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SYNTHESIS AND CHARACTERIZATION OF POLYMERIC RESINS BASED ON METHYL METHACRYLATE AND DIVINYLBENZENE

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Received: November 18, 2011 / Revised: November 22, 2011 / Accepted: March 27, 2012

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Abstract. Porous spherical materials can be obtained by suspensions polymerization using a solvent pair. In this work porous resins based on methyl methacrylate and divinylbenzene were synthesized and characterized in terms of apparent density, specific area, pore volume, morphology, and swelling percentage. The results show that the diluents system (toluene/heptane or methylethylketone/cyclohexane) affect significantly the polymer properties. Furthermore, differences in the solubility parameters of the monomers and diluents affect the morphological structure of beads.

Keywords: synthesis, characterization, methyl methacrylate, divinylbenzene, acrylic copolymers, solubility.

1. Introduction

Suspension polymerization is a process employed in the polymer industry to produce materials in the form of beads, normally in the size range of 5–1000 μm [1-6]. During suspension polymerization, products are added to increase the stability of the monomer droplets. The majority of these droplet stabilizers used in suspension polymerization are water-soluble polymers or small inorganic particles that are adsorbed at the oil-water interface [7]. An important characteristic of the polymers obtained by suspension polymerization is the morphology of the inside part and external surface. This morphology is related to the degree to which the polymer dissolves, swells or precipitates in the monomer phase. Polymers are produced in the form of beads, which can be hard or soft depending on the monomer's composition and presence of a miscible diluent. The particle's morphology can also be influenced by the use of a diluent in the monomer, which

should be a good or a bad solvent for the polymer chains and must be extracted after polymerization. Careful choice of the diluent and the concentration/type of reticulation agent can produce a large porosity range in the beads [3].

In applications such as immobilization of enzymes and chromatographic columns, the porosity of the particles and presence of functional groups at the bead surface are important factors. The bead size and porosity are used to increase the diffusion and help prevent pressure drop. Many studies have been carried out on the effects of varying the concentration and type of porogenic diluent used. For oil-in-water systems, the porogenic diluents are generally saturated hydrocarbons, including alkanes, aromatics (toluene), aliphatic alcohols and carboxylic acids. The pore size obtained will depend on the mutual solubility of the monomer and diluent mixture and also the structure and polarity of the diluent [8, 9].

The objective of this work was to use different pairs of porogenic diluents (TOL/HEP and MEK/CH) to obtain MMA-DVB copolymers with different morphological structures.

2. Experimental

2.1. Materials

Commercial divinylbenzene (DVB) (55 % divinylbenzene, donated by Nitriflex S.A. – Rio de Janeiro – Brazil) and methyl methacrylate (donated by Metacril S.A., Bahia – Brazil) were utilized as received. Benzoyl peroxide (BPO) was used as an initiator at the concentration of 1 % (in relation to the number of total moles of the monomers). The solvents toluene (TOL), heptane (HEP), methyl ethyl ketone (MEK), and

cyclohexane (CH), of P.A. purity grade, were acquired from VETEC Ltda., Rio de Janeiro – Brazil. The porogenic diluent pairs used in the syntheses were TOL/HEP and MEK/CH. The suspension agents used were gelatin (GEL) and CaCO_3 , at the concentrations of 0.1 % (w/v) and 1.0 % (w/v), respectively. The salt to promote the salting out effect was Na_2SO_4 , at the concentration of 6.0 % (w/v).

2.2. Preparation of the Aqueous and Organic Phases

Before carrying out the polymerization, it is necessary to prepare the aqueous and organic phase separately. The aqueous phase was prepared by dissolving the suspension agents (GEL and CaCO_3) and inorganic salt (Na_2SO_4) in water. The organic phase was prepared by mixing the monomers (MMA and DVB) and the initiator (BPO) in an inert atmosphere at room temperature. The organic phase was pre-polymerized at 323 K for 30 min, under magnetic stirring. After this reaction time, a mixture of diluents was added to the pre-polymerized solution, under continued stirring for homogenization of the system. The reactions were conducted while varying the diluent system (TOL/HEP and MEK/CH) and its concentration [10, 11].

