

Effect of the crosslinking agent on porous networks formation of hema-based copolymers

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Abstract

New copolymers of ethylene glycol dimethacrylate/2-hydroxyethyl methacrylate [poly(EGDMA-*co*-HEMA)], 2,2',2''-nitritotriethyl triacrylate/2-hydroxyethyl methacrylate [poly(NTETA-*co*-HEMA)] and pentaerythritol tetraacrylate/2-hydroxyethyl methacrylate [poly(PETA-*co*-HEMA)] were obtained by suspension polymerization at 70 or 85 °C, using cyclohexane (Cyc) as porogen. In this work, the influence of the crosslinking agent (di, tri, or tetra vinyl monomer) on the morphology of the polymeric networks was investigated. Swelling studies, Fourier Transform Infrared (FTIR) and mercury intrusion porosimetry, demonstrated that when both the vinyl groups number and molecular chain length between double bonds of the crosslinking agent decreased, networks with high porosity and crosslinking degree were generated.

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1. Introduction

Macroporous polymers have been used in several applications like in catalysis, enzyme immobilization, HPLC supports, in release of active substances, as adsorbents and many others [1–6]. These applications are consequence of their remarkable morphological properties, such as high crosslinking degree, rigid network structure in both swollen and dry state and presence of macropores that improves the accessibility into the polymeric network. Besides, these networks possess low apparent density (d_0), and high porosity (%*P*) and specific surface area (S_s). Therefore, the study of their synthesis is of great interest in polymer science.

Generally, these matrices are synthesized by suspension polymerization using monovinyl and polyvinyl (crosslinking agent) monomers and a porogen (diluent). In accordance with other authors [7–10], it is known that

during the process of copolymerization, crosslinking and phase separation occur, leading to the development of a porous structure, which depends on kind and concentration of porogen, monovinyl monomer and crosslinking agent [11,12], temperature [12] and agitation.

Depending on suspension polymerization experimental conditions, expanded or heterogeneous (porous) networks could be obtained, as a consequence of the phase separation process before or after gelation point [13,15]. A phase separation prior to gelation point, leads to development of networks with stable pores (heterogeneous) that do not collapse during the drying [13,14]. Besides, according to Dusek et al. [16], heterogeneities may appear in both poor and good solvents due to the polymer–solvent incompatibility (χ -induced syneresis) and to the increase in crosslinking density (ν -induced syneresis), respectively.

According to Okay [17], the networks can be classified in three groups taking into account the distribution of the diluent in the network structure after its formation:

1. *Expanded(preswollen) networks.* Expanded networks structures are obtained if the diluent present during the network formation remains in the gel throughout the

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polymerization process. Expanded networks are thus nonporous. During drying, the expanded network collapses, but reversibly, since addition of a good solvent allows it to re-expand to its previous state.

2. *Heterogeneous dry networks*. The diluent separates totally outside of the network phase during the polymerization and acts as a pore-forming agent.
3. *Heterogeneous swollen networks*. The diluent separates partially outside the network phase during polymerization. Thus, it distributes between network and diluent phases after synthesis. A part of the diluent acts as a pore-forming agent whereas the other part remains in the network structure.

The choice of polymerization conditions on macroporous polymers synthesis should be selected for each system in particular, since there are no general rules for this aim [8].

In previous papers [18,19], we studied the effects of some reaction conditions: type of porogen, free radical initiator rate, polymerization temperature and structure of monomers on the morphology of poly(EGDMA-co-HEMA) networks. Sorption-expansion ratio (H) was the main swelling parameter used as indicator of porosity in swollen network. H parameter reflects the balance between the amount of liquid sorbed and the expansion degree reached by the network [18,19]. Therefore, maximum values of H were used as marker to compare and to select the best conditions that allowed us to obtain macroporous polymers. Current work seeks to enlarge this analysis and take into account that crosslinking agent molecular structure is a variable that has not been thoroughly investigated [20,21]. Its effect on the polymeric network morphology is presented in this work. Polymerization conditions previously reported to attain HEMA-containing copolymers were used in this work [18,19]. In this occasion, crosslinking agents: divinyllic (EGDMA), trivinyllic (NTETA) and tetravinyllic monomers (PETA) were reacted with HEMA by suspension polymerization, to obtain the respective copolymer beads. Cyclohexane (Cyc) and benzoyl peroxide (BPO) were used as porogen and radical initiator, respectively, at 70 or 85 °C.

