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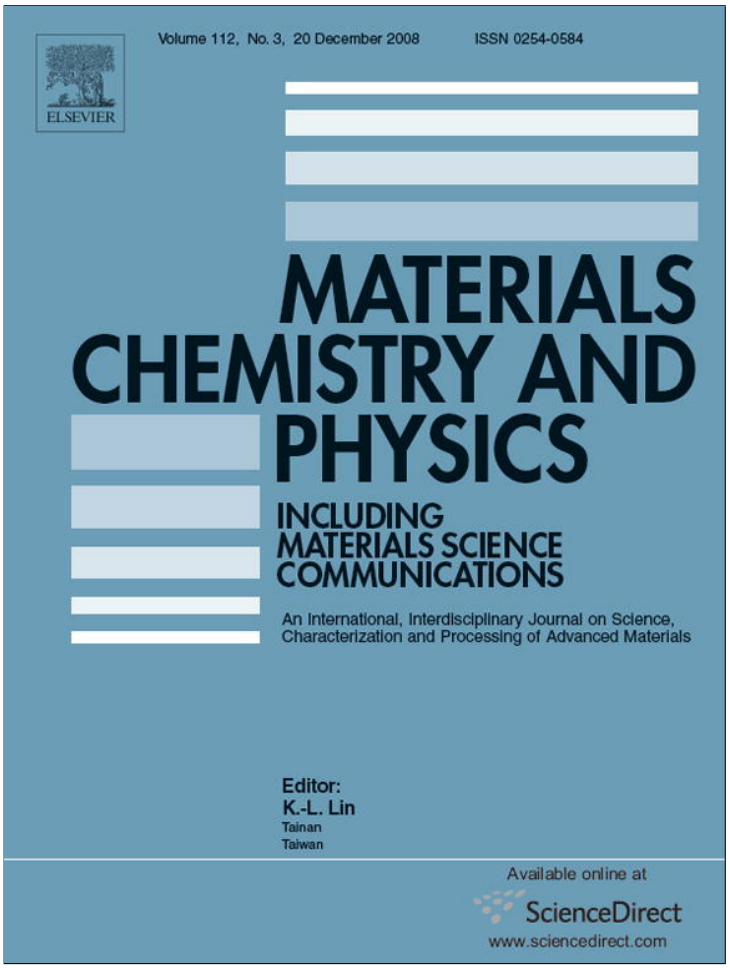

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Materials Chemistry and Physics 112 (2008) 1055–1060

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Preparation of polymeric macroporous rod systems: Study of the influence of the reaction parameters on the porous properties

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ARTICLE INFO

Article history:
Received 10 March 2008
Received in revised form 26 June 2008
Accepted 3 July 2008

Keywords:
Macroporous polymers
Chemical synthesis
Porous properties
Monoliths

ABSTRACT

Polymeric macroporous rod systems were prepared using *N*-acryloyl-tris(hydroxymethyl)aminomethane (NAT) and glycidyl methacrylate (GMA) as mono-vinyl monomers and *N*,*N*′-methylenebisacrylamide (BIS) or trimethylolpropane trimethacrylate (TRIM) as crosslinking agents. The reactions were performed in the presence of a ternary porogenic diluent (composed by dimethylsulfoxide, tetradecanol and poly(ethylenglycol) 6000 (PEG 6000)) and azobisisobutyronitrile (AIBN) as initiator, by free-radical crosslinking copolymerization. The effect of polymerization temperature, porogenic mixture and crosslinker was analyzed. The results showed that a lower polymerization temperature and an increase in the amount of non-solvating diluents (tetradecanol and PEG 6000) in the reaction mixture led to products with higher porosity. The prepared monoliths were promising as potential base supports for different chromatography processes, especially those synthesized with GMA, since its incorporation allows to bind different ligands in a direct coupling reaction.