2.2.1. Synthesis of the copolymers

The prepared organic phase was then added to the aqueous phase under mechanical stirring at $41.89 \text{ rad}\cdot\text{s}^{-1}$, producing a suspension. This suspension was maintained at 363 K for 3.600 s in the suspension polymerization itself. The aqueous/organic phase ratio was kept at 3/1 (v/v) in all the reactions.

2.2.2. Purification of the copolymers

At the end of the reaction, the MMA/DVB beads were first treated with a solution of HCl 1M, for hydrolysis of the CaCO_3 , and then were washed in deionized distilled water to remove the acid traces. After this pre-treatment, the beads were washed completely in distilled water to remove the suspension agent, and with ethanol to remove the residual diluent mixture and monomers, until the filtrate was soluble in water. The beads were then screened in a Retsch model AS-200 hydraulic sieve shaker, using sieves with meshes of 25, 45, 100, 140, 200, 270, and 325. The particles with the size range between 45–100 mesh were washed with methanol and dried in a chamber with forced air at 333 K for 172, 800 s [10].

2.2.3. Characterization of the copolymers

The apparent density of the MMA-DVB copolymer beads was determined using an adaptation of the ASTM D1895 method [12]. The specific area was determined by nitrogen adsorption data, at different relative pressures, at liquid nitrogen temperature, by the BET method [13], using a Micromeritics ASAP 2010 adsorption analyzer. The pore volume of the copolymers was determined by the mercury porosimetry technique, using a Micromeritics Autopore 9420 instrument [14]. The external morphology of the polymer beads was observed under an Olympus SZ10 microscope with an Olympus camera attached. The swelling percentage was determined by the difference between the volume of the swollen copolymer in different solvents and the dry volume [4, 5].

3. Results and Discussion

The MMA-DVB polymers were synthesized in varying proportions with the aim of obtaining materials with different degrees of reticulation and hydrophilicity. All the polymers were obtained with varied diluent proportions to obtain porous structures. Two diluent pairs were used in the synthesis, TOL/HEP and MEK/CH.

3.1. MMA/DVB Resins Obtained with TOL/HEP

3.1.1. Characterization of the dry state

The influence of the reaction conditions on the structure of MMA/DVB polymers was significant. The formation of the morphological structure of the polymers obtained was investigated as a function of the different diluent pairs (TOL/HEP and MEK/CH), the variation of the ratio between the diluents in the reaction mixtures (100/0, 70/30, 30/70 and 0/100) and the molar ratio of the MMA/DVB monomers, which was done at 25/75, 50/50 and 75/25. All the other parameters were held constant.

The Hildebrand solubility parameter theory has in many cases proved effective in predicting the physical characteristics of reticulated polymers. Table 1 shows the values of the solubility parameters (d) for the diluents and monomers used to synthesize the MMA/DVB polymers. The difference between the solubility parameters (Δd) of the monomer and diluent are also shown to evidence the similarities between the solubilities of each pair [15].

The variation of the TOL/HEP proportions generated polymer structures with very different physical characteristics. In this case, the toluene acted as the solvent diluent and heptane as the non-solvent diluent. The difference between the solubility parameters of the MMA and DVB monomers and the heptane was about

3.07 MPa^{1/2}. Therefore, the formation of a more porous polymer structure could be expected because of the low affinity of the diluent for the polymer, which is formed

during the polymerization reaction. This can be confirmed by the results of the characterization of the synthesized polymers in the dry state (Table 2).

