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Synthesis of crosslinked resin based on methacrylamide, styrene and divinylbenzene obtained from polymerization in aqueous suspension

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Abstract

A series of porous copolymer beads based on methacrylamide (MA), styrene and divinylbenzene (DVB) was prepared by aqueous suspension polymerization in the presence of diluents to act as precipitants. As MA is totally soluble into aqueous phase, the use of two types of phase transfer agent was investigated, namely: TritonX-100™ [polyoxyethylene-(10)-isooctylphenyl-ether] and tetrabutylammonium perchlorate. The effect of the diluents on the surface appearance and the porous structure of copolymer beads was studied. Suitable particle stabilisation was achieved by using a combination of two suspension agents, namely: gelatin and 2-hydroxy-ethyl-cellulose. The network resins were characterized by optical and scanning electron microscopy, IR spectroscopy, elemental analysis (CHN), apparent density, swelling in different solvents and specific area by BET method. It was observed that the MA incorporation was more effective when Triton™ was employed as phase transfer agent.

Keywords: Crosslinked resin; Methacrylamide; Suspension polymerization

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1. Introduction

Functional polymer networks have gained great importance in many fields of scientific research as well as for industrial applications. The interest stems from the variety of possible modifications of their chemical and physical properties [1–4]. Increasing environmental concerns in wastewater treatment has lead to the use of organic ligands anchored to solid supports in order to remove and recover important metal ions from aqueous solution [4–6]. In addition, network materials with porous structure are precursors for the preparation of various types of ion exchange resins, as inert supports for some types of chromatography (e.g. size exclusion chromatography, SEC), as supports for classical catalysts (e.g. acid catalysis for esterification or enzymes in biosynthesis) and as membranes for different purposes [7–11].

Porous polymer beads have been prepared by suspension copolymerization of vinyl monomers and crosslinking agent such as divinylbenzene (DVB) in presence of an inert diluent [12–14]. The detailed studies relating to the suspension copolymerization of styrene

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(ST) with DVB has been first developed by Kun and Kunin [15]. The porous structure formation has been attributed to phase separation of the copolymer formed during the polymerization process. Consequently, the selection of a diluent as a precipitant important in determining the porous structure of the polymer beads. For many applications, the presence of meso- and/or macropores is a key requirement to minimize diffusional limitations [3]. Almost all porous polymers are characterized by a relatively broad pore size distribution. Typically they contain micropores smaller than 2 nm in diameter, mesopores with sizes in the range varying from 2 to 50 nm and macropores with diameters larger than 50 nm. The pores are irregular voids between clusters of globules (mesopores) or voids inside a globule (micropores). Access to the pores is controlled by the hydrodynamic volume of the dissolved molecules. Molecules will only enter into those pores that are able to accommodate their size while smaller pores remain inaccessible for steric reasons [9,16].

Polymers and copolymers based on acrylamide, methacrylamide (MA) and their derivatives with very high molecular weights have gained more and more technical attention due to their uses in many fields, e.g. reversed-phase liquid chromatography (RPLC), chelating ion exchange resins etc. The literature sites many methods to prepare these polymers in bead form; inverse emulsion processes which usually lead to monodisperse submicrometer particles [17]; dispersion polymerization, in the course of which polymers precipitate from the reaction mixture in the form of very small particles [18]. The polymerization in a water-in-oil dispersion is also used to generate very high molecular weights. This process has advantages with respect to the low viscosity of the reaction mass and consequently, good heat transfer [17]. Aqueous suspension seems to be insuitable due to the solubility of acrylamide and MA into water.

Literature described porous polymers based on ST or (meth)acrylates in which the porous structure is achieved by use of inert diluent. This diluent should act as a good solvent for the monomer, but a rather poor solvent for the polymer network, promoting phase separation and porosity during the polymerization process. The wide variety of organic solvents which are not miscible with water makes "normal" suspension polymerization a very versatile and reliable procedure for manipulating the porous structure. However, in applications using hydrophobic resins based on ST/DVB, insufficient exchange rates in aqueous media were achieved [19,20]. For applications in aqueous systems, in particular in biomedicine or polymer supported reactions using enzymes, it is of interest to have a hydrophilic (wetting) polymer matrix. In this respect, to the best of our knowledge the use of phase transfer agents in aqueous suspension polymerization has not been evaluated to prepare copolymers beads based on MA, ST and DVB.

The aim of this work is, therefore, to obtain basic information about the synthesis of the copolymers based on MA and ST crosslinked with DVB using an aqueous suspension polymerization and also about the morphological control of these copolymers.