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1. Introduction

Macroporous polymeric rods are a particular type of rigid polymers that consists of a monolithic piece containing interconnected pores of great size or large channels [1]. The pores provide the desired surface area required for the specific interaction, while the channels allow a high flow rate at moderate pressures [1]. These polymers may be synthesized in a simple way from a homogenous mixture, which contain the monomers, the crosslinker, the porogenic solvents and the radical initiator. The polymerization and crosslinking reaction are carried out in a mold at the temperature of reaction to obtain finally a polymeric material with the form of the reactor used. Therefore, polymer rods of different shapes, i.e. as tubes [2–4], disks [5], or cylinders [6] have been synthesized and reported. The porous characteristics of these polymers allow them to be used in different processes, such as microfluidic chips technology [7], as stationary phases for HPLC [1,8,9] or in capillary electrochromatography [10,11].

Depending on the monomers used in the synthesis, macroporous monoliths with different surface chemistry are obtained. Thus, hydrophilic polymer rods based on hydrophilic acrylates [4,12,13] and acrylamide monomers [9,14] and non-polar monoliths formed from different styrene-based monomers [15] can be obtained. All the polymeric systems were obtained carefully studying the reaction parameters that influence the porous architecture of the monoliths yielded.

Different di-vinyl crosslinkers such as di-vinylbenzene [15], ethyleneglycol dimethacrylate [12,13] and *N*,*N*′-methylenebisacrylamide (BIS) [16–18] were used to the synthesis of macroporous monoliths. Besides, a tri-vinyl containing crosslinking agent, trimethylolpropane trimethacrylate (TRIM), was used in several cases to synthesize macroporous polymeric materials [3,4,19–21] since it can provide a high degree of crosslinking, so ensuring the rigidity and the mechanical stability necessary in applications such as chromatographic supports.

We have recently reported [16] the synthesis of hydrophilic macroporous rods based on *N*-acryloyl-tris(hydroxymethyl)aminomethane (NAT) as mono-vinyl monomer and BIS as crosslinker. We found that the porous properties of these polymers can be controlled through different parameters such as porogenic mixture, reaction temperature and concentration of the crosslinker monomer. From those results, the synthesis of macroporous polymeric rods containing NAT monomer under different conditions (effect of porogenic mixture, reaction temperature, presence of glycidyl methacrylate (GMA) as co-monomer and type of crosslinker) is discussed in this

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doi:10.1016/j.matchemphys.2008.07.019

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work. The polymeric systems considered were named as follows: poly(*N*-acryloyl-tris(hydroxymethyl)aminomethane-co-*N*,*N*′-methylenebisacrylamide) [poly(NAT–BIS)], poly(*N*-acryloyl-tris(hydroxymethyl)aminomethane-co-trimethylolpropane trimethacrylate [poly(NAT–TRIM)] and poly(*N*-acryloyl-tris(hydroxymethyl)aminomethane-co-glycidyl methacrylate-co-*N*,*N*′-methylenebisacrylamide) [poly(NAT–GMA–BIS)]. The rods were synthesized within glass tubes or in stainless steel HPLC columns as reactor.

2. Experimental

2.1. Materials

N-Acryloyl-tris(hydroxymethyl)aminomethane 93% (Aldrich, Steinheim, Germany); *N*,*N*′-methylenebisacrylamide 99% (Aldrich, Steinheim, Germany); trimethylolpropane trimethacrylate (technical grade; Aldrich, Steinheim, Germany); glycidyl methacrylate 97% (Aldrich, Steinheim, Germany); azobisisobutyronitrile (AIBN) 98% (Aldrich, Steinheim, Germany); dimethylsulfoxide (DMSO) 99.9% Anedra, Argentina); *n*-tetradecanol 95% (Fluka, Steinheim, Germany) and poly(ethylenglycol) 6000 (PEG 6000) (analytical grade; Fluka, Steinheim, Germany) were used as received.

