

Glycidyl Methacrylate-ethylene Glycol Dimethacrylate Copolymers with Varied Pore Structures Prepared with Different Reaction Parameters

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Copolymers based on glycidyl methacrylate (GMA) are considered attractive as sorbents because the epoxy groups can be easily converted into other groups. Studies involving the influence of the synthesis parameters on the morphological characteristics of these copolymers are scarce. This work investigates the synthesis of copolymers of poly(GMA-co-EGDMA) with different porosity degrees obtained by varying the synthesis parameters. GMA-EGDMA copolymers were synthesized by suspension polymerization employing varied conditions and characterized by measuring apparent density, surface area and pore volume distribution, optical and scanning electron microcopies, FT-IR, thermogravimetry and titration of epoxide rings. The copolymer with highest surface area and pore volume (260.4 m²/g and 0.5 cm³/g) was prepared employing cyclohexane as diluent, 80% EGDMA in monomeric composition and 100% of dilution degree. There was a relation between the epoxide content of the copolymers determined by titration and the residue content formed in the first decomposition stage.

Keywords: glycidyl methacrylate copolymers, polymer support, suspension polymerization

1. Introduction

Porous polymers can be employed in many areas, among which the most common are absorption and adsorption, such as sorption of CO₂¹ ion exchange processes², and support materials for immobilization of biocatalysts³. These polymers, with spherical shape, can be prepared by conventional heterogeneous polymerization processes, such as suspension, emulsion, dispersion and precipitation; multistage heterogeneous polymerizations, such as seeded suspension polymerization and seed assembly (to form supraballs); hypercrosslinking (Davankov approach); and polymerization of HIPEs (high internal phase emulsions)⁴.

Among the porous polymers extensively applied for adsorption and absorption processes and as supports are styrene-divinylbenzene (Sty-DVB) copolymers¹⁻³. These copolymers are commonly prepared by aqueous suspension polymerization, and can have gel-like or porous structures. The porosity of these copolymers can be controlled by the synthesis parameters, especially crosslinking degree, type of diluent and dilution degree⁵. Chemical modification of these copolymers is achieved normally by a sequence of reactions initiated by activation of benzene rings and various other reactions⁵. Synthetic routes with a high number of steps have disadvantages related to reagent consumption and residue production.

Copolymers based on glycidyl methacrylate (2,3-epoxypropyl methacrylate) (GMA) can be an important alternative to

substitute Sty-DVB copolymers⁶⁻¹⁵. The presence of epoxide groups in the polymeric matrix of GMA copolymers makes their functionalization easier, because the epoxide groups are very reactive⁶. Some works report copolymerization of the monomer GMA with a crosslinked monomer, commonly ethylene glycol dimethacrylate (EGDMA)^{6,9,11,12,15-18} or divinylbenzene (DVB)^{7,8,10,13} and N,N-methylene-bis-acrylamide (MBA)¹⁴.

Many works address the modification of microspheres of glycidyl methacrylate (GMA) through reaction with diamines such as ethylenediamine, diethylene triamine and tetraethylenepentamine, employed for coordination of metal ions such as Cu(II), Cd(II), Pb(II), Cr(VI) and U(VI). In this context, the works of Nastasovic and colleagues^{9,12}, Sadek and colleagues¹⁰, Makin and colleagues¹¹ and Donia and colleagues¹³ can be mentioned.

Aversa and colleagues⁷ described the synthesis of copolymers of GMA-DVB followed by reaction with diethylamine and finally quaternization with 1-bromobutane to prepare anion-exchange resins with polyquat structures. These materials were employed for sorption of phenol from aqueous solutions. Rizwan and colleagues¹⁵ described the preparation of GMA-EDGMA copolymers, modification of the particles with acetoxime followed of reaction with *p*-toluene sulfonic acid. The optimized polymer showed promising results for sorption of organic nitrogen species present in heavy gas oil (HGO). Danquah and colleagues¹⁶ described the preparation of GMA-EDGMA copolymers, functionalization of these copolymers through

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reaction with urea, 2-chloro-N,N-diethylethylamine hydrochloride or ammonia, and evaluation of the products for enrichment of plasmid DNA (pDNA), necessary for development of genetic vaccines and gene therapies.

Copolymers based on GMA also have been used to support enzymes like lipases and laccases, as reported by Milec and colleagues⁶ and Melo and colleagues¹⁷. Milec and colleagues⁶ reported the impregnation of lipases of *Candida antarctica* (*CalB*) on GMA-EDGMA beads with different surface areas, pore volumes and average pore sizes. The biocatalysts produced were evaluated for ring-opening polymerization of ϵ -caprolactam (ϵ -CL). They also showed that the activity of the biocatalysts produced was strongly dependent of the porosity characteristics of the GMA-EDGMA copolymers. The increase of pore size of the beads resulted in a pronounced increase in polymerization degree of ϵ -CL and in the polymers molecular weight.