Table 1

Hildebrand solubility parameters [15]

Components	δ , (MPa) ^{1/2}	Component pairs	$\Delta\delta$, (cal/cm ³) ^{1/2*}
Toluene (TOL)	18.20	TOL/DVB	0.00
Heptane (HEP)	15.14	HEP/DVB	3.07
Cyclohexane (CH)	16.77	TOL/MMA	0.20
Methyl acetone (MEK)	19.02	HEP/MMA	2.86
Divinylbenzene (DVB)	18.20	CH/MMA	1.23
Methyl methacrylate (MMA)	18.00	MEK/MMA	1.02
PolyDVB	18.41	CH/DVB	1.43
PolyMMA	18.43	MEK/DVB	0.82

* ($\delta_1 - \delta_2$); δ_1 – solubility parameter of the polymer; δ_2 – solubility parameter of the monomer

Table 2

Characterization of the MMA/DVB (TOL/HEP) polymers

Resin ^a	MMA/DVB, % molar	Diluents TOL/HEP, v/v	$d_{ap} \cdot 10^3$, kg/m ³	$V_p \cdot 10^{-3}$, m ³ /kg	$A^d \cdot 10^3$, m ² /kg
MMA/DVB01	75/25	100/0	0.67	0.10	0
MMA/DVB02		70/30	0.58	0.27	39
MMA/DVB03		30/70	0.36	0.79	68
MMA/DVB04		0/100	0.31	0.89	32
MMA/DVB05	50/50	100/0	0.51	0.25	79
MMA/DVB06		70/30	0.45	0.41	198
MMA/DVB07		30/70	0.35	-	183
MMA/DVB08		0/100	0.31	0.96	209
MMA/DVB09	25/75	100/0	0.49	0.27	278
MMA/DVB10		70/30	0.46	0.40	385
MMA/DVB11		30/70	0.33	0.96	406
MMA/DVB12		0/100	0.31	1.10	314

Notes: ^a aqueous/organic phase ratio = 3/1; ^b d_{ap} is apparent density; ^c V_p is pore volume and ^d A is specific surface area

3.1.2. Apparent density, pore volume and specific area

The polymers obtained were characterized in the dry state for specific area, apparent density and pore volume, for a particle size range of 45–100 mesh ($f_{mean} = 2.05 \cdot 10^{-4}$ m). Table 2 shows that the increase of the DVB content in the composition of the monomer phase generated structures with greater specific areas, as a consequence of the increased reticulation promoted by the DVB. The changes in the diluent ratio caused significant changes in the MMA/DVB polymeric resin structures obtained. The three MMA/DVB series presented reduction of the apparent density and an increase in the

pore volume as increasing the *n*-heptane content, due to its incompatibility with the polymer.

The expected relationship between specific area and porous volume was not observed. In this case, in general, the specific area increases with the increase of the porous volume. It can be related to the MMA/water interfacial tension (11.7 mN/m) that is lower than that for the DVB/water (29.5 mN/m) due to the less non-polar MMA character. The difference in the interfacial tensions influences the coalition of the organic droplet: the lower the interfacial tension the higher the possibility of losing diluent to the water phase. Indeed, a higher quantity of toluene in the organic mixture leads to a lower amount of total voids in the resin. And, the lower the total voids the lower the specific area.

The influence of MMA-water interfacial tension is more significant for the systems containing a higher MMA/DVB ratio.

3.1.3. Optical microscopy

The macroporosity features can also be observed under an optical microscope. The declining solvent power leads to the formation of more heterogeneous structures, causing greater refraction of the light passing through the beads, which is observed by the increase in opacity of the polymers.

Fig. 1 presents micrographs of the MMA/DVB (50/50) samples, obtained with different TOL/HEP diluent ratios, showing the external visual aspect of the polymer materials. As the proportion of heptane increased, the surfaces became more opaque, which means the material

might have more porous characteristics. It can be observed that the material synthesized with 100 % toluene is transparent (Fig. 1a), and as the heptane content was increased in the diluent mixture, the transparency decreased. The polymer material obtained with TOL/HEP (70/30) is translucent, with a milky aspect (Fig. 1b). The one obtained with TOL/HEP (30/70) (Fig. 1c) is opaque, but with a shiny aspect to the beads. The polymer material synthesized with 100 % of heptane (Fig. 1d) presents a loss of transparency (opaque) and the beads are no longer shiny. Since heptane acts as a pore-forming agent, this material is highly porous. The other resins obtained with different MMA/DVB ratios (25/75 and 75/25) showed the same loss of transparency as the content of the non-solvent diluent (heptane) increased.

