_0	Volume of pores V_d (cm^3 g^{-1})	Unreacted double bonds (mmol g^{-1})	Unreacted double bonds (mol %)
100 PENTA	—	0.5	0.52	0.77	7.6
80 PENTA	0.43	0.5	0.57	0.56	6.6
60 PENTA	1.2	0.5	0.56	0.34	5.1
40 PENTA	2.6	0.5	0.21	0.17	3.6
40 PENTA/2	2.6	0.33	0.08	0.17	3.6
40 PENTA/3	2.6	0.25	0.08	0.11	2.4
40 PENTA/4	2.6	0.20	0.00	0.16	3.4
20 PENTA	7.4	0.5	0.00	0.07	2.8

V_0 = initial fraction of monomers in mixture of monomers and diluents.

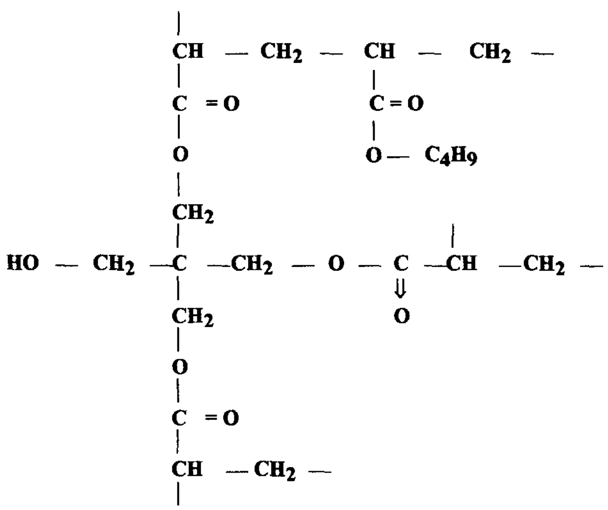

Figure 1 Pentaerythritol triacrylate and butyl acrylate copolymer.

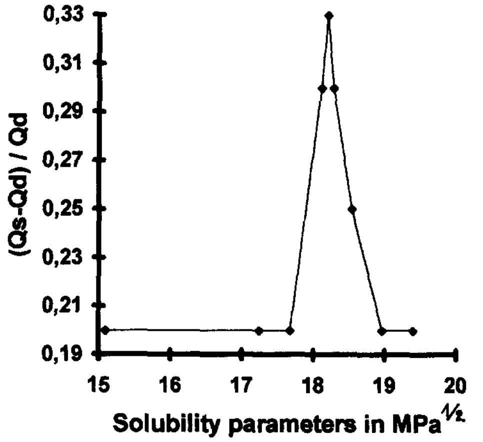

Figure 2 Solubility parameter for poly(pentaerythritol triacrylate).

constant weight. The apparent density (d_o) of the sample swollen in the solvent was also determined pycnometrically and the porosity and pore volume (V_s) were calculated. The variable B is estimated from the Dusek equation: $B = d_o/d + W(d_o/d_1)$, where d_1 is density of solvent[16].

ISEC method

Inverse size exclusion chromatography (ISEC) was performed using an apparatus equipped with an LC-6A pump (Shimadzu, Japan), a 7255 injector (Rheodyne, USA) and an RIDK-102 or UV–LCD 2563 refractive index detector (Ecom, Czech Republic). Tetrahydrofuran was in the mobile phase for polystyrene standards (Aldrich) and water was used for dextranes (Pharmacia). The flow velocity was 0.1 cm^3 min^{-1}. The pore structure parameters [mean pore radius (R) and distribution of pores] were calculated according to Ref.[17].

Unreacted double bonds

The unreacted double bonds in the polymer (in mmol g^{-1} or mol%) were determined by the bromination method[8]. In our case, tetrachloromethane was replaced by ethylene dichloride since it is characterized by a smaller density and a good ability to swell PENTA copolymers. Ten cubic centimetres of 0.26 M bromine solution in ethylene dichloride were added to 0.5(±0.01) g of a polymer and left for 24 h at a room temperature then refluxed for 7 h. When necessary, an additional portion of 0.26 M bromine solution was added. After cooling, the sample was placed in a glass sintered funnel and washed with ethylene dichloride, methanol and acetone. The concentration of bromine in a dry sample was determined by the Schoniger method.

