Synthesis of Isobutyl Maleate–Divinylbenzene Microspheres by Different Techniques of Heterogeneous Polymerizations

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ABSTRACT: Copolymers of isobutyl maleate–divinylbenzene in the form of microspheres were obtained. In their preparation, the following techniques of heterogeneous polymerization were used: emulsion, modified emulsion, precipitation, suspension, and multistep swelling polymerization. Among the obtained microspheres, those synthesized by modified emulsion and multistep swelling polymerizations have a size suitable for HPLC purposes, whereas the product of suspension polymerization can be used as packing material for gas chromatography. Their porous structure was studied in detail. The influence of the polymerization technique on the particle size and morphology is discussed. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 2008–2015, 2004

Key words: copolymerization; crosslinking; porous structures; emulsion polymerization; microspheres

INTRODUCTION

The preparation of monosized polymeric beads is a subject of interest of both scientists and producers. Most frequently, polymeric beads are made by heterogeneous polymerization. The term "heterogeneous polymerization" includes a number of techniques. The most important are emulsion, dispersion, precipitation, suspension, and polymerization in the presence of seed particles. Depending on the type of heterogeneous polymerization, polymeric beads of different sizes can be obtained.[1]

In emulsion polymerization, the monomer is insoluble or scarcely soluble in the polymerization medium, but it is emulsified in it with the aid of a surfactant. The initiator is soluble in the medium and not in the monomer. Under these conditions, the monomer is present in the mixture partly in the form of droplets (about 1–10 μm) and partly in the form of soap-coated micelles (ca. 50–100 Å). These droplets act as the monomer reservoir. The initial locus for polymerization occurs in a solution (not in the emulsion droplets or micelles) to form radical oligomers, and, subsequently, the locus of polymerization is in the micelles. The monomer is transferred from the droplets into micelles to replace the monomer that has reacted. This process continues as long as monomer droplets exist.[2–5] Typically, monosized beads of a diameter in the range of 0.5–1 μm are obtained by this technique.[6–10]

In dispersion polymerization, the monomer and the initiator are both soluble in the polymerization medium, but the medium is a poor solvent for the resulting polymer. At an early stage of the process, the formation of primary particles takes place. These primary particles are swollen by the polymerization medium and/or the monomer. As a result, polymerization proceeds largely within the individual particles, leading to the formation of spherical particles of a diameter of 0.1–10 μm.[11–14]

In precipitation polymerization, the initial state of the reaction mixture is the same as that in dispersion polymerization. However, in this case, primary particles do not swell in the medium, and the polymerization is literally "precipitation polymerization."[16,17] Precipitation polymerization produces irregularly shaped and polydisperse particles. In suspension polymerization, the initiator is soluble in the monomer, and these two are insoluble in the polymerization medium. The monomer phase is suspended in the medium in the form of small droplets by using a suitable suspension agent. Diameters of the obtained beads are in the range of 0.05–2 mm.[3,18,19] An important advantage of this method is that it allows for the formation of porous products.[20–25]

Another method allowing for preparation of porous materials is polymerization in the presence of seed particles. Recently, it has gained growing importance as the technique that ensures preparation of monosized microspheres. The synthesis of porous polymeric particles with diameters of 5–20 μm is challenging, as such materials are widely used as column
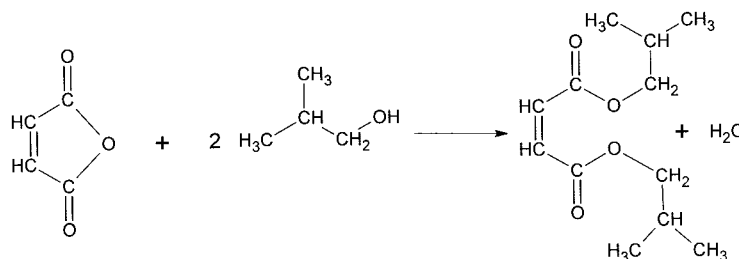
Figure 1 Synthesis of isobutyl maleate.

packing in high—performance liquid chromatography (HPLC) and gel permeation chromatography (GPC). Thus, the research connected with the production methods and formation mechanism of uniform macroporous particles have been intensively carried out.[26–30]

Unfortunately, the above methods have important limitations: Suspension polymerization gives a product with a broad particle-size distribution and polymerization in the presence of seed particles requires isolation of monosized polymeric seeds for further treatment. In this article, the synthesis of a new monomer isobutyl maleate is presented. This compound was used for the syntheses of polymeric microspheres by copolymerization with divinylbenzene. In preparation of polymeric microspheres, different techniques of heterogeneous polymerization were used. Attention was focused on the synthesis of porous monosized particles.