2. Experimental part

2.1. Materials

ST and DVB (consisted of 60% *meta*- and *para*-isomers of DVB and 40% ethylvinylbenzene) were kindly donated by Petroflex (Brazil) and Nitriflex (Brazil), respectively and used as received. Azo-α,α'-bisisobutyronitrile (AIBN) was kindly offered by Metacril (Brazil) and used after recrystallization from methanol. TritonX-100^{TM} and tetrabutylammonium perchlorate (TBA) were purchased from Aldrich Chemical Co. (USA) and Eastman Kodak Co. (USA), respectively and used as received. MA was purchased from Aldrich Chemical Co. (USA) and used without further purification. Other reagents and solvents were commercially purchased and used as received.

2.2. Synthesis of polymers

The suspension copolymerizations were performed in a 1 l, three-necked, round-bottomed flask reactor fitted with mechanical stirrer, reflux condenser with a silicon oil seal at its top and a nitrogen gas inlet tube. A typical recipe is described as following. The monomer phase has consisted of 0.49 mol of ST, 0.21 mol of MA, 0.20 mol of DVB, AIBN as initiator (1 mol% in relation to monomers) and diluent system. The content of the diluent mixture was fixed at 100% in ralation to the volume of the monomer mixture and its composition was varied according to the data given in Table 1. The aqueous phase has consisted of 520 ml of a 2 wt.% aqueous solution of Na_3PO_4, 2-hydroxy-ethyl-cellulose (HEC), gelatin and phase transfer agent (TritonX-100^{TM} or TBA) in according to the data shown in Table 1. It was also conducted a polymerization without the soluble monomer in water (MA). In a first stage, the aqueous medium was prepared by dissolving a suspension stabilizer (HEC or gelatin) or a mixture of them, during 24 h under stirring. Then Na_3PO_4 and phase transfer agent (TBA or Triton^{TM}) were dissolved. The aqueous phase is stirred (mechanical stirrer at 400 rpm) and the monomer phase was added to it and kept stirring at room temperature during 10 min. The suspension was maintained at 70 °C during 24 h. The copolymer particles obtained were thoroughly washed successively with water (four portions of 500 ml), hot water (eight portions of 500 ml) and acetone in a Soxhlet extractor. The water removes the salt, HEC, gelatin, TBA or TritonX-100^{TM}, MA

Table 1
Paramaters of copolymer synthesis

Polymerization #	Monomer mole ratio (MA/ST/DVB) (%)	Diluent Hep/Tol (%)	Transfer agent type/(%)[a]	Suspension agent type/(%)	Yield (%)
1	0/80/20	70/30	Triton™/20	Gelatin/0.5 and HEC/0.5	95
2	30/50/20	70/30	TBA/20	Gelatin/0.5 and HEC/0.5	60
3	60/20/20	70/30	Triton™/10	Gelatin/0.2	65
4	30/50/20	100/0	Triton™/30	–[b]	75
5	30/50/20	100/0	Triton™/20	–[b]	82
6	30/50/20	100/0	Triton™/10	–[b]	72
7	30/50/20	100/0	TBA/30	–[b]	64
8	30/50/20	100/0	TBA/20	–[b]	73
9	30/50/20	100/0	TBA/10	Gelatin/0.4	57
10	30/50/20	100/0	Triton™/10	Gelatin/1.0	75
11	30/50/20	100/0	TBA/10	Gelatin/1.0	73
12	30/50/20	100/0	Triton™/10	Gelatin/0.5 and HEC/0.5	58
13	30/50/20	50/50	Triton™/10	Gelatin/0.5 and HEC/0.5	70
14	30/50/20	100/0	Triton™/10	Gelatin/0.7 and HEC/0.7	70

Hep—heptane; Tol—toluene; TBA—tetrabutylammonium perchlorate; TritonX-100™—[polyoxyethylene-(10)-isooctylphenyl-ether]; HEC—2-hydroxy-ethyl-cellulose; MA—methacrylamide; ST—styrene; DVB—divinylbenzene. Polymerization conditions: time: 24 h; temperature: 60 °C; initiator: AIBN (1% M); monomer molar ratio: 30% methacrylamide/50% styrene/20% DVB; dilution: 100%; Na_3PO_4: 2% wt./v; organic phase/aqueous phase relation: 1/4.

[a] % Molar in relation to methacrylamide.

[b] No suspension agent.

homopolymer and unreacted one. As well as ketone removes the unreacted monomers (DVB and ST) and the diluent (heptane or/and toluene). The polymers were dried in an oven at 60 °C overnight.