2.2. Polymerization reactions

All polymerization mixtures were prepared in a glass tube (0.8 cm i.d. and 20 cm length). Firstly, a mono-vinyl monomer (NAT or a mixture of NAT:GMA) and a crosslinker (BIS or TRIM) were dissolved in a ternary porogenic mixture of DMSO, tetradecanol and PEG 6000. Since NAT and BIS are solid, their dissolution in the porogenic mixtures was carried out at the reaction temperature. At this temperature a homogeneous reaction mixture was attained. After the monomers were dissolved, the mixtures were purged with nitrogen for 10 min. Then, AIBN was added (1 wt.% with respect to monomers), and the glass tubes were sealed. Thus, each polymerization mixture was kept in the reaction vessel for 24 h at the selected temperature (55 or 70 °C). After this time, the glasses were broken and the rod polymers [poly(NAT–BIS)1-2-3; poly(NAT–TRIM)1-2-3 and poly(NAT–GMA–BIS)1-2-3] were cut into pieces and extracted with methanol in a Soxhlet apparatus for 24 h, and dried under vacuum to constant weight. The conversion was calculated from the weight of the crosslinked polymers as compared with the weight of the monomers in the feed solution. The experimental conditions used are summarized in Table 1.

In another set of experiments, poly(NAT–BIS) and poly(NAT–GMA–BIS) were also prepared within a stainless steel column (100-mm × 4.6-mm i.d.) giving poly(NAT–BIS)4 and poly(NAT–GMA–BIS)4. For this, each polymerization mixture was prepared in a glass tube, the AIBN was added and then, the final mixture was transvasated into the stainless steel column. In these cases, 70 °C and a porogenic mixture ratio of 72:14:14 of DMSO:$C_{14}H_{29}OH$:PEG 6000 were used. These experimental conditions are summarized in Table 2. The steel columns were sealed with PTFE plugs and put into the reaction vessel in which the polymerization occurred. After the reactions were completed, the plugs were replaced by column end fittings and the rods were exhaustively washed with methanol. Subsequently, the products were pushed out of the columns, cut into pieces and dried under vacuum to constant weight to study their porous properties.

2.3. Porous properties in dry state

The pore size distribution of the monolithic materials was determined by mercury intrusion porosimetry using an Autopore II 9220 Micromeritics (Norcross, USA), and their surface morphology was studied by Environmental Scanning Electron Microscopy (ESEM) using Philips XL-30 TMP PW 6635/45 equipment (Eindhoven, Netherlands). The images were recorded with a magnification of 20,000×. IR spectra were recorded on a Nicolet 5-SXC spectrometer (Madison, USA) on KBr disks. The thermogravimetric analyses (TGA) were performed with a TA Instrument H1-Res TGA 2950 (TA Instruments, New Castle, Delaware, USA). Samples (1.5–3.0 mg) were weighed in aluminum pans and heated at a scan rate of 10 °C min^{-1} between 25 and 500 °C in atmosphere of nitrogen.

3. Results and discussion

Polymer rods were prepared by free-radical crosslinking polymerization. Poly(NAT–BIS)1-4, poly(NAT–TRIM)1-3 and poly(NAT–GMA–BIS)1-4 consisted in solid rods; monomer conversion was close to 100%. Two different crosslinkers were used in the synthesis: BIS and TRIM; an epoxy containing monomer, GMA, was used as co-monomer to introduce oxirane functional groups into the supports. Tables 3–4 summarize their porous properties. The products were macroporous rods (which maintain their porosity in dry state and in a swollen state) since their porosity percentages were over 40% [22] and pore size was larger than 50 nm in all cases.

IR spectra of these rods showed the following characteristic signals (cm^{-1}):

Poly(NAT–BIS): 3670–3580 and 3460–3420 (–OH and –NH stretching vibrations, respectively), 1680–1630 (C=O stretching vibrations, amide band I), 1570–1515 and 1305–1200 (combination bands of N–H deformation and C–N stretching vibrations, amide bands II and III, respectively), 1280–1260 and 1075–1000 (–C–O stretching and O–H in-plane deformations of primary alcohol).
Poly(NAT–GMA–BIS): These products presented similar patterns to poly(NAT–BIS) in addition to new bands at 1726 and 802, due to the presence of the carbonyl absorption band of ester and epoxy groups, respectively.
Poly(NAT–TRIM): These products showed all the characteristic bands corresponding to the amide groups assigned for poly(NAT–BIS) products and a new band at 1732, due to the presence of the carbonyl ester group.