2. Experimental

2.1. Reagents and equipment

The following chemicals were purchased and used: 2-hydroxyethyl methacrylate (HEMA), Fluka; ethylene glycol dimethacrylate, (EGDMA), Fluka; pentaerythritol tetraacrylate, (PETA), Aldrich; benzoyl peroxide (BPO), Riedel de Haen; poly(vinylpyrrolidone) (PVP), (Kollidone 90), FLUKA; cyclohexane (Cyc), Anhedra; 2,2',2''-nitrioltriethyl triacrylate (NTETA), was obtained from our laboratory. Synthesis, purification and characterization of NTETA were report in a previous paper [19].

The polymeric networks were synthesized using a magnetic stirrer 04644-Series Digital Hot Plate/Stirrer (Cole Parmer). An AutoPore III Micromeritics 9410 was used in characterization by mercury intrusion porosimetry (pores diameter range: 4–500,000 nm).

2.2. Polymerization reactions

Networks preparation was carried out by suspension polymerization using a mol ratio of 3.0:1.0:9.3:2.5 × 10² of HEMA (6.20 ml), crosslinking agent [EGDMA (3.20 ml); NTETA (5.272 g); PETA (5.974 g)], Cyc (17.20 ml) and water (77.00 ml), respectively, to obtained 10 g of dry product. In each case, the free radical initiator BPO (0.411 g) in a rate of 2.44 mol% (vinyl monomers + BPO) and the suspension stabilizer PVP (0.777 g) in a proportion of 10 mg/ml with respect to total mixture, were used.

In a 250 ml flask, the mixture reactions were stirred at 450 rpm for 2 h with a magnetic stir bar, 3 cm long and 1.5 cm wide. The temperatures assayed were 70 or 85 °C. Copolymers were exhaustively washed with distilled water and ethanol. Next, samples were dried in an oven at 70 °C to constant weight. The yield of each reaction was calculated through the percentage of dry matrix obtained versus total grams of vinyl monomers used.

3. Methods

FTIR spectra were recorded on a Nicolet 5-SXC spectrometer on KBr disks. The absorbance ratio (AR) corresponding to the stretching vibration of both vinyl group carbon-carbon double bond and ester group carbon-oxygen double bond ($A_{C=CH_2}/A_{C=O}$) was used to confirm the conversion degree of pendant vinyl groups in the copolymers. The carbonyl and vinyl bands at 1735 and 1630 cm⁻¹, respectively, were used to calculate AR. Straight lines that linked the points of the spectrum at 1103, 994, 927, 799 and 536 cm⁻¹ were regarded as the baselines for peak intensity standards to correct the background.

As the crosslinking agents have different carbonyl groups number (N), AR of the networks were normalized according to Eq. (1), with N : 2, 3 and 4 for EGDMA, NTETA and PETA-based copolymers, respectively.

$$\text{NAR} : (A_{C=CH_2}/A_{C=O})N \quad (1)$$

Swelling studies were carried out in distilled water (pH: 6.5). Copolymer samples (0.10 g) were left in contact with water in a special funnel (with a very small hole in a closed chamber) for 24 h followed by 24 h drainage in the same closed chamber. Then the wet samples were weighed in an analytical scale and the weights were measured at different evaporation times (each 15 s for 7–8 min after the sample was removed from the chamber). The data were processed using a plot of weight of wet sample (g) versus evaporation

time (s), taking the weight of the sample in swollen state (W_{sw}) at time zero, which is achieved by extrapolation. Subsequently, the samples in an oven at 70 °C for 48 h were dried, weighed to obtain the dry sample weight (W_{dry}) and equilibrium weight swelling ratio (q_w) was calculated according to Eq. (2).