Solubility parameters

The solubility parameter of poly(PENTA) was calculated from the volume of the bead swollen to equilibrium in heptane and tetralin solvents. The volume swelling in equilibrium was calculated from the volume of the bed before (Q_d) and after swelling (Q_s) as $(Q_s - Q_d)/Q_s$ (*Figure 2*). The solvating ability of the solvent mixture was calculated on the basis of the following formula $\delta_m = V_1\delta_1 + V_2\delta_2$, where V_1 and V_2 stand for the volume fractions of the mixture components and σ_1 and δ_2 stand for their solubility parameters.

RESULTS AND DISCUSSION

Characteristics of copolymers

Synthesis of PENTA–BA copolymers was carried using mixture of monomers diluted with polar solvents: cyclohexanol and 2-ethylhexanol. Such solvents increased the accessibility of the hydroxyl group present in a PENTA molecule by interacting with them during polymerization. The solubility parameter of the solvent mixture was 20.4 MPa$^{1/2}$; the solubility parameter of poly(PENTA), which is $\delta = 18.2$ MPa$^{1/2}$, was determined from the dependence of the volume swelling in toluene and tetralin mixture (*Figure 2*). Since the solubility parameter of poly(BA) is 17.05 MPa$^{1/2}$, it can be seen that the increase of BA concentration in the monomer mixture decreases the

Table 2 Characteristics of pentaerythritol triacrylate and butyl acrylate copolymers swollen in solvents: tetrahydrofurane and toluene

Symbol	Solvent regain (g g^{-1})			Volume of pores, V_s (cm3 g^{-1})		Mean pore radius, R_{THF} (nm)
	THF	Toluene	B in toluene	THF	Toluene	
100 PENTA	0.54	0.57	1.01	0.61	0.65	2.50
80 PENTA	0.62	0.66	1.01	0.70	0.75	2.30
60 PENTA	0.65	0.72	1.01	0.73	0.82	2.25
40 PENTA	0.82	0.91	1.01	0.92	1.04	1.15
40 PENTA/2	1.74	1.76	1.02	1.95	1.96	1.70
40 PENTA/3	2.53	2.54	1.03	2.85	2.82	2.00
40 PENTA/4	2.68	2.71	1.04	4.55	3.00	1.55
20 PENTA	1.04	1.16	1.01	1.10	1.33	1.25

B = volume swelling ratio[16].

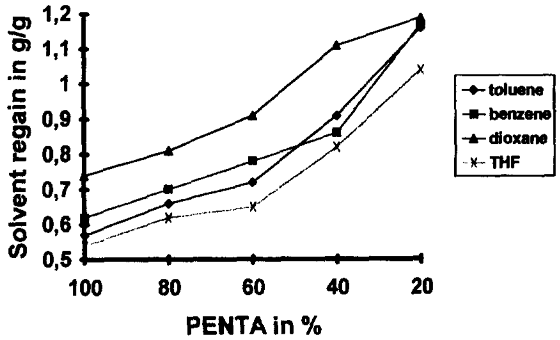

Figure 3 Solvent regain of pentaerythritol triacrylate and butyl acrylate copolymers.

solvating conditions for the formed network. In addition, it should be emphasized that the solvents used for dilution are not good enough even for poly(PENTA). Considering the above, one may assume that the porous structure of poly(PENTA), as well as of the copolymers containing a considerable amount of PENTA, results mainly from the increase of the cross-linking degree, whereas in case of the copolymers with a large amount of BA, it has the effect of making solvating conditions worse.

The composition of the monomer mixtures and characteristics of the polymers in the dry state are listed in *Table 1*. In the case of the polymers with 60–100% PENTA, the pore volume is the same and does not depend on the cross-linking degree. For copolymers with 40% of PENTA, the influence of BA on the porosity can easily be observed and the pore volume decreases by half in comparison to 60 PENTA. In the dry state, poly(BA) is an elastomer and the copolymers with high amounts of BA-mers are non-porous.

During the polymerization of a triacrylic monomer such as PENTA, elastic chains without bulky side groups should undergo cyclization more easily than TMPMA chains[10]. This suggests that the concentration of unreacted double bonds becomes larger together with the increase of the content of PENTA in the monomer mixture. It should be stressed, however, that some of the unreacted double bonds are not determined by chemical methods and some remain inaccessible in the particles of the swollen polymer[8,18]. It was found that the higher the concentration of PENTA in the copolymer, the higher the number of double bonds. However, simultaneously, accessibility decreases, so the actual concentration of unreacted double bonds in poly(PENTA) is probably greater than that determined. According to Rosenberg and Flodin[1–5], the number of unreacted double bonds depends on the polymerization conditions. In the above example, the conditions lead to the creation of an expanded structure in which the accessibility of unreacted bonds should be good and hence the undetermined amount should be small (*Table 1*).