All the products resulted very stable with the temperature. The samples poly(NAT–BIS), poly(NAT–GMA–BIS) and poly(NAT–TRIM) begins to decompose at 205.0, 193.6 and 200.1 °C, respectively. Their decomposition peaks temperatures were found to be 383.85, 398.32 and 432.02 °C.

All the products presented mono-dispersed pore size distribution profiles which may be very important in real applications. Representative porosity data are shown in Fig. 1.

By SEM analysis performed on the various monoliths, it was found that all the products showed heterogeneous surfaces that consisted of large microglobules aggregated into clusters with

Table 1
Copolymerization conditions to obtain macroporous poly(NAT–BIS)1-3, poly(NAT–TRIM)1-3 and poly(NAT–GMA–BIS)1-3 products

Polymer	Mono-vinyl:crosslinking monomers (mol%)[a]	*T* (°C)	DMSO:PEG 6000:$C_{14}H_{29}OH$ (vol.%)
Poly(NAT–TRIM)1[b]	60:40	55	72:14:14
Poly(NAT–TRIM)2[b]	60:40	70	72:14:14
Poly(NAT–TRIM)3[b]	60:40	70	64:18:18
Poly(NAT–BIS)1[c]	60:40	55	72:14:14
Poly(NAT–BIS)2[c]	60:40	70	72:14:14
Poly(NAT–BIS)3[c]	60:40	70	64:18:18
Poly(NAT–GMA–BIS)1[d]	40:20:40	55	72:14:14
Poly(NAT–GMA–BIS)2[d]	40:20:40	70	72:14:14
Poly(NAT–GMA–BIS)3[d]	40:20:40	70	64:18:18

[a] Total mol monomers: 0.010.
[b] Total volume of the porogenic mixtures: 2.9 mL.
[c] Total volume of the porogenic mixtures: 3.6 mL.
[d] Total volume of the porogenic mixtures: 3.7 mL.

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Table 2
Copolymerization conditions of macroporous poly(NAT–BIS)4 and poly(NAT–GMA–BIS)4 within obtained into stainless steel columns

Polymer	Mono-vinyl:crosslinking monomers (mol%)[a]	T (°C)	DMSO:PEG 6000:$C_{14}H_{29}OH$ (vol.%)
Poly(NAT–BIS)4[b]	60:40	70	72:14:14
Poly(NAT–GMA–BIS)4[c]	30:30:40	70	72:14:14

[a] Total mol monomers: 0.010.
[b] Total volume of the porogenic mixtures: 3.6 mL.
[c] Total volume of the porogenic mixtures: 2.9 mL.

Table 3
Influence of temperature over porous properties of macroporous poly(NAT–BIS)1-2, poly(NAT–TRIM)1-2 and poly(NAT–GMA–BIS)1-2 products

Polymer	T (°C)	Dp, max[a] (nm)	Porosity (%)
Poly(NAT–TRIM)1	55	725.4	39.2
Poly(NAT–TRIM)2	70	558.2	40.2
Poly(NAT–BIS)1	55	225.9	51.0
Poly(NAT–BIS)2	70	129.0	46.0
Poly(NAT–GMA–BIS)1	55	57.5	55.5
Poly(NAT–GMA–BIS)2	70	68.1	49.4

[a] Pore size at the highest peak in the pore size distribution profile.

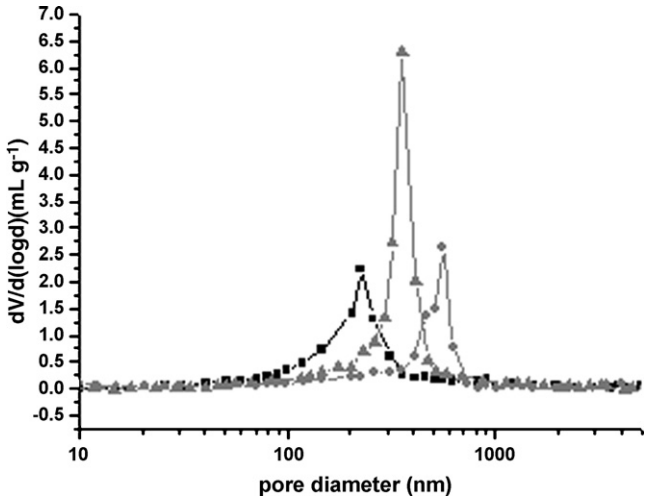

Fig. 1. Curves of pore size distribution from poly(NAT–BIS)1 (-■-), poly(NAT–TRIM)2 (-●-) and poly(NAT–GMA-BIS)3 (-▲-).

irregular voids. Some of the results are shown by way of example in Fig. 2.