2.3. Copolymer characterization

The pore size and surface area of copolymer samples (specific surface area, $S_{s,BET}$ in m^2/g) were determined by BJH and BET methods from low temperature nitrogen adsorption isotherms after degassing at 100 °C/1 mPa for 3 h on a Micromeritics apparatus. The shape and surface texture of the particles have been monitored by observation with a stereomicroscope Olympus SZ 10 and with a scanning electron microscope Zeiss DSM960. In order to observe the samples by scanning electron microscopy (SEM), they were coated with carbon and observed with 20 kV electron acceleration voltage. IR spectroscopy of the particles was carried out using a Perkin–Elmer or Nicolet FTIR spectrometer from KBr pellets. The elemental analyses were conducted using a CHN Perkin–Elmer 2400 apparatus. The apparent density of the particles was determined using ASTM D 1895-69 method [21]. The swelling was conducted in different solvents (toluene, methanol and water).

3. Results and discussion

In order to investigate the inert component content influence on the copolymers porous structure, several samples were synthesized keeping the monomer mixture content constant as can be seen in Table 1 (samples #2, #12 and #13). It is well know the MA is totally soluble in water. Hence, all copolymerizations were conducted using a phase transfer agent. By comparing the results shown in Table 2 and FTIR spectra, the use of Triton™ has been effective at some reaction conditions. As it can

Table 2
Elemental analyses (CHN) of resins

Polymer #[a]	Elemental analysis (CHN) (%)			
	Carbon	Hydrogen	Nitrogen	Oxygen
1	91.18	8.80	0	0
2	91.05	8.90	0	0
3	81.73	5.95	4.22	8.10
4	89.76	5.95	1.19	3.10
5	87.98	6.06	1.32	4.56
6	89.41	6.06	1.61	2.92
7	89.02	5.77	0.63	4.58
11	90.20	8.32	0.30	1.18

[a] The polymers are the same described in Table 1. Each CHN determination was made four times.

been seen in Table 1, the preparation of copolymer beads was always performed under a fixed dilution (100%) and monomer mixture (MA/ST/DVB = 3/5/2 mole proportion), except for the first and third copolymers (samples #1 and #3) and at the same reaction conditions. The FTIR spectra showed absorption bands attributed to: ν_{NH} and ν_{NH2} of primary amides at 3629 and 3197 cm^{-1} and $\nu_{C=O}$ of carbonyl of primary amide at 1664 cm^{-1}. Table 2 suggests the reaction conditions employed to produce the polymer of sample #3 has been more effective at incorporating MA into the polymer composition. Some spectra have presented an absorption due to $\nu_{C=O}$ of carbonyl of carboxylic acid at 1735 cm^{-1}. This indicates that some amide groups were probably hydrolyzed at the polymerization conditions employed in this work [22]. In fact, some reactions have produced a strong ammonia smell that was confirmed by Nessler reactive ($KI/HgCl_2/H_2O$) [23]. The presence of acrylic acid unit (hydrolysis product of MA unit) on the copolymer composition could be confirmed by results of elemental analysis (CHN) showed in Table 2, indicating very low total nitrogen content for copolymers of samples #4, #5 and #11. Although the copolymer of sample #3 has the highest nitrogen content, the oxygen content was also high indicating the hydrolysis process. This result could be confirmed by the FTIR spectrum which an absorption band due to $\nu_{C=O}$ of carboxylic acid at 1735 cm^{-1} is present.

The results shown in Tables 3 and 4 suggest that the surface characteristics and the porous structure of the copolymer have varied considerably depending on the employed diluent and monomer composition. The higher values of apparent density and swelling of the resin were achieved with a toluene/heptane mixture maybe due to an increased microporous nature (gel

Table 3
Resin characteristics—swelling and apparent density

Polymer #[a]	Apparent density (g/ml)	Swelling (%)		
		Toluene	Methanol	Water
1	0.46	80	10	10
2	0.45	85	10	10
3	0.25	60	55	50
4	0.26	28	40	25
5	0.29	25	35	20
6	0.33	35	35	20
7	0.31	35	28	15
8	0.30	38	13	13
9	0.39	55	25	15
10	0.29	43	15	15
11	0.36	40	20	15
12	0.44	43	30	20
13	0.63	115	30	20
14	0.34	33	37	27

[a] The polymers are the same described in Table 1.

Table 4
Paramaters of porous structure of copolymers

Polymer #[a]	Surface area (m^2/g)	Average pore diameter (nm)	Specific pore volume (cm^3/g)
1	70	160	0.12
2	75	90	0.05
3	130	178	0.10
4	30	260	0.28
7	11	nd	nd
9	89	nd	nd
10	68	nd	nd
11	30	290	0.27
12	20	250	0.14

nd—not determined.