Equilibrium volume swelling ratio (q_v) was obtained by the ratio of the volume (Eq. (3)) of samples in swelling equilibrium state (V_{sw}) and the volume of samples in dry state (V_{dry}). It was performed using graduated tubes after the dry samples (particle size range, 40–70 mesh) have been soaked 24 h in an excess of distilled water. The assays were performed four times and the results showed an error less than 5%.

Then, sorption–expansion ratio (H) was determined by Eq. (4) [18].

$$q_w = W_{sw}/W_{dry} \quad (2)$$

$$q_v = V_{sw}/V_{dry} \quad (3)$$

$$H = q_w/q_v \quad (4)$$

4. Results and discussion

Poly(EGDMA-*co*-HEMA), poly(NTETA-*co*-HEMA) and poly(PETA-*co*-HEMA) networks were obtained by suspension polymerization at 70 or 85 °C, using Cyc and BPO as porogen agent and radical initiator, respectively. In general, the reaction yields of insoluble white beads polymers were higher than 85%. Nevertheless, although NTETA copolymer synthesized at 85 °C exhibited a high yield, it reached the value of 10% at 70 °C. This behavior can be attributed to the fact that the polymerization kinetics is not favored by the reaction conditions used in this particular case, since the presence of a nitrogen atom in the crosslinking agent would be affected its solubility in Cyc at that temperature.

In this study, the effect of the molecular chain length between double bonds and vinyl groups number of the crosslinking agent (EGDMA, NTETA and PETA) on the morphology of copolymers is presented. Networks characterization was carried out by mercury intrusion porosimetry, swelling studies and FTIR.

4.1. Mercury intrusion porosimetry

Mercury intrusion porosimetry is a method routinely used to evaluate pore size in the range of mesopores and macropores of different materials [22,23]. From this technique, the pores size distribution ($dV/d \log d$), specific volume of pores (V_p), area of specific surface (S_s), apparent density (d_0) and porosity percentage ($\%P$) of networks were thus obtained.

Porosity percentage ($\%P$) values were calculated

according to the Eq. (5) [14]:

$$\%P = V_p d_0 \times 100 \quad (5)$$

As shown in Figs. 1 and 2, in all cases the copolymer networks presented high porosity and low d_0 values, showing morphological properties of heterogeneous networks from a phase separation process at a low conversion rate. This assay could not be achieved for poly(NTETA-*co*-HEMA) synthesized at 70 °C, since its reaction yield was only 10%. Furthermore, poly(EGDMA-*co*-HEMA) and poly(NTETA-*co*-HEMA) networks showed (Figs. 1–3) higher porosity and total S_s , and lower d_0 values than poly(PETA-*co*-HEMA). This could be due to the agent crosslinking molecular structure effect on crosslinking density (v -syneresis induced) or solubility (χ -syneresis induced) of the chains during their formation, affecting phase separation and network porosity. For PETA-based copolymers, four vinyl groups present in the molecular structure of PETA, would lead to late phase separation producing low porosity in the network. It could be due to prevalence of cyclization and intramolecular crosslinking over intermolecular crosslinking as result of the high local concentration of pendant unsaturations in a small region of the space.

On the other hand, a long molecular chain between double bonds in the crosslinking agent generated a network with high flexibility due to the large distance among the crosslinking points. So, a collapse of the network is generated during the drying process with the consequent diminution in specific surface area. This behavior is in agreement with the results found by Jovanovic et al. [21].

In Figs. 4 and 5 (pores diameter range: 4–500,000 nm), the presence of three pore size dispersions inside a determined range of diameters (4–50, 50–6000 or 6000–500,000 nm) in the total pore size distribution from synthesized networks can be observed.

These size dispersions showed empty gaps between different types of clusters generated in each copolymer, as consequence of crosslinking agent type effect on the phase

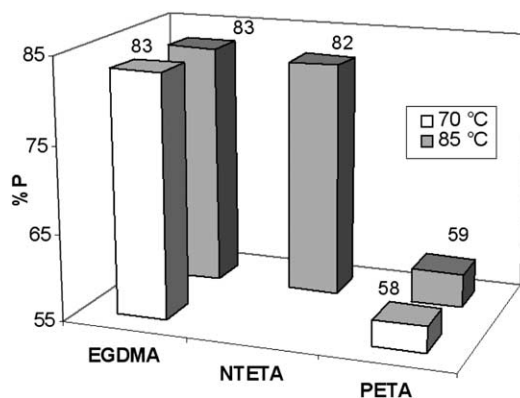


Fig. 1. Crosslinking agent type effect on HEMA-based copolymers porosity.