This type of macroporous monolith materials was obtained by solution polymerization in a mold. They present a pore structure that allows a flow of a liquid through its large pores. There is an accepted mechanism of pore formation in a polymerization between mono-vinyl monomers (as glycidyl methacrylate and acrylamide) and di-vinyl monomers (ethyleneglycol dimethacrylate, di-vinylbenzene and *N*,*N*′-methylenebisacrylamide), initiator and porogenic solvent (poor solvent for the polymer) [12], summarized as follows. The formed radicals start the reaction in solution after which the polymers precipitate when become insoluble in the reaction medium. The nuclei swell with the monomers (as glycidyl methacrylate) present in the surrounding liquid, and the polymerization continues in solution but preferably within the swollen nuclei (the local concentration of the monomers is higher in them because the monomers are thermodynamically better solvating agent for the polymer than the porogen). If the monomers are solid (as acrylamide) and were dissolved to react, they probably tend to leave a less polar medium in order to stay within the more polar swollen nuclei, which also leads to a higher local concentration of monomers in the swollen nuclei than in the surrounding solution. The polymer chains in formation are captured by the growing nuclei and further increase their sizes. The nuclei associate in clusters being held together by polymer chains that crosslink the neighboring nuclei. So, the interconnected and grown clusters form a final porous matrix within the polymerization system.

3.1. Effect of the polymerization temperature

In general, the polymerization temperature–porous structure relation is a consequence of the increasing decomposition rate of the initiator (and the overall polymerization rate) on increasing the temperature [12,22].

Table 3 shows the porous properties of the different polymeric systems obtained at 55 and 70 °C. In general, it can be seen that an increase in the temperature leads to monoliths with pores of small size. This effect has already been observed in other macroporous polymer rods [2,12]. This behavior may be explained on the basis of the number of radicals formed per unit time. At lower temperatures, the rate of polymerization is slow, the number of free radicals formed is lower and, considering that the global monomer concentration in the polymerization mixture is the same for all cases, they are likely to form a smaller number of polymeric nuclei and microspheres of greater size. Therefore, the polymers present greater clusters and consequently the pore size (voids between clusters) is greater [22]. Contrarily, at higher reaction temperature, the greater is the number of free radicals generated per unit of time and the greater the number of nuclei and microspheres formed. Increasing

Table 4
Influence of the composition of porogenic mixtures on macroporous poly(NAT–BIS)2-3, poly(NAT–TRIM)2-3 and poly(NAT–GMA–BIS)2-3

Polymer	DMSO:PEG 6000:$C_{14}H_{29}OH$ (vol.%)	Dp, max[a] (nm)	Vp[b] (mL g^{-1})	Ss[c] (m^2 g^{-1})	Porosity (%)
Poly(NAT–TRIM)2	72:14:14	558.2	0.583	49.0	40.2
Poly(NAT–TRIM)3	64:18:18	823.8	0.622	48.3	41.3
Poly(NAT–BIS)2	72:14:14	129.0	0.565	87.1	46.0
Poly(NAT–BIS)3	64:18:18	206.1	0.899	41.9	56.6
Poly(NAT–GMA–BIS)2	72:14:14	68.1	0.719	86.9	49.6
Poly(NAT–GMA–BIS)3	64:18:18	355.3	1.133	38.4	56.4

[a] Pore size at the highest peak in the pore size distribution profile.
[b] Total pore volume.
[c] Specific surface area.

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the number of nuclei and microspheres necessarily decreases their sizes so that smaller voids or pores between them appear in the final copolymer.