EXPERIMENTAL

Materials

Divinylbenzene (DVB, Merck, Darmstadt, Germany) was washed with a 5% aqueous sodium hydroxide to remove the inhibitors. Sodium dodecylsulfate (SDS) bis(2-ethylhexyl)sulfosuccinate sodium salt (DAC, BP), α,α'-azoisobutyronitrile (AIBN), polyvinylpyrrolidone K 90 (PVP), 1-hexadekanol (cetyl alcohol), benzoyl peroxide (BPO), and potassium peroxodisulfate, purchased from Fluka AG (Buchs, Switzerland), were used without purification. Toluene, dodecane, acetone, methanol, and ethanol (reagent grade) were from POCh (Gliwice, Poland), whereas styrene was from the Chemical Plant "Dwory S.A. (Oświęcim, Poland).

Tetrahydrofuran and acetonitrile were HPLC grade from Merck. Alkylophenones and phthalates were laboratory reagent grade, obtained from a number of sources. Polystyrene standards were from Toyo Soda (Tokyo, Japan) and Merck.

Synthesis of diisobutyl maleate

Maleic anhydride, 98 g, isobutyl alcohol, 362 mL, and H_2SO_4, 0.05 mL, were placed in a 1000-mL round-bottomed flask equipped with a distillation head and heated until the water evolution stopped. The excess of isobutyl alcohol was distilled off under reduced pressure. The received isobutyl maleate (MIB) was

TABLE I
Polymerization Recipe

| Method of polymerization	Monomers (g)		Diluents (mL)		Specific surface area (m^2/g)	Pore volume (cm^3/g)	Most probable pore diameter (Å)
	MIB	DVB	Toluene	n-Dodecane			
Suspension polymerization	5.530	9.470	—	22.5	475	0.699	—
			3.4	19.1	540	1.021	300
			11.25	11.25	565	1.207	150
			19.1	3.4	623	1.015	120
			22.5	—	447	0.507	25
Modified emulsion polymerization	5.530	9.470	19.1	3.4	578	1.280	93/250
Multistep swelling polymerization	5.530	9.470	19.1	3.4	616	1.300	315
Emulsion polymerization	5.530	9.470	—	—	348	0.918	43
Precipitation polymerization	0.553	0.947	—	—	489	0.320	63
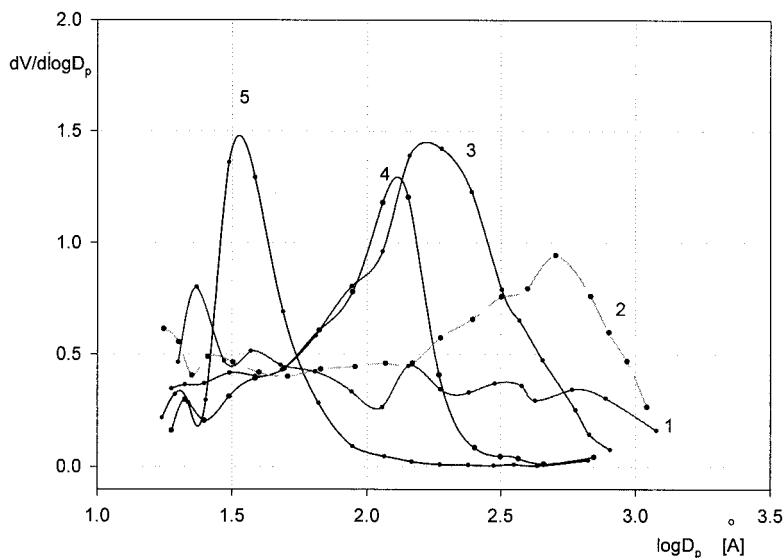
Figure 2 Differential PSD as a function of the log of pore diameter, D_p, for the studied copolymers obtained by suspension polymerization in the presence of a diluent containing different amounts of toluene: (1) 0%; (2) 15%; (3) 50%; (4) 85%; (5) 100%.

washed with distilled water (3 × 100 mL) and dried with anhydrous magnesium sulfate. The scheme of its synthesis is presented in Figure 1.