Rolland and colleagues¹⁸ proposed the preparation of enantiomerically enriched GMA-EDGMA copolymers (containing chiral epoxy residues) based on copolymerization of (*R*)- or (*S*)-glycidyl methacrylate monomers with ethylene glycol dimethacrylate. These copolymers were reacted with several achiral and homochiral amines. The amino alcohol polymers produced were coordinated with ruthenium and the complexes formed were evaluated as asymmetric catalysts for reduction of acetophenone.

Many of these studies are related to modification of GMA copolymers and evaluation of the products as ion exchangers, chelating groups, catalysts, sorbents or stationary phases, etc. The relationship between the morphological characteristics of these copolymers and efficiency of the products was not covered in many of these works. However, the porosity degree of glycidyl methacrylate copolymers influences the accessibility of reactants to epoxide (oxirane) groups, and consequently the extent of the modification reactions of these copolymers.

In relation to works related to synthesis of Sty-DVB copolymers, some researchers have studied the reactional parameters that can provoke alterations of morphologic characteristics of GMA-EDGMA copolymers. In this context, the works of Jovanovic and colleagues¹⁹, Hercul and colleagues²⁰ and Ferreira and colleagues²¹ can be cited. Hercul and colleagues²⁰ prepared enantiomerically enriched GMA-EDGMA copolymers by precipitation polymerization employing (*R*) or (*S*) glycidyl methacrylate. The polymerizations were conducted by varying crosslinker degree, molecular weight of polyvinylpyrrolidone (PVP) used as stabilizer, proportion of PVP in monomeric mixture, and volumetric ratio between monomer mixture and ethanol (employed as diluent). The influence of these factors was related only with the polydispersity of the particles produced. Jovanovic and colleagues¹⁹ studied the preparation of GMA-EDGMA copolymers by varying the type of diluent (porogenic agent) present in the organic phase. The diluents studied were cyclohexanol (100%) and mixtures of cyclohexanol and alcohols of different chain lengths (butanol, octanol, decanol, dodecanol, tetradecanol, hexadecanol) in proportion of 90:10. The specific surface area of the particles (S_{BET}) varied from 13.2 to 68.2 m²/g. The authors reported a slight increase of specific volume and pore diameter and a decrease

of specific surface area when the chain length of aliphatic alcohol was increased.

Ferreira and colleagues²¹ prepared three series of GMA-EDGMA copolymers by aqueous suspension polymerization with varying diluent composition, agitation velocity and polymerization reaction temperature. The diluent composition was constituted of a mixture of cyclohexanol-dodecanol or mixtures of cyclohexanol-toluene in proportions of 100:0, 80:20 and 20:80. According to the authors, cyclohexanol is considered a solvating solvent to chains of GMA-EDGMA, while dodecanol and toluene are non-solvating solvents to these polymeric chains. The surface area and pore volume values of the particles prepared in the presence of cyclohexanol-toluene were higher than for the particles synthesized with cyclohexanol-dodecanol.

There is a need for more studies involving preparation of GMA-EDGMA copolymers by varying the synthesis parameters, especially the type of diluent, dilution degree of monomeric phase and crosslinker content. Thus, in this work we investigated the influence of synthesis parameters, namely diluent type (cyclohexane, cyclohexanol, n-butanol or toluene), dilution degree (50 or 100%) and monomer composition (20 or 80% crosslinker), on the morphological characteristics of glycidyl methacrylate-ethylene glycol dimethacrylate (GMA-co-EGDMA) prepared by aqueous suspension polymerization.

2. Materials and Methods

2.1 Chemicals

Glycidyl methacrylate (GMA) (97%) and ethylene glycol dimethacrylate (EGDMA) (95%) (both monomers containing 90-110 ppm of monomethyl ether hydroquinone as inhibitor) were supplied by Sigma-Aldrich Brasil Ltda (São Paulo, Brazil) and used as received. 2,2-azo-bis(isobutyronitrile) (AIBN) (granular form, commercial degree) was purchased from Mig Química Ltda (São Paulo, Brazil) and used after recrystallization with methanol (ACS reagent, 99.8%). Cyclohexane (ACS reagent, 99%), cyclohexanol (ACS reagent, 98%), n-butanol (ACS reagent, 99.4%) and toluene (ACS reagent, 99.5%) and other reagents and solvents employed on this work were purchased from Sigma-Aldrich Brasil Ltda (Rio de Janeiro, Brazil) and used as received.

2.2 Synthesis of GMA-EGDMA copolymers

GMA-EGDMA copolymers were synthesized by aqueous suspension polymerization in a 1 L three-necked round-bottom reactor flask equipped with a mechanical stirrer and a reflux condenser. The organic phase was composed of GMA and EGDMA, in proportions of 80:20 and 20:80 mol/mol (Table 1), AIBN, 1% mol in relation to total mols of monomers, and different diluents regarding dilution degrees in the monomer mixture, as described in Table 1. The aqueous phases were PVA and NaCl, both at 1.0% w/v in relation to water content. Volumetric ratio between the aqueous and organic phase was 3:1 (v/v). The aqueous phase was prepared and transferred to the flask. The organic phase was prepared and also transferred to the same flask. The system was stirred continuously at 350 rpm at 85 °C for 24 hours.