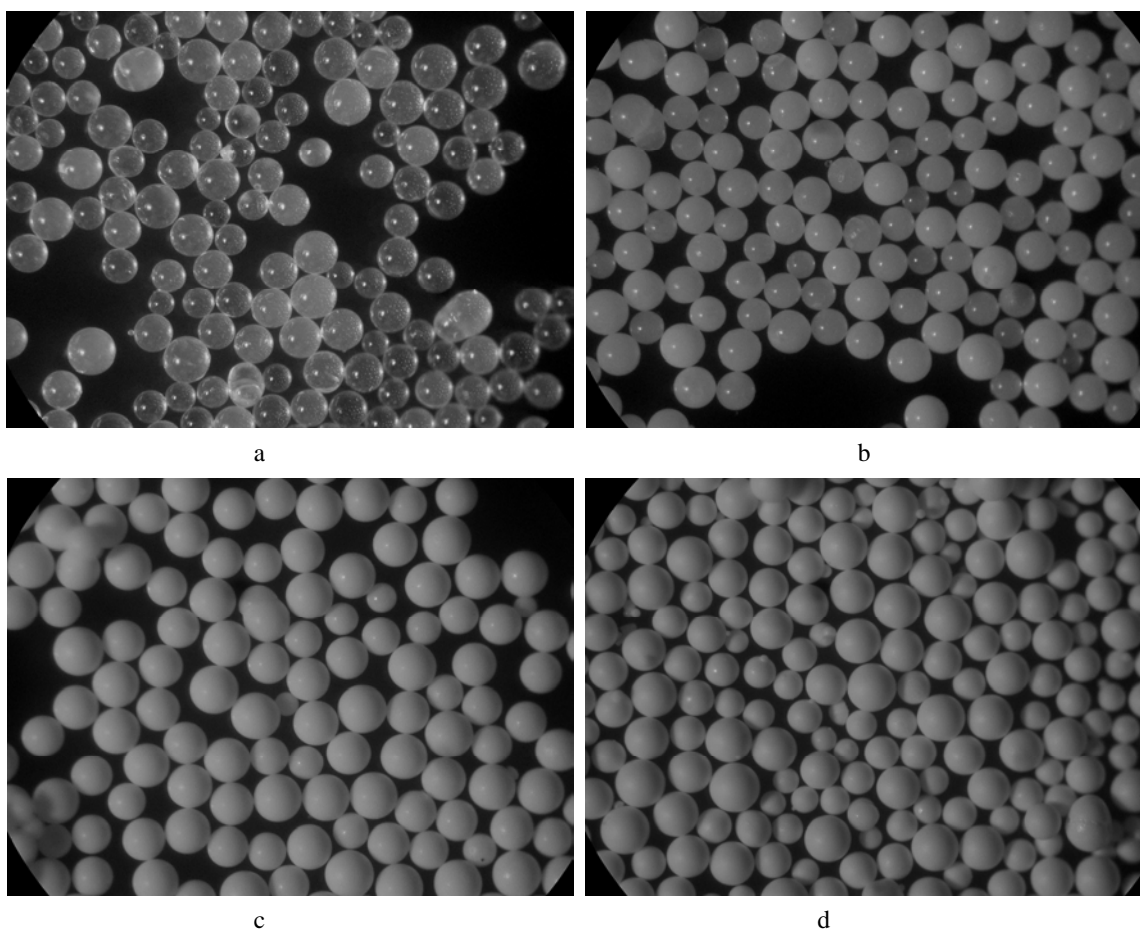


Fig. 1. Optical microscope micrographs of the outside surface of the MMA / DVB (50/50) polymers with different diluent ratios (TOL/HEP): 100/0 (a); 70/30 (b); 30/70 (c) and 0/100 (d); magnification of 45X

3.1.4. Characterization in the moist state

The characterization in the moist state was carried out to observe the behavior of the resins' morphological structure when in contact with different solvents having distinct solubility parameters. The objective of this study

was to verify the affinity between the polymers and solvents. Table 3 presents the results of the swelling percentage of the polymer materials based on MMA and DVB.