Suspension polymerization

Copolymerization was performed in an aqueous suspension medium. In a typical experiment, 195 mL of distilled water and 6.5 g of poly(vinyl alcohol) used as the suspension stabilizer were stirred for 6 h at 80°C in a three-necked flask fitted with a stirrer, water condenser, and thermometer. Then, the solution containing 15 g of the monomers and 0.075 g of AIBN in 22.5 mL of the diluents (toluene plus n-dodecane) was prepared and added while stirring to the aqueous medium. Copolymerization was performed for 20 h at 80°C. Porous beads formed in this process were sucked off, washed with hot water, and extracted in a Soxhlet apparatus with acetone, toluene, and methanol. The purified beads were separated into fractions
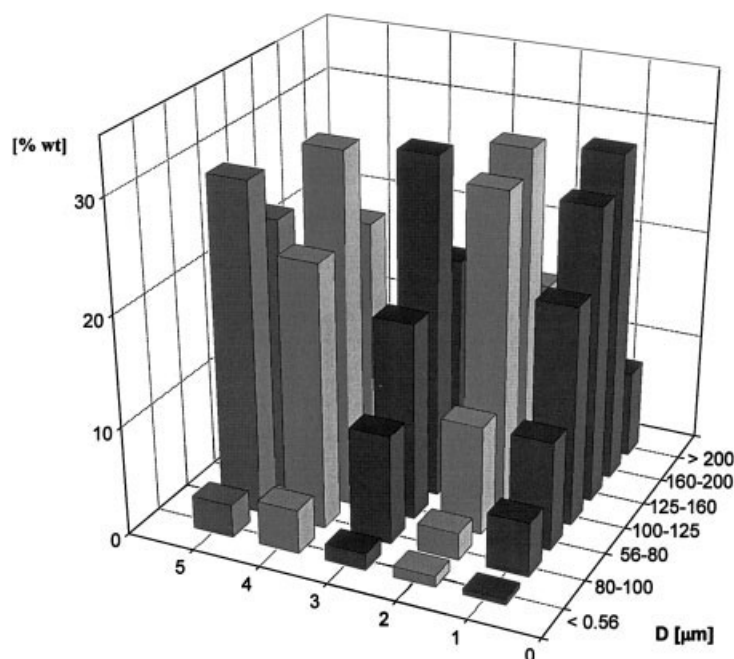
Figure 3 PSD of the MIB–DVB heads obtained by suspension polymerization in the presence of different toluene concentrations: (1) 0%; (2) 15%; (3) 50%; (4) 85%; (5) 100%.

by the sieving. The size distribution of the polymeric microspheres was obtained by using standard sieves (VEB Metallwerberei Neustadt, Germany). The bead-size distribution was reported as the percentage of the weight of the bead.

Emulsion copolymerization

Copolymerization was performed in an aqueous medium. In a typical experiment, 190 mL of distilled water and 2.2 g of the surfactant (DAC, BP) were stirred for 0.5 h at 80°C in a three-necked flask fitted with a stirrer, a water condenser, and a thermometer. Then, 15 g of the monomers were added while stirring. After 5 min, 0.15 g of the initiator (potassium peroxodisulfate) dissolved in 5 mL of water was added. Polymerization was performed for 20 h at 80°C. The particle-size distribution of the obtained latex was determined on an Zeta Plus/pals apparatus (Brookhaven Instruments Corp., USA).