Table 1. Data of apparent density, specific area, pore volume to GMA-EGDMA copolymers

Copolymer	GMA-EGDMA / (mol:mol)	Diluent	Dilution degree (%)	dap (g cm ⁻³)	S (m ² g ⁻¹)	V _p (cm ³ g ⁻¹)	Epoxide ring (mmol g ⁻¹)
P-01	80:20	Cyclohexane	50	0.61	6.5	0.06	2.47
P-02		Cyclohexanol	50	0.82	0.2	nm	2.67
P-03		n-Butanol	50	0.78	0.04	nm	3.96
P-04		Toluene	50	0.78	0.7	0.003	2.82
P-05	20:80	Cyclohexane	50	0.44	126.3	0.4	1.03
P-06		Cyclohexane	100	0.37	260.4	0.5	0.48
P-07		Cyclohexanol		0.39	18.5	0.1	0.44
P-08		n-Butanol		0.31	175.1	0.4	0.40
P-09		Toluene		0.48	110.4	0.2	0.40

GMA: Glycidyl methacrylate; EDGMA: Ethylene glycol dimethacrylate; dap: apparent density (determined by graduated cylinder method); S: Surface area and V_p: pore volume distribution (determined by nitrogen adsorption measurements following the BET and BJH methods); nm: not measurable.

The microspheres obtained were washed several times with hot water (70 °C, 6 portions of 500 mL), ethanol (500 mL) and methanol (250 mL), and finally dried at atmospheric pressure for 48 h at 60 °C^{7,10,17,21}.

2.3 Characterization of the copolymers

The porosity of GMA-EGDMA copolymers was characterized by determining apparent density by the graduated cylinder method²², and surface area and pore volume distribution by nitrogen adsorption measurements following the BET and BJH methods, respectively (Micromeritics ASAP 2010 apparatus)²³.

The specific surface area, pore volume and pore diameter of the GMA-EDGMA copolymers were determined by using nitrogen (inert gas) adsorption data at different relative pressures. The copolymer beads (200-300 mg) were pretreated at 120 °C for 4 hours for drying and degassing before analysis. Isotherms were plotted correlating the amount of gas adsorbed by the beads (cm³g⁻¹) (n) as a function of the variation of relative pressure (P / P₀). These isotherms can be of different types (types I, II, III, IV, V and VI). The shape of these isotherms is related to the type of porosity of the material, type of coverage of the material surface (monolayer or multilayer) and interactions between adsorbate and adsorbent molecules. The plot 1/[Q(P₀/P-1)] x P/P₀ (where Q is the adsorption heat) generates a line (y = a + bx) and the determination of the linear and angular coefficients permits determining the volume of gas necessary to recover of material with the monolayer of gas (V_m) that is applied in the BET equation (Equation 1), to determine the specific surface area of the material¹⁹:

$$(P/V(P_0 - P)) = [(1/V_m c) + (c - 1/V_m c)(P/P_0)] \quad \text{(Equation 1)}^{23}$$

Where: c = exp[(Q₁ - Q_L)/RT], Q_L: molar adsorption heat, Q₁: monolayer adsorption heat, R: gas constant, T: absolute temperature.

The BJH method (mathematical method proposed by Barret, Joyner and Halenda) is based on application of Kelvin equation (Equation 2) and assumes the progressive emptying of the pores filled with N₂ (in liquid state) with decreasing pressure. Pore size determination by applying Kelvin equation is limited to the pores with cylindrical

format in the range of 10-250 Å, this being the principal limitation of BJH method²³.

$$\ln(P/P_0) = -(2\gamma M_v \cos\theta / RT r_m) \quad \text{(Equation 2)}^{23}$$

where γ : surface tension of the condensed, M_v: molar volume of the adsorbate, θ : contact angle between the solid and the condensed phase, R: gas constant, T: absolute temperature, r_m: mean radius of curvature of the liquid meniscus.

Appearance and morphology of the copolymers were analyzed by optical microscopy (Olympus SZ10) and scanning electron microscopy (SEM) (JEOL-JSM 6460 LV). For optical microscopy, the samples were submitted to magnification of 50 x. For SEM, the samples were spread on conductive tape and sputtered with gold. The analysis was conducted at 20 keV and magnification of 5000 x.

GMA-EDGMA copolymers were also characterized by Fourier-Transform Infrared spectrometry (FT-IR), thermogravimetric analysis (TGA and DTG) and determination of epoxide rings by titration. FT-IR spectra (4000 – 400 cm⁻¹) were recorded with a Perkin-Elmer Spectrum One spectrometer (4 scans and 4 cm⁻¹ resolution) in the form of KBr pellets. TGA and DTG curves of the copolymers were obtained using a TA Q50 instrument in a temperature range of 30–650 °C at a constant heating rate of 20 °C min⁻¹ under nitrogen atmosphere and a flow rate of 60 mL min⁻¹.

The method adopted to determine the epoxide groups of GMA-EDGMA copolymers was based on reaction with tetramethylammonium bromide in glacial acetic acid followed by titration with 0.1 N perchloric acid in glacial acetic acid and acetic anhydride in the presence of crystal violet indicator²⁴.