[a] The polymers are the same described in Table 1.

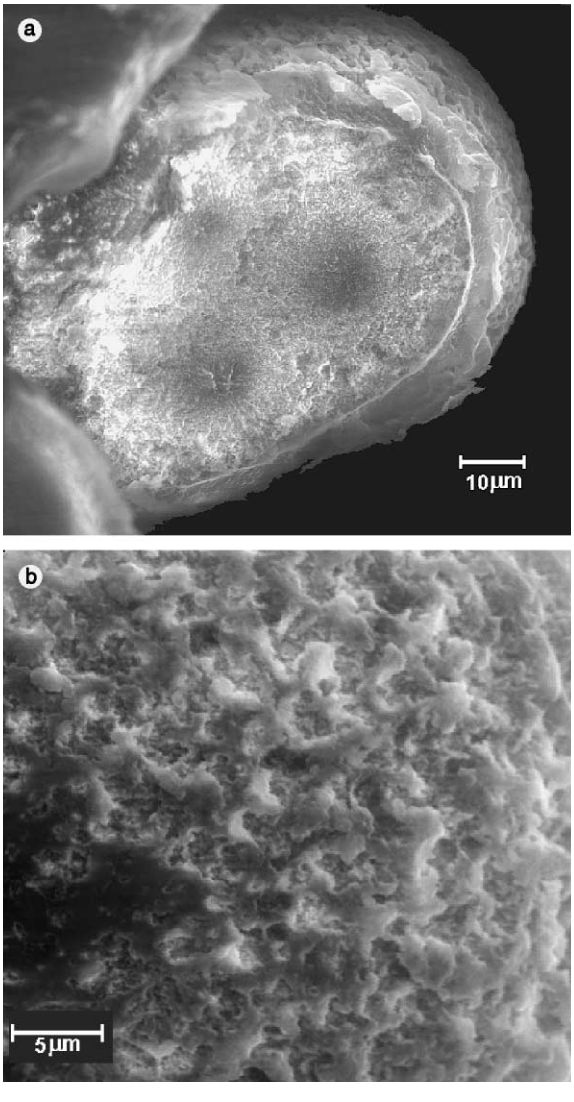

Fig. 1. Scanning electron micrographs of resin #12: (a) resin showing both external and internal parts; (b) external part.

phase). The larger pore diameters and the lower surface areas were achieved with heptane due to an increased meso/macroporous structure. Fig. 1a shows that the resin synthesized only with heptane (sample #12) presented two different domains. The external part (Fig. 1b) is more heterogeneous than the internal part. These differences between internal and external parts could be attributed to the migration of MA to monomer phase made by phase transfer. This transference of MA could produce a rugosity on the surface of polymer particles. The resin #13 was prepared with a mixture of toluene and heptane at 50/50 volume ratio. A bead of this resin was observed by SEM (Fig. 2). The internal part of a broken bead can be seen with more details in Fig. 2b, showing details of the dense internal part. It is possible to observe that this resin presents more homogeneous surface compared to the other ones. These characteristics could be attributed to the solvatant properties of toluene used as diluent [12–14]. Fig. 3 shows a stereomicroscopy micrograph of the resin #3 prepared with a mixture of heptane and toluene at 70/30 volume ratio. This micrograph shows clearly that the surface is very rugous. At these polymerization reaction conditions, the beads of copolymer did not agglutinate as it was observed in the other resins. The greater incorporation of MA (Table 2) into this copolymer disturbs the interface of nuclei and produces a surface rugosity. In addition, the coalescence of beads of other resins could be attributed to the combination of the action of the phase transfer agent and the MA migration from aqueous phase. Table 4 shows that this copolymer presents a larger value of specific area (S_s). All BET values of average pore diameter showed that the resins are mesoporous. The average pore diameter of the resins # 7, #9 and #10, probably larger than the other ones, were not determined by this method because the BET method is not sensible for macroporous.

Fig. 3. Stereo micrograph of resin #3 (magnification ×70).