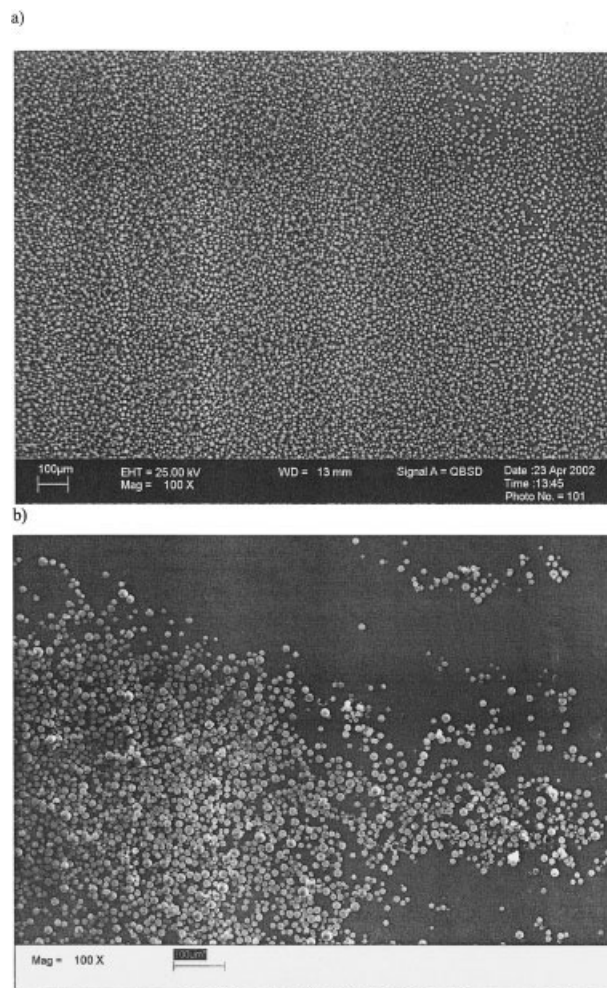## Modified emulsion polymerization

The copolymerization procedure was nearly the same as in emulsion polymerization: Only the water-soluble initiator (potassium peroxodisulfate) was replaced by an oil-soluble one (AIBN).

Preparation of polystyrene seed particles

Monodisperse polystyrene seed particles were produced by dispersion polymerization in an ethanol me-

Figure 4 Scanning electron micrographs of the MIB–DVB microspheres obtained by (a) modified emulsion and (b) multistep swelling polymerizations.

dium. PVP, 1.25 g, and cetyl alcohol, 0.5 g, were dissolved in 65 g ethanol in a 250/mL three-necked round-bottomed flask equipped with a mechanical stirrer, a thermometer and a reflux condenser. Then, a solution of 0.25 g AIBN in 25 g of styrene was added while stirring. Polymerization was carried out at 75°C for 24 h. After a typical centrifugal purification method, the seed particles were dispersed in the ethanol/water (1:1; v/v) mixture for further use.

Multistep swelling polymerization

The multistep swelling polymerization procedure was as follows: Six milliliters of an ethanol/water dispersion of polystyrene seed particles (0.07 g/mL) was placed in a 250-mL flask.

> I step swelling:
> An emulsion (droplet size <1 μm, verified by microscopy) was prepared from dibutyl phthalate

TABLE II
Average Size of the Particles Obtained by Different Techniques of Polymerization

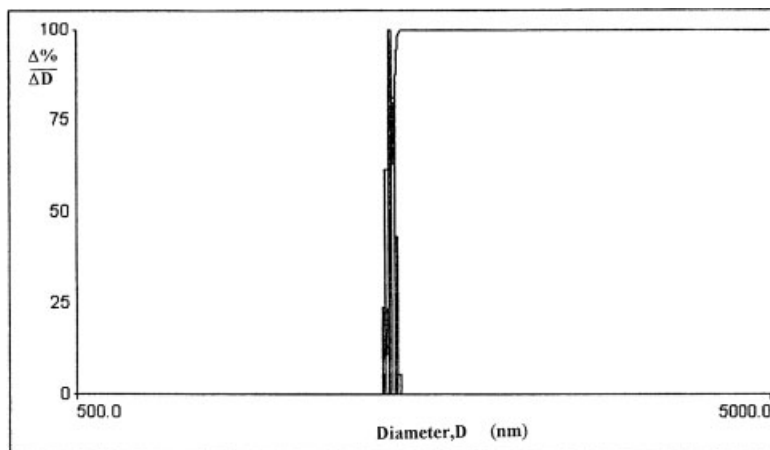| Technique	Average diameter (μm)	Weight percent (%)
Suspension polymerization	<56	2
	56–80	14.3
	80–100	19.5
	100–125	24.6
	125–160	20
	160–200	13.6
	>200	6
Modified emulsion polymerization	<15	35
	15–20	47
	>20	18
Multistep swelling polymerization	<15	24
	15–20	67
	>20	9
Precipitation polymerization	3–20	