For organic solvents with slightly apolar characteristics (methanol, ethanol and acetone), there was

a tendency for the swelling to decline as the content of the non-solvent diluent increased. This variation is more evident for the resins with MMA/DVB ratio of 75/25. This behavior was expected, since in the system containing a higher non-solvent diluent content there is an earlier phase separation, generating materials with more rigid structures, and hence with less capacity to swell. With respect to the influence of the MMA/DVB proportion, it can be observed that in general the swelling increased with the reduction of the DVB content in the mixture of monomers. This behavior was also expected, since a lower DVB content produces a less reticulated material, that is, less subject to swelling and having greater affinity with the solvents used than the DVB, generating greater expansion of the network. Further in

relation to the swelling behavior in less apolar solvents, in general the percentage was greater in acetone, since among the solvents tested, it has a solubility parameter nearest to that of MMA, promoting greater polymer-solvent interaction.

In general, when the DVB content was kept constant, the swelling diminished with increasing heptane content in the mixture of diluents. The increase of heptane favors the formation of more rigid structures, hence less prone to swell. The resins synthesized with a monomer ratio of 50/50 presented swelling percentages with less variation for all the solvents studied. In this case, the slightly more apolar character of the MMA appears to offset the rigidity of the polymer chain caused by the increased DVB content.

Table 3

Influence of the reaction variables on the swelling percentage of the MMA/DVB (TOL/HEP) polymers

Resin	MMA/DVB, % molar	Diluents TOL/HEP, v/v	Swelling percentage				
			Methanol	Ethanol	Acetone	Toluene	Heptane
MMA/DVB01	75/25	100/0	73	88	85	-	-
MMA/DVB02		70/30	57	67	77	84	65
MMA/DVB03		30/70	24	26	33	70	41
MMA/DVB04		0/100	13	16	21	28	10
MMA/DVB05	50/50	100/0	43	52	51	52	77
MMA/DVB06		70/30	48	43	48	49	67
MMA/DVB07		30/70	25	22	27	33	31
MMA/DVB08		0/100	20	22	19	28	29
MMA/DVB09	25/75	100/0	45	46	51	60	51
MMA/DVB10		70/30	47	48	52	58	48
MMA/DVB11		30/70	21	20	22	25	28
MMA/DVB12		0/100	14	13	23	14	15

Note: - not determined

Table 4

Characterization of the MMA/DVB (MEK/CH) polymers

Resin ^a	MMA/DVB, % molar	Diluents MEK/CH, v/v	$d_{ap}^b \cdot 10^3$, kg/m ³	$V_p^c \cdot 10^3$, m ³ /kg	$A^d \cdot 10^3$, m ² /kg
MMA/DVB04	75/25	100/0	0.71	-	0
MMA/DVB03		30/70	0.68	-	0
MMA/DVB02		70/30	0.48	0.34	63
MMA/DVB01		0/100	0.41	0.61	73
MMA/DVB08	50/50	100/0	0.47	0.35	131
MMA/DVB07		30/70	0.55	-	155
MMA/DVB06		70/30	0.47	0.42	207
MMA/DVB05		0/100	0.36	0.73	242
MMA/DVB12	25/75	100/0	0.36	0.31	-
MMA/DVB11		30/70	0.45	0.34	-
MMA/DVB10		70/30	0.47	0.50	-
MMA/DVB09		0/100	0.45	0.62	419

Notes: ^a aqueous/organic phase ratio = 3/1; ^b d_{ap} is apparent density;