Swelling of copolymers

Regain of solvents by the porous matrix is carried out by filling in the pores and by the swelling of chains between the network cross-links until equilibrium between osmotic pressure and network elesticity is reached. This can happen with or without volume changes. It has been noted that swelling is a function of both the cross-linking degree and thermodynamical value of solvents. In the presence of a highly thermodynamic solvent, the change of bead volume should be observed (gel swelling), whereas only a change in pore diameter is noted in the poorly thermodynamic solvent. When in copolymer with a small degree of cross-linking, the good solvent is replaced by the poor solvent and contraction of the gel may be observed together with collapsing of the pores until a new equilibrium of swelling is reached.

Taking the above facts into consideration, one should not be surprised by a similar increase of the solvent regain of non-polar solvents and solvents with different polarity (toluene, $\delta = 18.2\ \mathrm{MPa}^{1/2}$; THF, $\delta = 18.6\ \mathrm{MPa}^{1/2}$; benzene, $\delta = 18.8\ \mathrm{MPa}^{1/2}$; and dioxane, $\delta = 20.5\ \mathrm{MPa}^{1/2}$) for the series of PENTA copolymers with a decreasing degree of cross-linking (*Table 2* and *Figure 3*). The presence of a hydroxyl group in PENTA-mers causes the highest sorption of dioxane-solvent characterized by the most distant solubility parameter. This is another example proving that describing the swollen state merely by means of Hildenbrandt parameters is imperfect.

Since the hydrophobicity of the matrix varies with the change in degree of cross-linking, copolymers act differently while swelling in alcohols (methyl, $\delta = 29.7\ \mathrm{MPa}^{1/2}$; ethyl, $\delta = 26.0\ \mathrm{MPa}^{1/2}$; butyl, $\delta = 23.3\ \mathrm{MPa}^{1/2}$) (*Figure 4*). Possessing hydrophobic hydrocarbon chains, butyl alcohol is best absorbed by the gel copolymer 20 PENTA. Water filled the expanded copolymer after previously treating it with good (toluene) solvents; poor solvents (acetone, methanol) led to the greatest microsyneresis of gel.

One may note an increase in porosity in the swollen state compared with that determined for the dry state (*Figure 5*). The 20 PENTA copolymer, which is not porous in the dry state, has the greatest porosity in toluene and, compared with 40 PENTA, displays a smaller porosity in dioxane (*Figure 6*). Poly(PENTA) shows the least change since the considerable cross-linking degree not only prevents the skeleton from contraction during drying, but also makes expanding during swelling impossible. It displays a slightly larger porosity in polar solvents as opposed to the 20 PENTA copolymer in non-polar solvents. In addition, 20 PENTA becomes a gel and loses its porosity after microsyneresis in water. It is noteworthy that the dependence of porosity on the composition is similar to the case of the dry state (*Figures 5 and 6*).

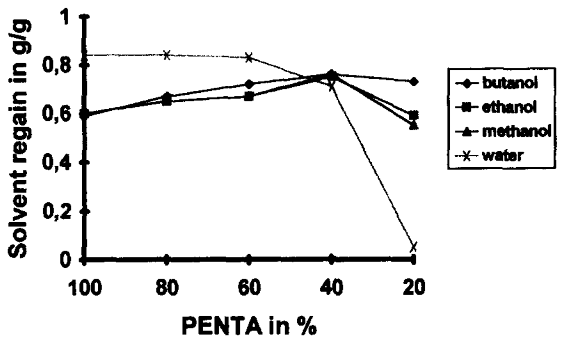

Figure 4 Alcohol regain of pentaerythritol triacrylate and butyl acrylate copolymers.

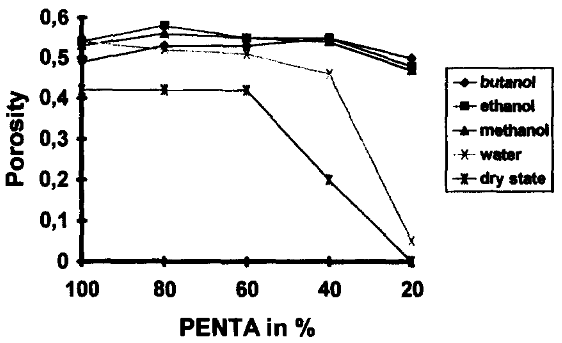

Figure 5 Porosity of pentaerythritol triacrylate and butyl acrylate copolymers swollen in alcohols and water.