Comparison of the three systems showed that the effect of temperature in the size of the pores is notorious in the poly(NAT–TRIM) system. At 55 °C, poly(NAT–TRIM)1 showed the greatest pore size at the highest peak in the distribution profile, at 725 nm. However, this polymer presented the lowest porosity (39.2%). Its morphology is shown in Fig. 2(b). It can be observed that the polymer chains could be greatly crosslinked between them as a consequence of the higher functionality (three vinyl groups) of the crosslinker used (TRIM) losing individuality. In spite of this, fewer pores, though of larger size, seemed to be formed.

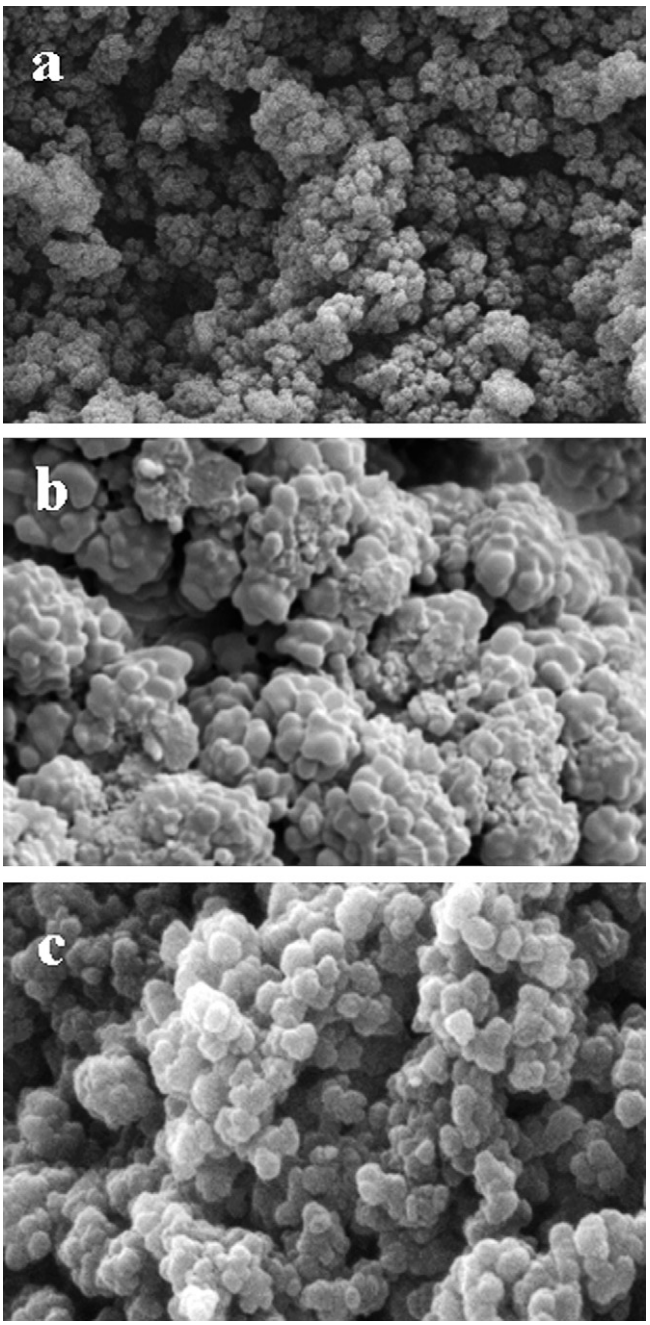

Fig. 2. Scanning electron micrographs (20,000×) of poly(NAT–BIS)1 (a); poly(NAT–TRIM)1 (b) and poly(NAT–GMA–BIS)1 (c) rods prepared at 55 °C.

Although the changes in the temperature reaction of the poly(NAT–BIS) and poly(NAT–GMA–BIS) systems did not cause important shifts in the maximum pore size distribution profiles, the monoliths obtained at 55 °C [poly(NAT–BIS)1 and poly(NAT–GMA–BIS)1] exhibited high porosity. In particular, poly(NAT–GMA–BIS)1 showed the highest porosity (55.5%). The pore volume and the specific surface area of this product were high (0.929 mL g^{-1} and 87.1 m^2 g^{-1}, respectively), which may be very important if the polymeric surface will undergo derivatization reactions.