^c V_p is pore volume and

^d A is specific surface area; - not determined

3.1.5. MMA/DVB resins obtained with MEK/CH

Characterization of the dry state. For the MEK/CH diluent pair, the cyclohexane has less affinity for the MMA/DVB polymer, acting as a non-solvent diluent, and the methyl acetone has a smaller solubility parameter difference with the polymer, tending to have greater affinity for the chains, acts as a solvent diluent. The difference of solubility parameters of this pair of solvents when compared to the TOL/HEP pair caused significant changes in the morphological structure of the polymers synthesized. Table 4 shows the morphological characteristics (apparent density, pore volume and specific area) of the MMA/DVB polymers obtained in the synthesis with the MEK/CH solvent pair, in varying proportions.

In general an increase in the DVB content led to the formation of more reticulated structures and fewer pores, resulting in an increase in the specific area. The specific area value of the polymers also increased when the diluent mixture was enriched with the non-solvent diluent (CH). This increase was most pronounced for 50 % DVB.

For a determined DVB content, the reduction in the proportion of CH in the diluent mixture, that is, the increase in the solvent power of the system, generated polymers with greater apparent density. The structure formed became less porous, because the pore volume declined. This behavior might be related to the occurrence of less pronounced phase separation, due to the diluent mixture's greater affinity for the polymer with increasing solvent diluent content, leading to the formation of less porous structures. The effect of the MEK/CH proportion on the degree of phase separation was observed for all the MMA/DVB series: the difference in the pore volume produced by different diluent mixtures was greater or less depending on the degree of cross-links. For the polymers synthesized with the highest quantity of DVB (75 %), the difference between the values was very small, while for the copolymers synthesized with 25 % and 50 % DVB this difference was more accentuated.

For specific area the behavior was the same as for the TOL/HEP diluent system, that is, the specific area increased when pore volume increased. The suggested explanation here is the same as for the TOL/HEP diluent system, except that for the MEK/CH system a more pronounced "escape" of the MEK to the aqueous phase would be expected than for the toluene. Indeed, a comparison of Tables 2 and 4 for the MMA/DVB 50/50 ratio and 100 % non-solvent diluent, the pore volume is $0.96 \cdot 10^{-3} \text{ m}^3/\text{kg}$ and specific area is $209 \cdot 10^3 \text{ m}^2/\text{kg}$ when heptane was used, and the pore volume is $0.73 \cdot 10^{-3} \text{ m}^3/\text{kg}$ and specific area is $242 \cdot 10^3 \text{ m}^2/\text{kg}$ when cyclohexane was

used. The non-solvent diluents do not have affinity for the aqueous phase, and hence would not be expected the diluents "escape", making specific area smaller when pore volume is greater. A comparison of the results for the same MMA/DVB ratio of 50/50 and 100 % solvent diluent, where some "escape" would be expected to the aqueous phase (due to the low interfacial tension between the aqueous and organic phases and also to the only slight affinity of these diluents for the aqueous phase), shows that the relation between the pore volume and the specific area did not follow the usually observed behavior. For example, for polyDVB [16, or when a more apolar diluent is used: for 100 % toluene, the pore volume is equal to $0.25 \cdot 10^{-3} \text{ m}^3/\text{kg}$ and the specific area is $79 \cdot 10^3 \text{ m}^2/\text{kg}$, and for the 100 % methyl acetone, the pore volume is $0.35 \cdot 10^{-3} \text{ m}^3/\text{kg}$ and the specific area is $131 \cdot 10^3 \text{ m}^2/\text{kg}$.

The optical micrographs show the external visual aspect of the MMA/DVB (50/50) polymer materials obtained with different CH/MEK diluent ratios (Fig. 2). These results are very similar to those obtained for the resins synthesized with the TOL/HEP diluent pair. An increase in the MEK proportion caused the formation of more transparent surfaces, meaning this material could be less porous. It can be seen that the material synthesized with 100 % CH is opaque (Fig. 2a), and as the MEK content increased, the resins became more transparent. The polymer material obtained with MEK/CH (30/70) appears translucent, with a milky aspect (Fig. 2b). In contrast, the polymer materials obtained with MEK/CH 70/30 (Fig. 2c) and 0/100 (Fig. 2d) appear in the form of transparent beads. We believe that polymers synthesized with 100 % of the diluent, which acts to form pores, are more porous (Fig. 2a). The other resins obtained with different MMA/DVB ratios (25/75 and 75/25) showed the same behavior of increasing transparency with increasing content of the solvent diluent (MEK).