Figure 1 shows the steps related to preparation, purification and characterization of GMA-EDGMA copolymers.

3. Results and Discussion

FT-IR spectra of GMA-EDGMA copolymer, named P-01 (Figure 2), showed broad absorption at 3468 cm⁻¹ involving OH association, an intense absorption at 1732 cm⁻¹ due C=O stretching, a band at 1153 cm⁻¹ due to C(=O)-O stretching, and absorptions at 1263 cm⁻¹ and 991 cm⁻¹ due to symmetrical and asymmetrical stretching of epoxide rings. These data suggest the incorporation of both monomers in the polymer structure²⁵.

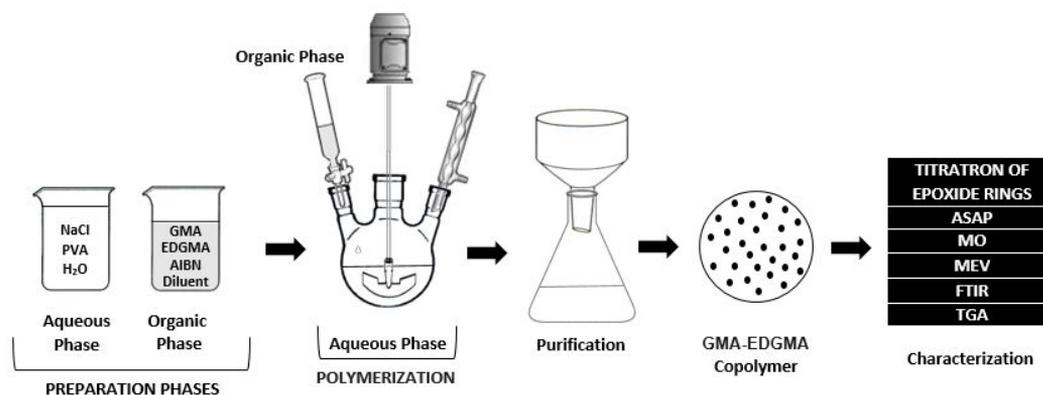


Figure 1. Schematic representation of the steps related to polymerization, purification and characterization of GMA-EDGMA copolymers.

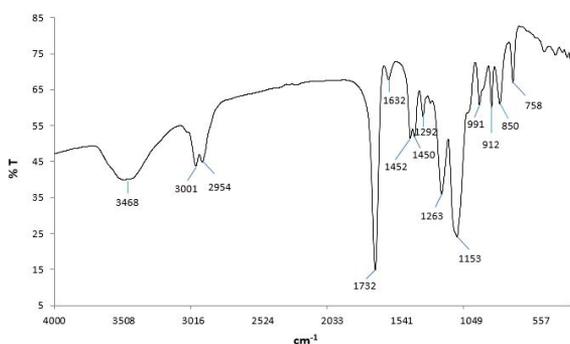


Figure 2. FT-IR spectra of P-01 copolymer.

Morphological characteristics of the polymeric supports influence the process of diffusion of reagents and products through the internal structure of these materials, controlling the extension of modification reaction of these supports as well as the accessibility of reagents to active groups and diffusion of products to the medium⁵. GMA-EDGMA copolymers are attractive as supports because the epoxy groups can be easily converted into other groups. Studies to establish relationships between synthesis parameters and physical and chemical characteristics of these materials are scarce. In this work, we employed different conditions to prepare diverse GMA-EDGMA copolymers. In order to prepare copolymers with different pore structures, the copolymerization of GMA and EGDMA was carried out using different diluents, crosslinker contents and monomer dilution degrees.

3.1 Influence of diluent type

The solvating power of the diluent employed for copolymerization has a strong effect on the phase separation and consequently on morphological characteristics of the copolymers prepared by suspension polymerization^{4,26}. When the monomers are polymerized in the presence of a diluent that does not solvate polymer chains in formation, the phase separation process occurs before the gel point via χ -induced syneresis, generating beads with larger pore diameters associated with low surface areas. On the other hand, when this polymerization is carried out with a good

solvent of polymer chains, the phase separation process occurs after the gel point via v -induced syneresis, generating gel-type particles with low surface areas or structures with high surface area and micropores. Besides the solvating power of the diluent, the morphological characteristics of the particles are also influenced by other parameters, such as monomeric composition, content of crosslinking monomer and dilution degree.

Crosslinked polymers did not undergo dissolution but did swell in different solvents/diluents. The swelling degree of a polymer can be predicted based on comparison of the solubility parameters between polymer and solvent. The classification of the diluent as a thermodynamically bad solvent (non-solvating) or good solvent (solvating) of the polymeric chains is based on solubility scales, such as Hildebrand solubility parameters and the three-dimensional solubility parameters of Hansen. The difference between the solubility parameters of the diluent and polymer (tabulated values) is employed for this classification²⁷.