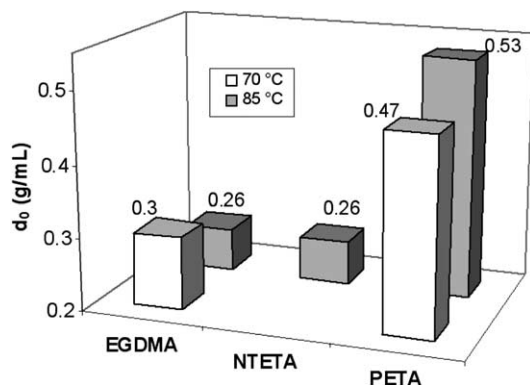


Fig. 2. Networks apparent density of HEMA-based copolymers.

separation. The pores between 10,000–500,000 nm correspond to the voids between the particles.

Poly(EGDMA-*co*-HEMA) and poly(NTETA-*co*-HEMA) synthesized at 85 °C presented similar pores size distributions (Fig. 5), showing networks whose pore size dispersion intensity increased with the pore diameter.

In Table 1, the values of V_p , S_s and average pore diameter (d_{ave} : $4000 V_p/S_s$) corresponding to each network pore size dispersion were listed. In their size dispersion, poly(EGDMA-*co*-HEMA) and poly(NTETA-*co*-HEMA) showed comparative values and higher than those found in poly(PETA-*co*-HEMA) networks. It is believed that, when the crosslinking agent used possessed a number of vinyl groups less than or equal to three, the phase separation was carried out at an early conversion rate. This behavior would indicate that phase separation is more dependent on vinyl group number present in crosslinking agents than molecular chain length between their double bonds.

Additionally, in general the d_{ave} values of the networks synthesized at 85 °C were higher than those obtained at 70 °C, which could be related to the higher crosslinking density and a smaller collapse of network generated at highest reaction temperature.

4.2. Swelling studies

Swelling studies in water, were used to analyze the

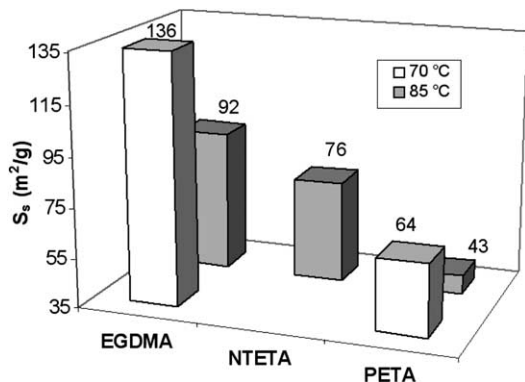


Fig. 3. Total S_s of networks synthesized at 70 or 85 °C.

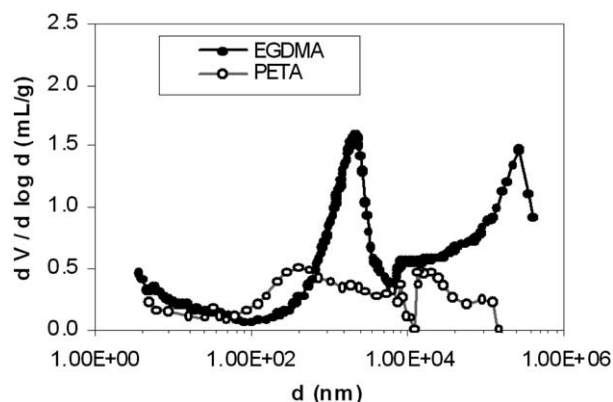


Fig. 4. Pores size distribution of networks synthesized at 70 °C.

behavior of the different polymeric networks in swollen state. This method constitutes a valuable tool for the characterization of macroporous polymers and a complement for mercury intrusion porosimetry.