Similar behaviors were observed for porous monolithic rods yielded from acrylamide and *N*,*N*′- methylenebisacrylamide as monomers [14] and alcohols of distinct lengths of chains as porogens. In this case, changes in the polymerization reaction between 70 and 55 °C produced few changes in the porous characteristics of the formed polymers yielding rods with pores of size and volume of approximately of 1000 nm and 1.6 mL g^{-1}, respectively.

3.2. Effects of the porogenic mixture

To obtain macroporous polymers, a pore-forming solvent (porogen, porogenic agent or inert diluent) is used in the polymerization mixture. The type and amount of porogenic mixture to be used is very important, because the porous properties may be affected according to the solvation of the polymeric chains in formation.

A solvating solvent, a non-solvating solvent or a linear polymer are the porogenic agents more frequently used. Mixtures of polymers and non-solvating solvents used as porogen have been reported [23–25]. In the previous work [16], we have obtained a macroporous polymer rod with both high porosity and large pore size using a ternary porogenic mixture constituted by DMSO as solvating solvent, and a mixture of tetradecanol and PEG 6000 as non-solvating diluents. In this work, the same ternary porogenic mixture has been used and the amount (percentage) of each solvent has been varied to obtain poly(NAT–BIS)2-3, poly(NAT–TRIM)2-3 and poly(NAT–GMA–BIS)2-3. The effect of this experimental condition on the porous properties was analyzed and quoted in Table 4.

As can be seen, an increase in the amount of non-solvating diluent (tetradecanol and PEG 6000) led to polymers with greater porosity shifting the maximum of the pore size distribution profiles towards a larger pore size. This effect could be explained by the phase separation occurring earlier in those systems that contain greater amounts of non-solvating diluent (tetradecanol and PEG 6000), because of a decrease in the solvating power of both monomers and polymer chains in formation [2]. Therefore, the nuclei of polymers in formation could segregate and capture preferably monomers from the local solution, and consequently increase their size. This process possibly occur since the monomers probably tend to pass from a less polar medium in order to stay within the more polar swollen nuclei in DMSO, which leads to a higher local concentration of monomers in the swollen nuclei than in the surrounding solution. The polymerization reaction would proceed principally in the swollen nuclei rather than in the solution. At the same time, the precipitated microglobules can attract the polymer chains in formation and coalesce with them, which would lead to a further increase in their size and therefore in the size of the pores formed between them [2,14]. Contrarily, if the solvating power of the solvent increases, the polarity within the nuclei is similar at that in the solution, the local monomer concentration is lower since the monomers are not forced to adsorb preferably into the nuclei and the polymerization occurs with formation of nuclei that keep individualized [14]. A large number of nuclei compete for the remaining monomers, leading a larger number of small globules that aggregate with small pores. So, as it was concluded previously [14], the

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Table 5
Porous properties of macroporous poly(NAT–BIS)4 and poly(NAT–GMA–BIS)4 rods obtained into stainless steel columns

Polymer	Dp, max[a] (nm)	Vp[b] (mL g^{-1})	Ss[c] (m^2 g^{-1})	Porosity (%)
Poly(NAT–BIS)4	177.3	0.884	83.5	56.0
Poly(NAT–BIS–GMA)4	264.7	0.793	45.9	46.6

[a] Pore size at the highest peak in the pore size distribution profile.
[b] Total pore volume.
[c] Specific surface area.

thermodynamic conditions that induce phase separation during the polymerization depend on the composition of the polymerization mixture containing monomers and the porogen.