Figure 5 PSD of the MIB–DVB microspheres obtained by emulsion polymerization.

(1.4 mL), BPO (0.24 g), SDS (0.15 g), and deionized water (100 mL) by sonication. Then, it was added to the dispersion of polystyrene seed and the first step of the swelling was carried out at room temperature for 24 h while stirring at 125 rpm.

II step swelling:

Dodecane, 19.1 mL, and toluene, 3.4 mL, were added and the mixture was stirred at room temperature for 12 h.

III step swelling:

The monomers and an aqueous solution of PVP (1.5 g in 35 mL of water) were added to the dispersion. The swelling was continued at room temperature for another 24 h while stirring at 125 rpm.

IV polymerization:

The dispersion was polymerized at 80°C for 20 h while stirring slowly.

After polymerization, the product was washed with hot water and extracted with acetone, methanol, and toluene in a Soxhlet apparatus to remove the stabilizer, surfactant, and unreacted monomers.

Precipitation copolymerization

Precipitation copolymerization was performed in a toluene/acetonitrile medium (30:70; v/v). The initiator (0.03 g of AIBN) was dissolved in a mixture of monomers (0.553 g of MIB and 0.947 of DVB). Then, the solution was added to the polymerization medium. Copolymerization was carried out at 70°C for 20 h.

Characterization of porous structure

Characterization of the porous structures was made using inverse exclusion chromatography (EC) and nitrogen adsorption–desorption measurements. The co-

polymers, in a dry state, were characterized using an adsorption analyzer ASAP 2405 (Micrometrics Inc, USA). Determinations were based on the measurements of the adsorption and desorption of nitrogen on the surface of the studied copolymer while cooling it to liquid nitrogen. The specific surface areas were calculated by the BET method, assuming that the area of a single nitrogen molecule is 16.2 $Å^2$.

In a swollen state, the copolymers were characterized by an inverse EC technique introduced by Halász and Martin.[15] The main assumption in this method is that, in the good solvent, chains of macromolecules form coils of a diameter corresponding to the polymer molecular weights. The diameter of the probe molecules (ϕ, in angstroms) was calculated from the equation[15]

$$\phi = 0.63 M_w^{0.59}$$

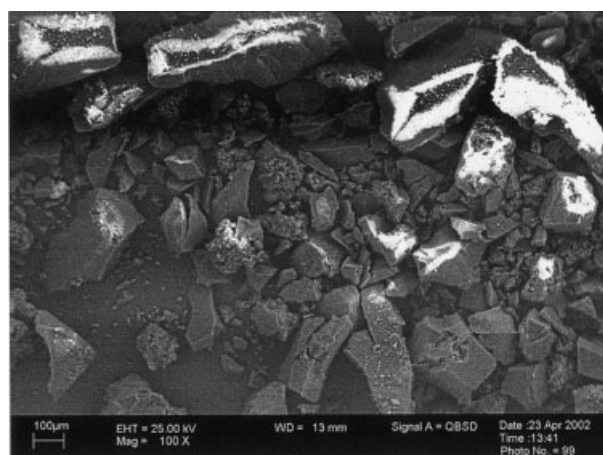where M_w is the Gram-molecular weight of the probe.

Figure 6 Scanning electron micrographs of the MIB–DVB copolymer obtained by precipitation polymerization.