Characterization of the moist state. Table 5 shows the swelling percentages of the polymer materials based on MMA and DVB. For the slightly more polar organic solvents (methanol, ethanol and acetone), there was only a clear relationship between the MEK/CH ratio and the swelling percentage for the polymers at a 25/75 MMA/DVB ratio. It appears that less reticulated systems are less subject to variations in the interaction between the polymer and the non-solvent diluent, because these systems did not present a linear relation between the DVB content/diluent ratio and the swelling properties. This can be noted from the fluctuation of the swelling percentages for the series with 75/25 and 50/50 MMA/DVB ratios. For the 25/75 MMA/DVB series, the swelling capacity declined as the MEK content increased in the diluent mixture. Although there was a variation in the swelling percentage with the change in the MEK/CH diluent ratio, this did not behave as expected. This suggests that the

system with greater content of DVB and MEK in the synthesis of the polymers may have caused instability in the reaction system.

The swelling of the polymers in the organic solvents used in the synthesis (cyclohexane, which is more apolar, and methyl acetone, which is less apolar)

behaved similarly to that observed for the more polar solvents (methanol, ethanol and acetone), that is, there was only a linear relationship between the diluent ratio and swelling for the MMA/DVB 25/75 polymers. In this case, the swelling clearly decreased with an increasing content of the solvent diluent (MEK).