ISEC measurements

The ISEC measurements made with polystyrene standards in THF and dextrane standards in water indicate the influence of the type of diluent used in polymerization on the changes which take place during swelling. A comparison has been made between the volume of pores filled by THF and water, V_s (expressed in $cm^3 g^{-1}$) (*Tables 2 and 3*) and the pore volume determined for polymers in the dry state, V_d (*Table 1*). For all copolymers with 60–100% PENTA, one may note that filling the pores with THF and changes in the copolymers are negligible (V_s:V_d close to 1) (*Figure 7*). Greater differences can be observed in copolymers with a smaller cross-linking degree in which swelling consists of the disentangling of chains; this is shown by the swelling of the gel. In case of THF, such swelling is stronger and is responsible for the displacement of chains in the polymer network and an increase in the bead volume is observed. A similar effect was described by Smigol[19]. In water, it is only segments of triacrylate containing hydroxyl groups which undergo hydration. As a consequence, the swelling of segments between cross-links takes place and the pore volume gets smaller. The mean pore radius of poly(PENTA) and of copolymers with a high PENTA content is smaller by half if compared with the same copolymers swollen in THF, which, according to the solubility parameters, is a very good solvent for a copolymer (*Figure 8*). The 40 PENTA copolymer, owing to the high content of BA-mers and a smaller PENTA content, also swells better in THF than water (*Figures 3 and 4*), and

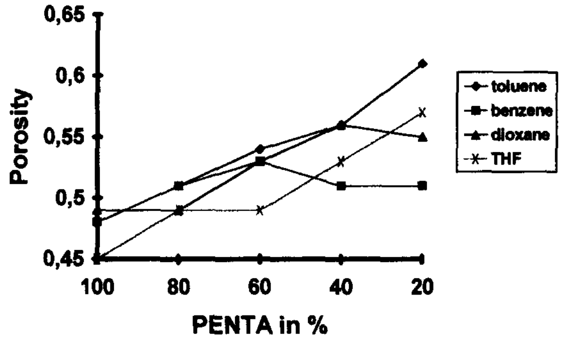

Figure 6 Porosity of pentaerythritol triacrylate and butyl acrylate copolymers swollen in various solvents.

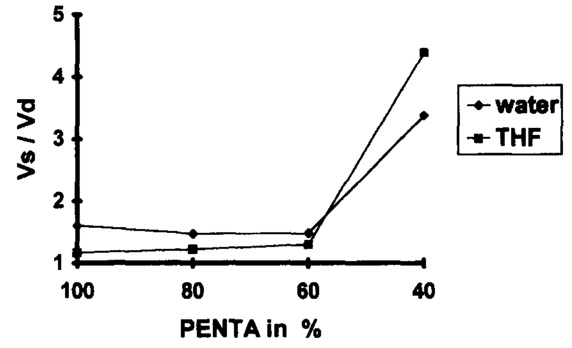

Figure 7 Ratio of pore volume of swollen (V_s) to pore volume of dry (V_d) copolymers as a function of pentaerythritol triacrylate and butyl acrylate copolymer composition.

Table 3 Characteristics of pentaerythritol triacrylate and butyl acrylate copolymers swollen in water

Symbol	Water regain (g g^{-1})	*B*	Volume of pores, V_s (cm3 g^{-1})	Mean pore radius, *R* (nm)
100 PENTA	0.83	1.01	0.83	0.95
80 PENTA	0.84	1.01	0.84	1.10
60 PENTA	0.83	1.01	0.83	1.25
40 PENTA	0.71	1.01	0.71	1.75
40 PENTA/2	0.86	1.03	0.80	1.70
40 PENTA/3	1.59	1.04	1.50	2.0
40 PENTA/4	1.44	1.06	1.31	1.55
20 PENTA	0.05	1.01	0.05	—

B = volume swelling ratio[16].