The Hildebrand solubility parameter is defined as the square of the cohesive energy density (CED), which is related with the energy of vaporization per cm^3 , and the attraction force between the molecules. Hansen parameters are determined considering the contribution of structural groups to the entire molecule²⁷. As previously defined by Valle and colleagues²⁸, when the difference between the Hildebrand solubility parameters of the polymer (δ_p) and solvent (δ_s) is low ($|\delta_p - \delta_s| \leq 1.5$), the solvent may be considered a good solvent (or solvating solvent) of that polymer. On the other hand, when this difference is high ($|\delta_p - \delta_s| \geq 1.5$), this solvent is considered a thermodynamically poor solvent of the polymer²⁸.

Table 1 shows data of apparent density, surface area, pore volume and epoxide ring content (determined by titration) of copolymers GMA-EDGMA prepared by employing different solvents as polymer chain diluents.

Table 2 shows the solubility parameters of the solvents employed as diluents for copolymerization of the monomers GMA and EGDMA and the monomer GMA. The determination of the Hildebrand solubility parameter for GMA-EGDMA copolymers is a difficult process because those polymers have highly crosslinked structures. Data in Table 2 indicate the difference of the Hildebrand solubility parameter between

Table 2. Solubility Parameters to solvents employed as diluents on polymerization of the monomers GMA and EDGMA²⁰

	δ_t MPa ^{1/2}	δ_d MPa ^{1/2}	δ_p MPa ^{1/2}	δ_H MPa ^{1/2}
Cyclohexane	16.8	16.8	0	0.2
Cyclohexanol	22.4	17.4	4.1	13.5
n-Butanol	23.1	16.0	5.7	15.8
Toluene	18.2	18.0	1.4	2.0
GMA monomer	19.36			

δ_t : Total Hildebrand Solubility Parameter; δ_d : dispersion component; δ_p : polar component; δ_H : hydrogen bonding component

toluene and GMA is low, while for the other solvents this difference is high.

Comparison of the data on apparent density and surface area of the copolymers P-01, P-02, P-03 and P-04 synthesized employing 20% EGDMA and dilution degree of 50% (Table 1) shows that P-01, which was prepared employing cyclohexane as diluent, had higher surface area and lower apparent density than the other copolymers of this series. This indicates that this copolymer had a more porous structure. The optical microscopic images of these copolymers (Figure 3) show that the copolymer P-01 had opaque beads while the other copolymers had translucent beads. Scanning electron micrographs of these copolymers also confirmed that P-01 had a porous structure while P-02, P-03 and P-04 showed non-porous surfaces. Probably in the presence of cyclohexane, the phase separation process occurred before the gel point, via χ -induced syneresis, contributing to generate more porous structures⁴.

Since cyclohexanol and n-butanol can interact with the polymeric structures, establishing hydrogen bonds with oxygen atoms of epoxides and ester groups, it can be presumed that these solvents are also good solvents of GMA-EGDMA copolymers. Jovanovic and colleagues¹⁹ and Ferreira and colleagues²¹ also classified these two alcohols as good solvents of GMA-EDGMA. Thus, probably in the presence of these alcohols the phase separation process occurred after the gel point, via v -induced syneresis, generating structures with low porosity degree. Even with higher content of EDGMA and dilution degree, the copolymers synthesized employing cyclohexanol as diluent presented low surface area and pore volume, corroborating the results of these studies. Since the difference of the Hildebrand solubility parameter between toluene and GMA is low (Table 2)²¹, this solvent is expected to be a solvating solvent of GMA-EGDMA, leading to structures with low porosity degree. However, Ferreira and colleagues²¹ classified toluene as a poor solvent of GMA-EDGMA copolymers, probably considering that this solvent is not structurally similar to this copolymer.

The porous characteristics of the GMA-EDGMA copolymers underwent notable changes when butanol and toluene were employed as diluents, in function of the alterations of the other reactional parameters (dilution degree and EDGMA content). Jovanovic and colleagues¹⁹ stated that morphological characteristics of copolymers were not related only to solubility parameters of the solvents used as diluents, but also other reactional parameters of the polymerization reactions.

Data of apparent density, surface area and pore volume of the copolymers P-06, P-07, P-08 and P-09 synthesized employing 80% EGDMA and dilution degree of 100% (Table 1)