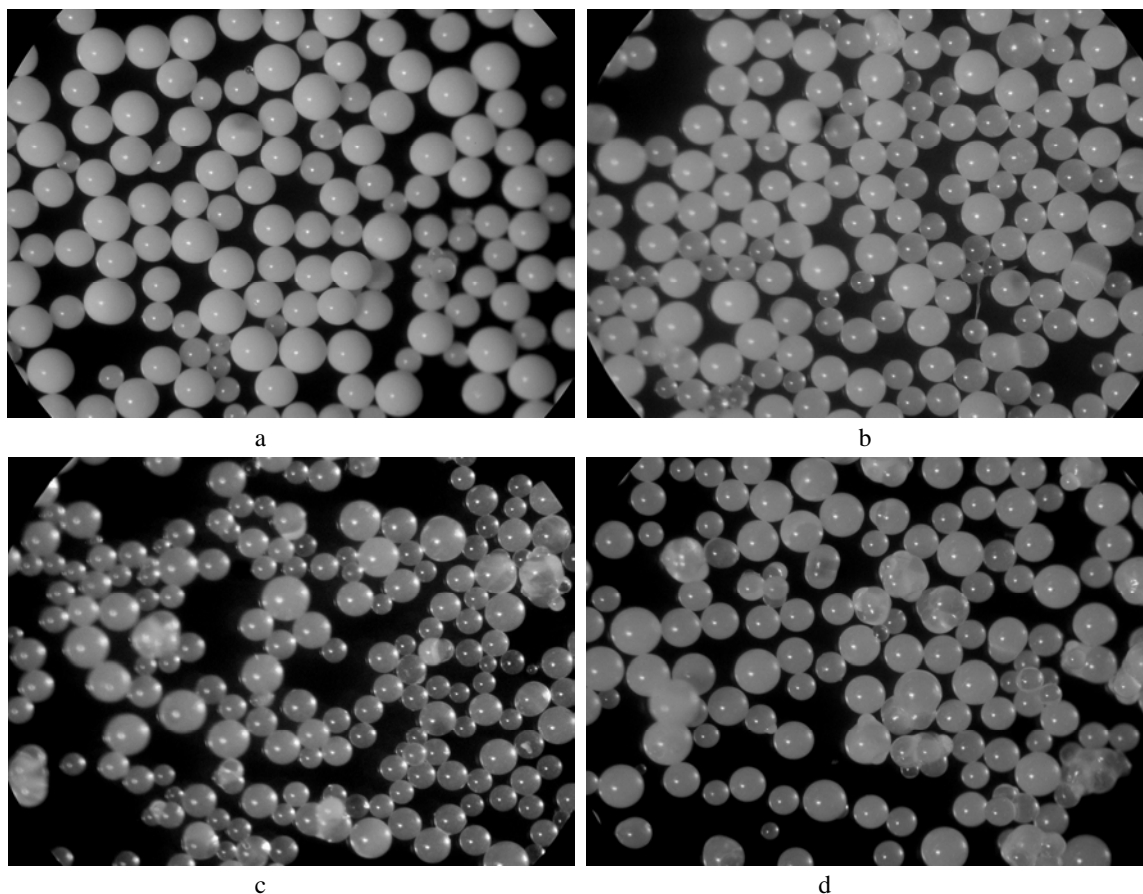


Fig. 2. Optical microscope micrographs of the outside surface of the MMA / DVB (50/50) polymers with different diluent ratios (MEK/CH): 0/100 (a); 30/70 (b); 70/30 (c) and 100/0 (d); magnification of 45X

Table 5

Influence of the reaction variables on the swelling percentage of the MMA/DVB (MEK/CH) polymers

Resin	MMA/DVB, % molar	Diluents MEK/CH, v/v	Swelling percentage				
			Methanol	Ethanol	Acetone	CH	MEK
MMA/DVB04	75/25	100/0	40	47	42	-	56
MMA/DVB03		70/30	47	51	56	-	67
MMA/DVB02		30/70	31	33	42	48	37
MMA/DVB01		0/100	30	38	55	27	46
MMA/DVB08	50/50	100/0	23	27	29	44	27
MMA/DVB07		70/30	33	35	39	73	40
MMA/DVB06		30/70	27	33	33	44	34
MMA/DVB05		0/100	23	26	29	50	32
MMA/DVB12	25/75	100/0	13	15	12	24	16
MMA/DVB11		70/30	30	26	27	31	28
MMA/DVB10		30/70	34	37	31	37	35
MMA/DVB09		0/100	40	41	45	39	43

Note: - not determined

4. Conclusions

The morphological characteristics of the polymer materials varied as a function of the ratio of monomers, type of diluent pair (TOL/HEP and MEK/CH) and proportion of solvent and non-solvent diluent. A reduction in the solvent/non-solvent diluent ratio caused a decline in the apparent density, an increase in the pore volume and led to the formation of more opaque beads. Differences in the solubility parameters of the monomers and diluents significantly affected the morphological structure of the polymers generated.

An increase in the MMA content facilitates the escape of the diluent that has greater affinity for the aqueous phase, reducing its quantity in the organic phase, and consequently, diminishing the total amount of voids in the resin, causing the resin formed to have a smaller specific area.

Acknowledgements

The authors thank to CNPQ, CAPES, FAPERJ and Petrobras for the financial support.

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СИНТЕЗ І ХАРАКТЕРИСТИКА ПОЛІМЕРНИХ СМОЛ НА ОСНОВІ МЕТИЛМЕТАКРИЛАТУ І ДИВІНІЛБЕНЗОЛА

Анотація. Полімеризацією суспензій з використанням суміші розчинників отримано пористі сферичні матеріали. Синтезовано пористі смоли на основі метилметакрилату і дивінілбензолу та визначено їх насипну густина, питому площу, об'єм пор, морфологію і відсоток набрякання. Показано, що система розчинників (толуол/гептан або метилетилкетон/циклогексан) значно впливає на властивості полімерів. Окрім того, відмінності в параметрах розчинності мономерів і розчинників впливає на морфологічну структуру кульок.

Ключові слова: синтез, характеристика, метилметакрилат, дивінілбензол, акрилові кополімери, розчинність.