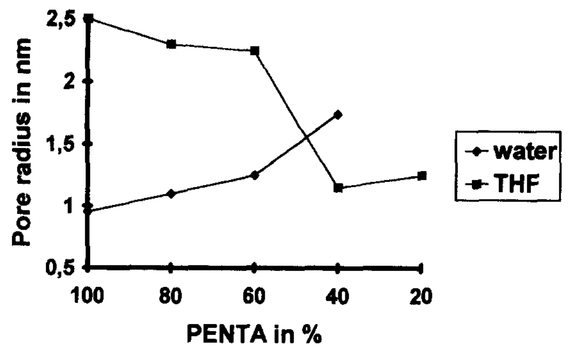

Figure 8 Mean pore radius of pentaerythritol triacrylate and butyl acrylate copolymers

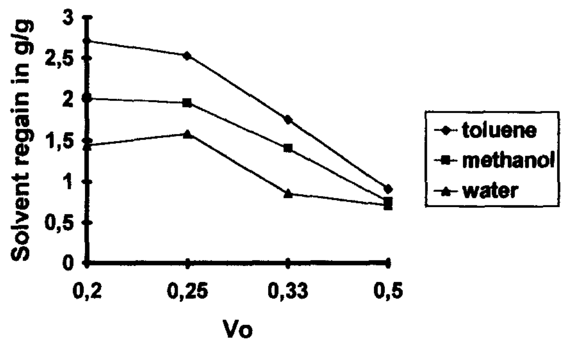

Figure 9 Solvent regain of pentaerythritol triacrylate and butyl acrylate copolymers (40 PENTA) as a function of fraction of monomers (V_0) in mixture of monomers and diluents

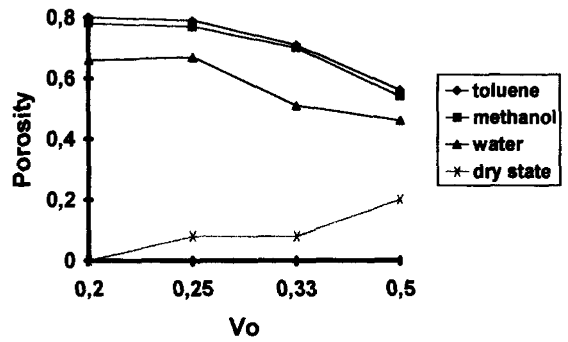

Figure 10 Porosity of the pentaerythritol triacrylate and butyl acrylate copolymers (40 PENTA) as a function of the fraction of monomers (V_0) in

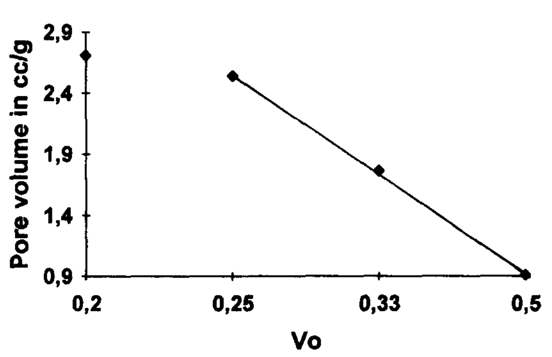

Figure 11 The dependence between pore volume of pentaerythritol triacrylate and butyl acrylate copolymers (40 PENTA) swollen in toluene and the fraction of monomers (V_0) in monomer mixture and diluents

therefore its mean pore radius determined in that solvent becomes smaller. The pore radius of 40 PENTA measured after filling with water is bigger than after swelling in THF due to the microsyneresis of the gel and the sufficient cross-linking degree. The 20 PENTA copolymer filled with water has a gel structure where the volume of the pores is very small (it is not possible to determine the micropores of the gels by the ISEC method).

Effect of monomer mixture dilution

The 40 PENTA copolymer, being an example of a material with sufficiently porosity and, at the same time, with a considerable amount of hydrophobic monomer, enabled us to examine the influence of diluting the monomer mixture with inert solvents (cyclohexanol and 2-ethylhexanol) on the polymer structure. We have observed an expected decrease in the number of unreacted double bonds which are more accessible and create cycles more easily in a system with a greater dilution (*Table 1*). However, the copolymer obtained from a monomer mixture with the highest monomer:diluent ratio is quite different.