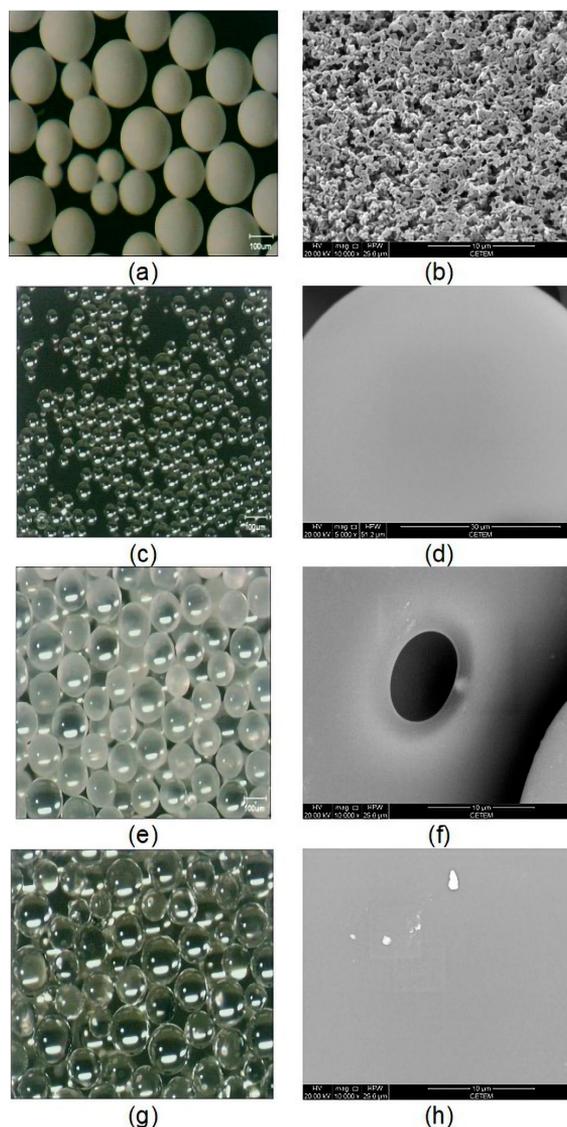


Figure 3. Optical (OM) and scanning electron (SEM) microscopic images of the copolymers P-01 OM: (a), SEM: (b); P-02 OM: (c), SEM: (d); P-03 OM: (e), SEM: (f) and P-04 OM: (g), SEM: (h).

also confirm that the presence of the diluent cyclohexane generated more porous structures, with larger areas and pore volumes. Electron microscopic images of these copolymers (Figure 4) confirm the formation of a more porous structure when cyclohexane was employed as diluent in the monomer mixture. Figure 5- a shows that for this series of copolymers,

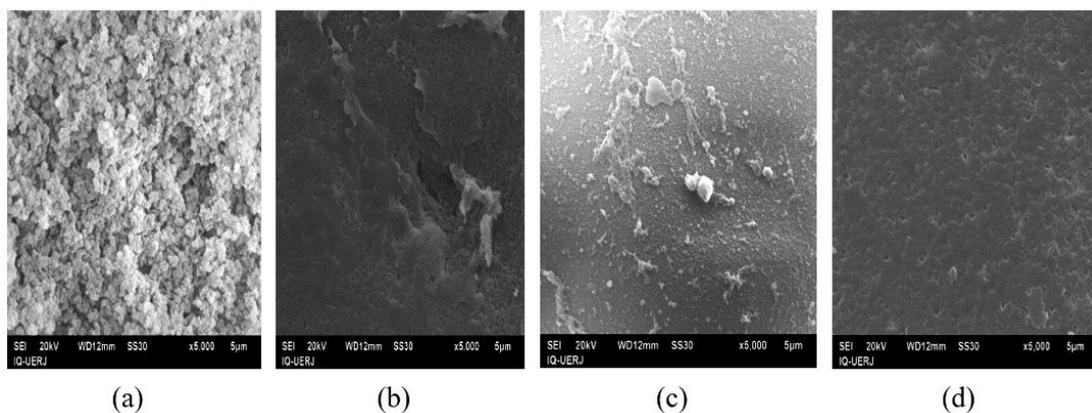


Figure 4. Scanning electron microscopic images of the copolymers P-06 (a), P-07 (b), P-08 (c) and P-09 (d).

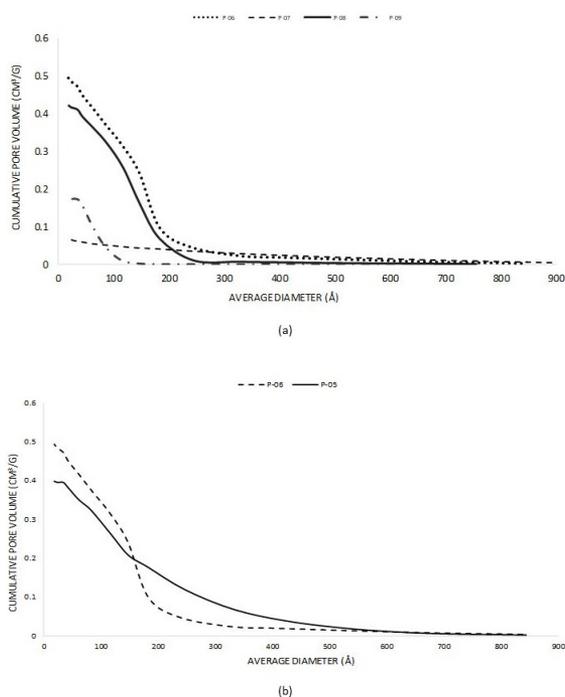


Figure 5. (a) Pore size distribution curves of the copolymers P-06, P-07, P-08 and P-09 (b) Pore size distribution curves of the copolymers P-05 and P-06.

unlike initially expected, the variation of diluent type did not provoke a significant variation of pore size distribution. These four copolymers presented average pore diameters in the range of 0–200 Å. As reported by Gokmen and Du Prez², the employment of non-solvating solvents as diluent commonly leads to structures with macropores via χ -induced syneresis and displacement of pore sizes to larger diameters.