It is well known that the swelling of the polymeric network is ruled by two separate processes. One of them consists on the filling of pores with the swelling liquid determined by the diluent volume separated out of the phase network during polymerization. The other consists on solvation of the network chains, which is determined by the volume of the diluent remainder in the structure of the network. In addition, the solvation process depends on both the crosslinking density and the interaction between the swelling liquid and the chains of the network [9,17].

As can be seen in Fig. 6, parameter H , related to the porosity of swollen networks, displayed a similar behavior to that found in % P (Fig. 1) of networks in dry state. This is a consequence of a smaller change in the network structure during the passage of dry-to-swollen state in the swelling process, which corroborates the existence of highly crosslinked structures. Besides, Fig. 6 showed that maximum H values were reached when short molecular chain between double bonds and low number of vinyl groups in crosslinking agent were used at highest polymerization temperature.

On the other hand, it is known that q_v parameter (Fig. 7)

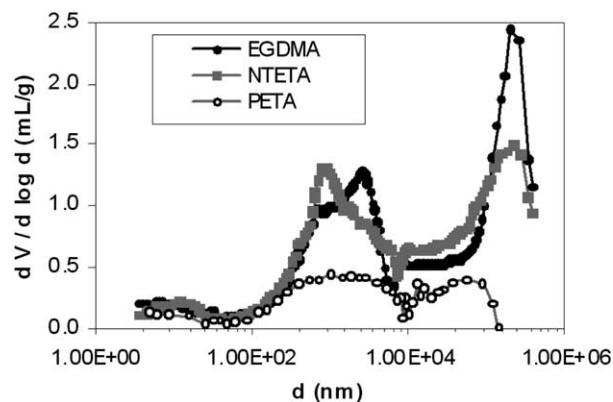


Fig. 5. Pores size distribution of networks synthesized at 85 °C.

Table 1
Effect of crosslinking agent on network morphology by mercury intrusion porosimetry

	70 °C		85 °C		
	EGDMA	PETA	EGDMA	NTETA	PETA
V_p (ml/g)	0.25 ^a 1.07 ^b 1.43 ^c	0.14 ^a 0.69 ^b 0.39 ^c	0.18 ^a 1.30 ^b 1.76 ^c	0.16 ^a 1.31 ^b 1.67 ^c	0.09 ^a 0.62 ^b 0.42 ^c
S_s (m ² /g)	128.0 ^a 7.3 ^b 0.2 ^c	55.4 ^a 8.5 ^b 0.1 ^c	82.6 ^a 8.9 ^b 0.2 ^c	66.0 ^a 9.4 ^b 0.2 ^c	37.4 ^a 5.1 ^b 0.1 ^c
d_{ave} (nm)	8 ^a 587 ^b 33,647 ^c	10 ^a 324 ^b 19,500 ^c	9 ^a 586 ^b 37,053 ^c	10 ^a 557 ^b 33,400 ^c	10 ^a 486 ^b 24,000 ^c

^a Diameter range of pore size: 4–50 nm.

^b Diameter range of pore size: 50–6000 nm.

^c Diameter range of pore size: 6000–500,000 nm.

is related with the network expansion degree [7]. This parameter depends on both the network crosslinking density and affinity of the chains by the swelling liquid. From Fig. 7, it can be seen that polymeric networks synthesized at 85 °C showed lower q_v values than those synthesized at 70 °C. A major diffusion of the monomers at highest polymerization temperature would lead to high crosslinking density.

Moreover, a large molecular chain between double bonds in the crosslinking agents would generate crosslinking points with wide separation, which would lead to a highly expandible network. As can be noticed in Fig. 7, when molecular chain length between double bonds in the crosslinking agents decrease, NTETA>PETA>EGDMA, q_v values of the respective copolymers synthesized at 85 °C do too. So, it shows the influence of molecular chain length between double bonds on network crosslinking degree.

Poly(EGDMA-co-HEMA) obtained at both temperatures, presented the most rigid networks with the major porosity values, whereas NTETA-based copolymer synthesized at 85 °C showed high values in both porosity and expansion degree.