It was found that increasing the dilution of the monomer mixture with solvents resulted in an increased regain of all solvents. The largest of these can be observed for toluene and the copolymer formed with the highest dilution ($V_0 = 0.2$), i.e. 40 PENTA/4. Its toluene regain is about 2.5 times bigger than in case of the 40 PENTA copolymer with dilution equal to 0.5 (*Figure 9*). The 40 PENTA copolymers which were obtained in the presence of a large amount of diluents have an expanded structure which undergoes a higher contraction of the skeleton. At the same time, porosity of the copolymers in the dry state decreases, resulting in a non-porous copolymer at dilution $V_0 = 0.2$ (*Figure 10*).

The regain of toluene is a linear function of dilution. It can be described by the following equation $W = 0.815V_d + 1.19$, where the linear correlation factor is 0.9997. Since a similar dependence was obtained by Okey for styrene–divinylbenzene copolymers[20,21] as well as poly(ethylene glycol dimethacrylate)[18], one may treat the above equation as a general dependence, which makes it possible to predict the influence of the monomer mixture dilution during suspension polymerization on the network swelling in a good solvent.

The pore volumes in a polymer swollen to equilibrium in toluene (V_s) as a function of the dilution of monomer mixture changes in linearly until dilution $V_0 = 0.25$ according to the equation $V_s = 0.895V_d + 0.15$. The value of $0.15\ \mathrm{cm}^3\ \mathrm{g}^{-1}$ is the pore volume of a copolymer in a swollen state obtained without a diluent. When dilution increases below 0.25, aberrations from linearity can be observed (*Figure 11*).

As has been previously mentioned, the solvent regain refers to the total quantity of the solvent present in the pores and in the gel. The value of the volume swelling determines which part of the solvent can be found in the gel. Assuming an isotropic swelling of the network, the value of volume swelling was calculated on the basis of Dusek's equation [16,22]. Data displayed in *Tables 2 and 3* show that the volume swelling, B, of the analysed copolymer series in toluene is constant (1.01–1.04) and does not depend on the dilution degree. The amount of the solvent in the gel is constant and the difference in weight swelling results from the various pore volume in a swollen state. The values referring to the volume swelling of polymers in water reveal slightly greater differences (1.01–1.06) (*Table 3*).

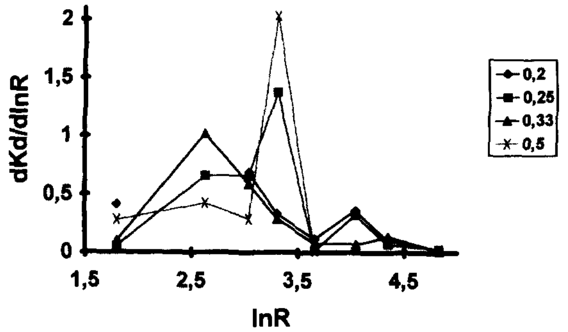

Figure 12 Pore distribution of pentaerythritol triacrylate and butyl acrylate copolymers swollen in water.

The pore volume distribution for the copolymers obtained from the monomer mixture diluted with various amounts of diluent was determined using the ISEC method after previous swelling in water (*Figure 12*). It was found that—with the X-axis as ln of the pore sizes in Å—a higher dilution (up to $V_0 = 0.25$) results in a greater content of small pores, thus the average pore size is reduced (*Table 3*). Only the copolymer with $V_0 = 0.2$ is an exception to this rule.

CONCLUSIONS

If we accept the solubility parameter determined for poly(PENTA), which is 18.2 $\mathrm{MPa}^{1/2}$, as the only criterion, PENTA copolymers should be considered hydrophobic. However, a more detailed analysis of the swelling and porosity of the PENTA–BA copolymer series reveals the influence of hydroxyl groups, as the above copolymers are characterized by a significant sorption of dioxane and, in the case of a small cross-linking degree, of water as well. For copolymers, swelling depends on the thermodynamic quality of the solvents. The most considerable changes occur in the case of copolymers obtained at a high dilution of monomers with diluents. Such copolymers undergo strong collapsing under the influence of thermodynamically poor solvents. Only copolymers with a high cross-linking degree are porous in the dry state and the porosity of copolymers obtained at a higher dilution of monomer mixture is smaller than that of those obtained at a smaller dilution. On the contrary, the swelling of copolymers with a higher dilution is greater in all the solvents. Swelling in good solvents consists of enlarging the bead volume; hence, the pore dimensions after swelling in THF are greater than in water which results from the influence of a hydroxyl group leading to the swelling of a triacrylate segment at the cost of the pore volume. Triacrylate polymer networks form a new interesting group of hydrogel and their hydrophobic–hydrophilic properties can easily be changed by modification[14].

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