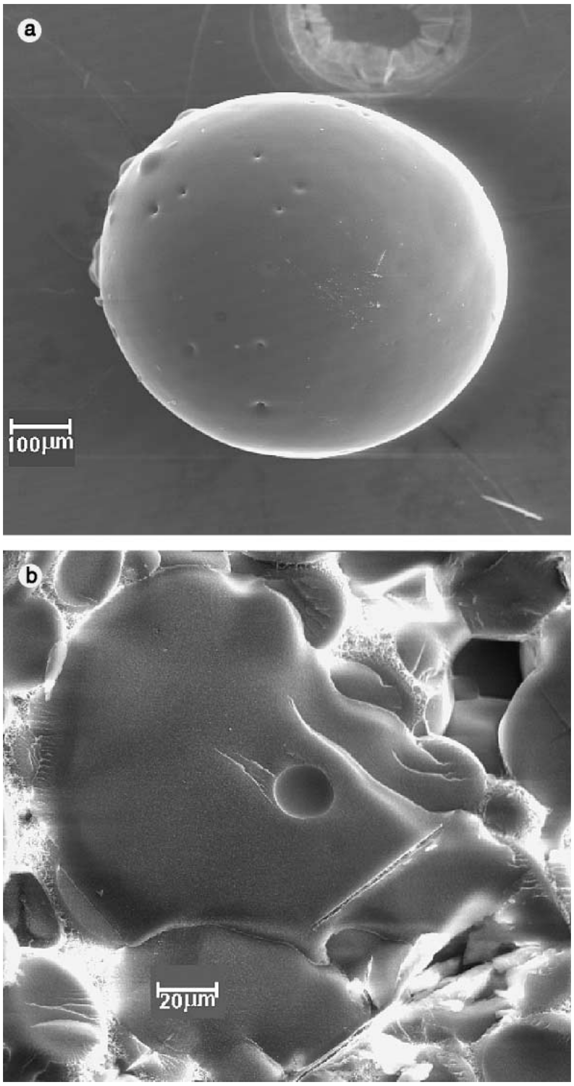

Fig. 2. Scanning electron micrographs of resin #13: (a) sphere—external part; (b) detail of internal part.

By swelling data of resin #3 and #4 (Table 3), it was possible to conclude that the hydrophilicity of beads increased. Hence, the beads swelling into water indicates also the incorporation of MA.

4. Conclusions

It is possible to copolymerize methacrylamide with ST and DVB by the aqueous suspension polymerization technique using phase transfer agent (Triton^{TM} and TBA). The incorporation of MA was more effective when Triton^{TM} was employed. The results presented in this work also show that the parameters of resins mesoporous based on methacrylamide, ST and DVB can be influenced by changing the type of diluent used.

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References

[1] Struck M, Widdecke H. Angew Makromol Chem 1996; 235:131–48.
[2] Bicak N, Sherrington D. React Funct Polym 1995;27:155–61.
[3] Kotha A, Raman RC, Ponrathnam S, Shewale JG. React Funct Polym 1996;28:227–33.
[4] Li W, Coughlin M, Albright RL, Fish RH. React Funct Polym 1995;28:89–96.
[5] Jovanovic SM, Nastasovic A, Jovanovic NN, Jeremic K, Savic Z. Angew Makromol Chem 1994;219:161–8.
[6] Jovanovic SM, Nastasovic A, Jovanovic NN, Jeremic K. Mater Sci Forum 1996;214:155–62.
[7] Abrams IM, Millar JR. React Funct Polym 1997;35:7–22.
[8] Sharma MM. React Funct Polym 1995;26:3–23.
[9] Smigol V, Svec F, Fréchet JMJ. Macromolecules 1993;26: 5615–20.
[10] Li WH, Li K, Stöver HDH. J Polym Sci, Part A: Polym Chem 1999;37:2295–303.
[11] Gauthier M, Frank PC. React Funct Polym 1996;31:67–79.
[12] Rabelo D, Coutinho FMB. Polym Bull 1993;31(50): 585–92.
[13] Rabelo D, Coutinho FMB. Eur Polym J 1994;30(6): 675–82.
[14] Kuroda H, Osawa Z. Eur Polym J 1995;31(1):57–62.
[15] Kun KA, Kunin R. J Polym Sci, Part A 1968;6:2689–701.
[16] Blondeau D, Bigan M, Despres P. React Funct Polym 1995;27:167–73.
[17] Baade W, Reichert K. Makromol Chem, Rapid Commun 1986;7:235–41.
[18] Lopour P, Sevcik S, Labsky J, Lednicky F. Angew Makromol Chem 1996;243:151–9.
[19] Rohr T, Knaus S, Sherrigton DC, Gruber H. Acta Polym 1999;50:286–92.
[20] Hering R, editor. Chelatbildende Ionenaustauscher. Berlin: Akademie-Verlag; 1977.
[21] ASTM D 1895-69, Apparent density, bulk factor and pourability of plastic materials.
[22] O'Connor Q. Rev Chem Soc 1970;24:553–64.
[23] Morita T. Assumpção RM. Manual de soluções, reagentes e solventes, Edgard Blücher Ltda., São Paulo, 1968. p. 329–30.