3.2 Influence of crosslinker content

The data in Table 1 on copolymers P-01 and P-05, synthesized in the presence of hexane as diluent and 50% dilution degree, show that increased EGDMA content led to the formation of beads with higher surface area associated with lower apparent density. In general, all copolymers synthesized with 80% EGDMA presented higher porosity than those

obtained with 20% EGDMA. Considering that EGDMA is a more active crosslinker than GMA, it is possible to suppose that a high EGDMA content generates more compact nuclei and microspheres, inducing phase separation at lower conversion rates and forming more porous structures^{29,30}.

As expected, the GMA-EGDMA copolymers containing 80% GMA (P-01, P-02, P-03 and P-04) presented higher epoxide ring content (determined by titration) than the copolymers with 20% GMA and 80% EGDMA in monomeric mixtures (P-06, P-07, P-08 and P-09) (Table 1). Comparison of the epoxide ring content of these copolymers with that of 80% GMA indicated that P-03, synthesized employing butanol as diluent, presented higher content of epoxide groups than the other copolymers of this series. Since this copolymer had the lowest surface area and consequently higher content of gel phase, it can be assumed that this structure presented high swelling capacity in the mixture employed in titration, which may have permitted high access of the reactants to epoxide groups located in the internal structure of this copolymer.

In general, the TGA curves of the copolymers prepared with 80% GMA and 20% EGDMA (P-01, P-02, P-03 and P-04) (Figure 6-a) show three decomposition stages. DTG curves (Figure 6-b) contain three peaks related to these three degradation stages. The first thermal degradation step (T_{onset} at around 200 °C) can be attributed to the decomposition of the epoxide groups.

The DTG peak associated with this stage of degradation is more intense for P-03, with higher epoxide ring content as determined by titration (Figure 6-b), supporting the correlation between data obtained by thermogravimetry and data from titration of epoxide rings. The second and third stages of decomposition can be attributed to the decomposition of the carbon chains of the copolymers. It can be assumed that the third degradation stage is related to the degradation of crosslinked domain regions, nuclei and more entangled microspheres formed in the initial stages of polymerization with high proportion of crosslinked monomer³¹. This third stage of degradation of the polymeric chains was more intense for copolymers with 80% EDGMA in relation to the copolymers prepared with 20% EGDMA (Figure 7), indicating that this last degradation step can be associated with decomposition of the crosslinked region³¹.

3.3 Influence of dilution degree

For the copolymers P-05 and P-06, synthesized in the presence of cyclohexane and 80% EGDMA in the monomeric mixture, increasing the dilution degree provoked a decrease

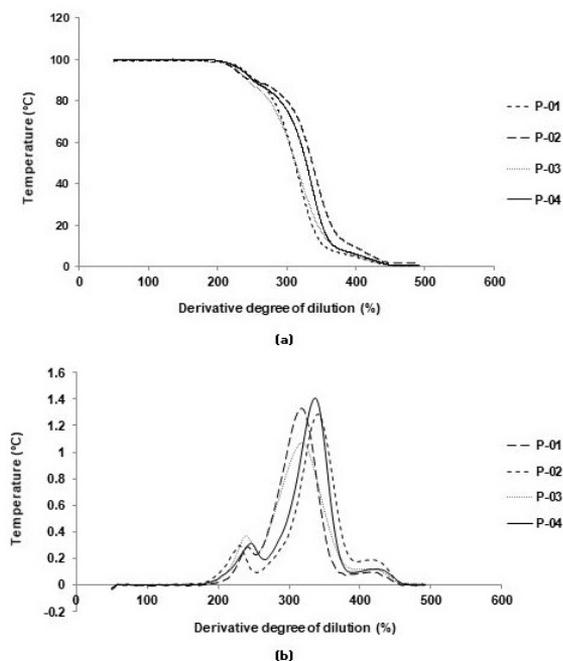


Figure 6. TGA (a) and DTG (b) curves of the copolymers P-01, P-02, P-03, P-04 and P-05.

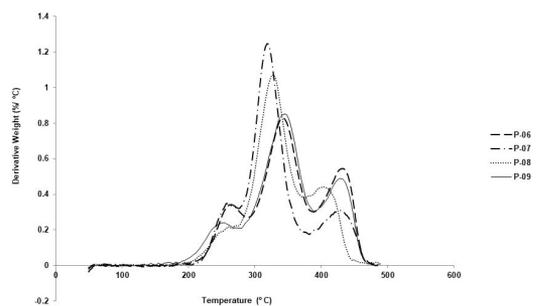


Figure 7. DTG curves of the copolymers P-06, P-07, P-08 and P-09.

of the apparent density and large increases of surface area and pore volume, indicating greater porosity of the beads. Other studies have also demonstrated that increasing the dilution degree contributes to generation of particles with higher porosity^{5,30}. The scanning electron microscopic images of these two copolymers (Figure 8) also confirm that P-06 possessed a more porous structure. Unlike expected, the pore size distribution curves of these two copolymers (Figure 5-b) are similar i.e., these two copolymers have pores with similar diameters. Costa and colleagues⁵ demonstrated that the pore size distribution curves of Sty-DVB copolymers shifted to higher diameters when the dilution degree increased.