Similar behaviors were observed for porous monolithic rods derived from systems formed by glycidyl methacrylate-co-ethyleneglycol dimethacrylate [2] and acrylamide-co-*N*,*N*′-methylenbisacrylamide [14]. In these, a diminution of the solvating power of the porogenic mixtures, allowed to yield porous monolithic rods with pores of great sizes. In the first case [2], increasing the amount of dodecanol as non-solvating diluent, rods with pores of approximately 2500 nm of size and volume and specific surface area of 1.39 mL g^{-1} and 6 m^2 g^{-1}, respectively, were obtained. In the second case [14], the solvating power of the porogenic mixture was changed using different alcohols of distinct lengths of chains. So, using dodecanol as non-solvating diluent, rods with pores of size and volume of 437 nm and 1.01 mL g^{-1}, respectively, were yielded.

Table 4 shows that an increase in pore volume and size was accompanied in all cases by a decrease in the specific surface area.

In particular, poly(NAT–GMA–BIS)3 presented a high porosity (56.4%), the highest pore volume (1.133 mL g^{-1}) and a considerable specific surface area (38.4 m^2 g^{-1}) for later derivatization reactions. This type of epoxy groups containing monoliths is very useful since these functional groups present in the matrices can be easily reacted with specific ligands to yield an affinity chromatography support.

On the other hand, the good porous properties of poly(NAT–TRIM)3 and the possibility of later activation of their hydroxyl groups to attain a specific ligand, turn it into a potential chromatography base support. It is known [26] that functionalized monoliths with pore size of about 700 nm yielded excellent separations in chromatography of proteins. So, the new material poly(NAT–TRIM)3 with a pore size of 823.8 nm can be compared with those reported previously by Josic et al. [26].

3.3. Polymerization reaction in stainless steel column

Synthesis of porous monoliths within molds of different walls, such as glass [14,27], HPLC columns [2,9,12], poly(propylene) (PP) [12] and poly(etheretherketone) (PEEK) tubes [28] has been reported previously. In this work, poly(NAT–BIS)4 and poly(NAT–GMA–BIS)4 have been synthesized directly within HPLC stainless steel columns. Table 5 shows the porous properties of these products.

Therefore, the porous properties and the specific surface area of these monoliths can turn them into promising supports to be used in processes requiring a high flow rate and enough surface area, such as various chromatography processes, solid-phase catalysis and solid-phase chemistry.

4. Conclusions

Three different macroporous monoliths systems were prepared using a ternary porogenic mixture. In all cases the monoliths consisted in solid and white rods, with monomer conversion near 100% and mono-dispersed pore size distribution profiles. The products presented the characteristics of macroporous rods with stable porosity in a dry state and in a swollen state, since their porosity percentages were over 40%. The results showed that a lower polymerization temperature and an increase in the amount of non-solvating diluents (tetradecanol and PEG 6000) in the mixture of reaction led to products with improved porous properties (larger pore size, pore volume and porosity).

In particular, two products proved promising. Firstly, poly(NAT–GMA–BIS)3 presented a high porosity (56.4%), pore volume (1.133 mL g^{-1}) and appreciable pore size at the highest peak in the distribution profiles (355.3 nm). This type of epoxy groups containing monoliths is very useful since these functional groups present in the matrices can be easily reacted with specific ligands to yield an affinity chromatography support. Secondly, poly(NAT–TRIM)3 presented the largest pore size at the highest peak in the distribution profiles (823.8 nm). Its good porous properties and the possibility of later activation of their hydroxyl groups to attain a specific ligand, turn it into a potential chromatography base support.

The porous properties of poly(NAT–BIS), poly(NAT–TRIM) and poly(NAT–GMA–BIS) resulted similar at those previously reported by another authors. So, we are contributing with new hydrophilic macroporous polymeric rods with potential applications in the chromatography field. Besides, we are presenting the synthesis of porous materials within stainless steel columns. This possibility is an advantage, for example, for the preparation of affinity chromatography supports with a very specific ligand, or for the immobilization of biological catalyst, or for the use as a separation medium for HPLC of a spectrum of molecules.

The modification of the yielded monoliths, in order to reach chromatography supports is being object of different assays.

Acknowledgements

The authors thank CONICET, FONCyT, ALFA II 0231 FI ELAPNET Polymeric Material and SECYT (Universidad Nacional de Córdoba) for their financial assistance. R.D. Arrua also acknowledges receipt of a fellowship from CONICET.

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