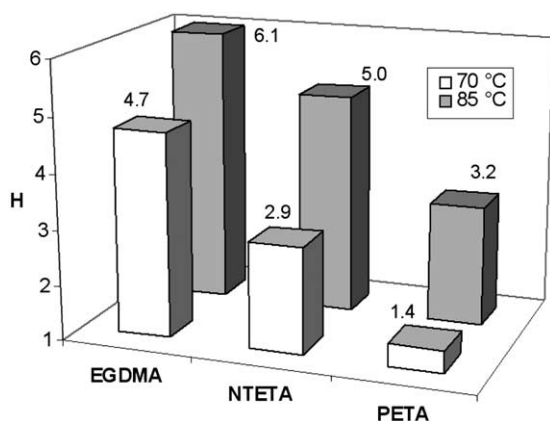


Fig. 6. Sorption-expansion ratio of the networks.

4.3. FTIR studies

Network crosslinking degree depends on both conversion rate of vinyl groups and molecular chain length between double bonds in the crosslinking agent. For that reason, conversion rate of vinyl groups of network was analyzed through NAR (Eq. (1)) corresponding to vinyl (1630 cm⁻¹) and carbonyl groups (1735 cm⁻¹).

As can be shown in Fig. 8, NAR of the networks increases with the crosslinking agent vinyl group number used (EGDMA < NTETA < PETA). The minor efficiency in the conversion as vinyl group number increases could be due to the diminution in the vinyl groups accessibility toward reactive centers by minor diffusion and major steric hindrance. In addition, higher conversion rates of pendant vinyl groups were reached at 85 than at 70 °C, due probably to the major diffusion of monomers at highest temperature.

5. Conclusions

From comparative analysis of the different morphological features corresponding to poly(EGDMA-co-HEMA), poly(NTETA-co-HEMA) and poly(PETA-co-HEMA), the

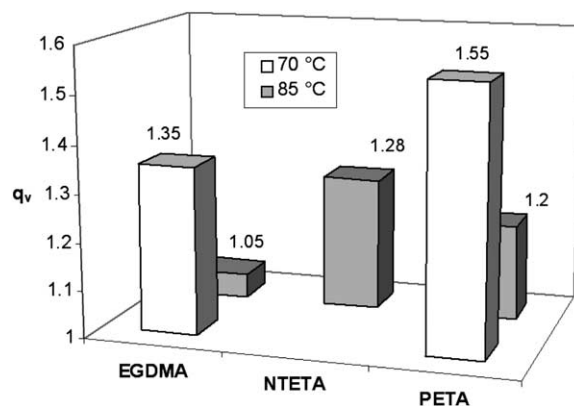


Fig. 7. Equilibrium volume swelling ratio of polymeric networks.

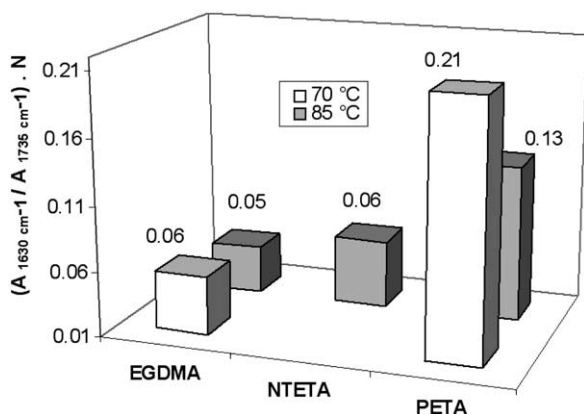


Fig. 8. NAR of HEMA-based networks.

effect of the molecular structure of the crosslinking agent on the formation of the polymeric networks was evaluated.

Taking in account the kind of crosslinking agent (structure and size), networks with different behavior of porosity and swelling could be obtained. Therefore, poly(EGDMA-co-HEMA) shows tendency to be classified as ‘heterogeneous dry networks’ while NTETA and PETA-based copolymers can be classified as ‘heterogeneous swollen networks’.

In these studied systems, it can be concluded that highly porous networks were obtained when equal or minor than three-vinyl groups number into the crosslinking agents were used (EGDMA and NTETA). This behavior showed a significant vinyl groups number effect on phase separation process. By another way, a minor molecular chain length between double bonds (EGDMA), originated networks with major crosslinking density (less expansible).

Acknowledgements

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