Copolymer P-05 contained twice the epoxide ring content of P-06 (Table 1), although these two materials were synthesized employing the same content of GMA in the monomeric mixture. Apparently, increasing the dilution degree of the monomer phase decreased the incorporation degree of the GMA in the polymeric chain. The increase of the dilution degree results in an increase of the organic phase volume and consequently a greater aqueous phase volume employed in the polymerization reactions. GMA and EGDMA can be considered partially hydrophilic monomers. Thus, the increase of dilution degree may have contributed to partial solubilization of GMA in the aqueous phase and consequently lower incorporation of this monomer in the polymeric chain. Data in Table 1 show that the other copolymers prepared with 100% dilution degree (P-07, P-08, P-09) also presented around 0.4 mmol of epoxide ring per gram of copolymer, confirming the low incorporation of GMA in the GMA-EGDMA copolymers when the diluent content of the organic phase increased.

Table 3 shows the thermal stability data obtained from TGA and DTG curves of copolymers P-01, P-05 and P-06. P-01 and P-05 contained residue contents after the first stage of degradation of 8.5 and 5.3% respectively. As expected, P-01 had high epoxide ring content, as determined by titration (Table 1), and higher residue content after the first decomposition stage (Table 3) (Figure 6), confirming that this copolymer possesses high content of GMA in its structure. This result also indicates that the first decomposition stage of GMA-EGDMA copolymers observed in TGA and DTG curves is related with loss of epoxide rings. P-01 did not present a degradation stage around 400 °C, which can be related to

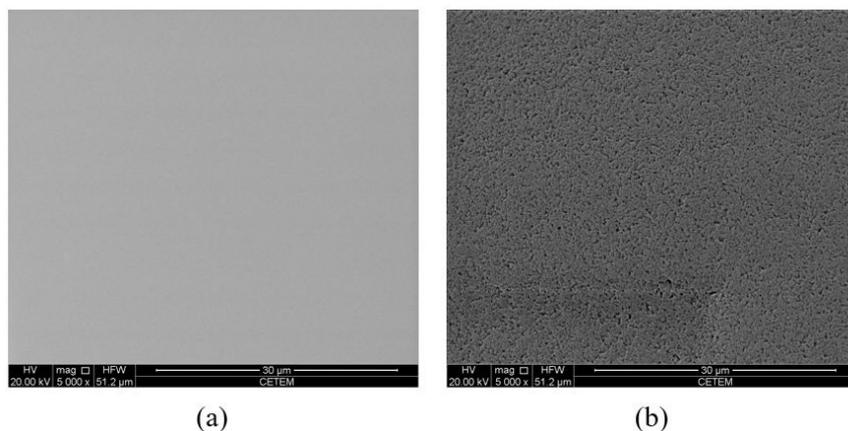


Figure 8. Scanning electron microscopic images of the copolymers P-05 (a) and P-06 (b).

Table 3. Thermal data to the copolymers P-01, P-05 and P-06

Copolymer	Stages of decomposition					
	1° Stage		2° Stage		3° Stage	
	T _{onset} (° C)	Residue (%)	T _{onset} (° C)	Residue (%)	T _{onset} (° C)	Residue (%)
P-01	225.4	8.5	287.9	84.2	-	-
P-05	225.7	5.3	307.2	75.3	411.5	17.7
P-06	-	-	303.9	65.7	406.4	29.0

GMA: Glycidyl methacrylate; EDGMA: Ethylene glycol dimethacrylate

its low content of crosslinking monomer (EDGMA). On the other hand, P-06 did not undergo the first degradation stage, confirming the low epoxide ring content of this material, as determined by titration.

4. Conclusions

It was possible to prepare GMA-EGDMA copolymers with varied morphological characteristics through aqueous suspension polymerization by varying the diluent, monomeric composition and dilution degree of the monomeric phase. The data on apparent density, surface area and pore volume, along with the optical and electron microscopies, indicated that these three parameters influenced the formation of the polymeric structures. Comparison of the copolymers synthesized with the same monomer composition and dilution degree reveals that the diluent cyclohexane led to the formation of more porous structures. The copolymers synthesized with 100% dilution degree and higher content of EDGMA (crosslinker monomer) had higher porosity than those synthesized with 50% dilution degree and high content of GMA. P-06 had the highest surface area and pore volume (260.4 m²/g and 0.5 cm³/g) among the all materials synthesized. This copolymer was prepared employing cyclohexane as diluent, 80% EDGMA in the monomeric composition and 100% dilution degree. In general, the copolymers presented three degradation stages. The first thermal degradation stage was attributed to the decomposition of the epoxide groups and the second and third stages to the decomposition of the carbon chains of these copolymers. There was a relation between the epoxide content of the copolymers determined by reaction with tetramethylammonium bromide and titration with perchloric acid and the residue content formed in the first decomposition stage.

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