TABLE III
Diameter (ϕ) and Retention Volume (V_R) of the Probes on the Porous Copolymers Obtained by Modified Emulsion and Multistep Swelling Polymerizations

				Retention volumes (mL)	
No.	Probe	Molecular weight (g)	ϕ (Å)	Modified–emulsion polymerization	Multistep swelling polymerization
1	Toluene	92.14	9.1	1.014	1.030
2	Acetophenone	120.15	10.6	1.012	1.027
3	Butyrophenone	148.20	12.0	1.009	1.011
4	Dimethyl phthalate	194.19	14.1	1.005	1.008
5	Diethyl phthalate	222.24	15.3	1.003	1.006
6	Dibutyl phthalate	278.35	17.4	1.001	1.003
7	Dinonyl phthlate	418.62	22.2	1.001	0.999
8	Didodecyl phthalate	502.78	24.7	1.001	0.997
9	Polystyrene	580	26.9	0.910	0.991
10	Polystyrene	666	29.2	0.907	0.889
11	Polystyrene	1050	38.2	0.902	0.883
12	Polystyrene	4000	84.1	0.890	0.765
13	Polystyrene	5100	97.0	0.871	0.654
14	Polystyrene	8000	126.5	0.773	0.544
15	Polystyrene	11,600	157.5	0.760	0.516
16	Polystyrene	30,300	277.6	0.663	0.495
17	Polystyrene	68,000	447.2	0.574	0.494
18	Polystyrene	120,000	625.3	0.554	0.494
19	Polystyrene	390,000	1253.3	0.550	0.494
20	Polystyrene	750,000	1843.4	0.550	0.494
21	Polystyrene	1,260,000	2503.6	0.550	0.494
22	Polystyrene	2,610,000	3847.3	0.550	0.494
23	Polystyrene	3,840,000	4831.7	0.550	0.494

The diameter of the probe molecule is associated with a pore diameter (ϕ) which corresponds to the smallest pore allowing unhindered access for the probe of a given molecular weight. For the pore-size probes, toluene, alkylphenones, phthalates, and polystyrenes were used.[11,12]

The cumulative pore-size distribution (PSD) was determined from the plot $1 - K_0(EC)$ versus lg ϕ, where $K_0(EC)$ is the distribution constant in EC calculated from the equation [15,16]

$$K_0(EC) = \frac{V_R - V_0}{V_p} = \frac{V_R - V_0}{V_i - V_0}$$

where V_R is the retention volume of the probe; V_0, the interstitial volume equal to the retention volume of a totally excluded molecule; V_i, the retention volume of a totally included molecule; and $V_p = V_i - V_0$, the pore volume. As previously, V_i is equal to the retention volume of toluene.[12]

The differential PSD $W(\phi)$ was obtained by computer differentiation of the polynomial-fitted cumulative curves (PSD) versus the logarithm of the probe pore diameter, lg ϕ. Six- to ten-order polynomials were used for fitting the experimental data.
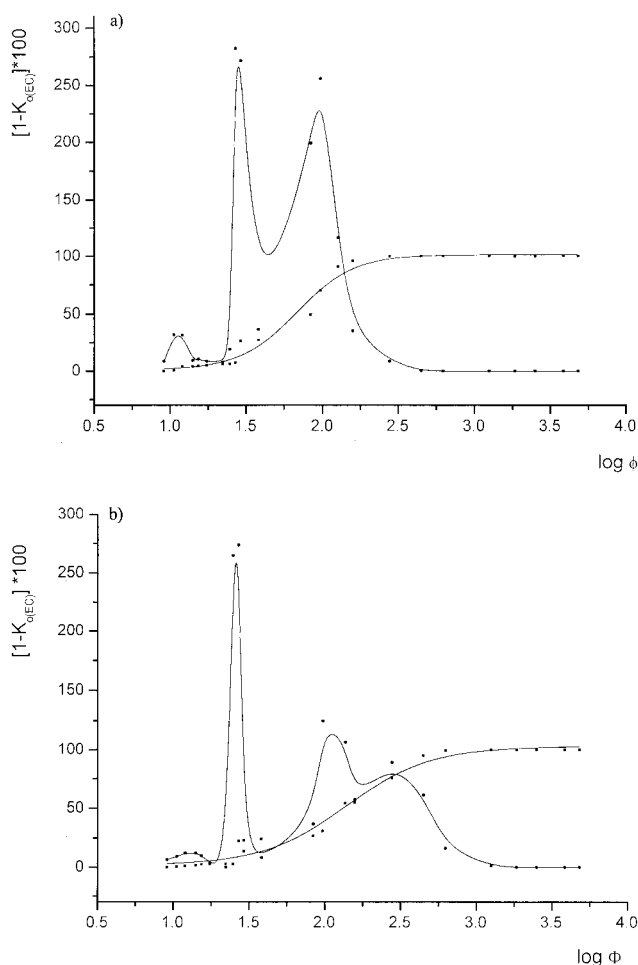
Swelling propensities of the copolymers (SP factors) were calculated according to Nevejans and Verzele[31]:

$$SP = \frac{p(THF) - p(H_2O)}{p(H_2O)}$$

where $p = P/\eta$ is the pressure relative to the mobile phase viscosity, η, and P is the column inlet pressure when THF and water were used as the mobile phases, respectively. The beads were imaged using a LEO 1430 VP numerical scanning electron microscope (Germany) with a countershaft and an energy-dispersive X-ray detector.

RESULTS AND DISCUSSION

The first attempts for the preparation of the MIB–DVB microspheres were made by suspension polymerization. This polymerization was carried out in the presence of pore-forming diluents: toluene and n-dodecane. The influence of a pore-forming composition on the porous structure of the beads was studied. For this reason, different concentrations of toluene in the mixture with n-dodecane were made in the syntheses, providing that other parameters such as the mol ratio of the monomers and the volume ratio of the diluents to the monomers were constant (Table I). By careful choice of the diluent composition, a wide range of porosities can be obtained. An increase of the toluene concentration causes an increase of specific surface

Figure 7 Cumulative and differential PSD curves for the MIB–DVB microspheres obtained by (a) modified–emulsion and (b) multistep swelling polymerizations.

polymers were shifted toward larger pore diameters (Fig. 2). Microspheres of a monodispersive PSD and the most probable pores of diameters of 120 Å suitable for chromatography purposes were obtained in the presence of a diluent containig 85% of toluene. Thus, such a composition of diluents was used in the syntheses by other techniques suitable for the preparation of porous materials.

As shown in Figure 3, the composition of the diluents affects also the size and the size distribution of the obtained microspheres. The smallest beads with the narrowest size distribution were produced in the presence of pure toluene. The fraction with diameters in the range 80–120 μm can be used as a stationary phase for gas chromatography.

The results from nitrogen-adsorption measurements show that the porous structure of the received microspheres depends on the methods of preparation. The same system of diluents employed in various techniques gives different values of the porous structure (Table I). The polymerization technique also affects the PSD. As usually, a broad particle size distribution was obtained for the MIB–DVB copolymer obtained by suspension polymerization (Table II).

Much smaller and uniform microspheres were obtained in a modified emulsion and multistep-swelling polymerizations (Fig. 4). In these cases, porous particles with diameters in the range of 5–20 μm were produced.

Regular microshperes of a narrow PSD were obtained in the emulsion polymerization (Fig. 5). Application of the precipitation technique for the preparation of an MIB–DVB copolymer led to the irregular particles presented in Figure 6.

Among the obtained microspheres, those synthesized by modified emulsion and multistep swelling polymerizations have a size suitable for HPLC purposes. Thus, these materials were packed into chromatographic columns to study their properties. As the packing in an HPLC column has a contact with organic solvents, its porous structure under such conditions should be known. From this reason, inverse EC measurements were made. The results are presented in Table III and Figure 7.

From these data and the weights of the copolymer in the chromatographic columns, the pore volume and the volume of micropores for the studied copolymers

areas. The largest specific area is observed for the copolymer obtained in presence of 85% (v/v) toluene. For the copolymer prepared in the presence of pure toluene, the specific surface area decreases significantly, reaching a smaller value than in the case of a copolymer obtained in the presence of pure n-dodecane. The diluent mixture composition also influences the pore volume and the average pore diameter. The system with a high concentration of toluene produces a structure with a small pore volume and small average pore diameters. By increasing the concentration of n-dodecane in this system, the PSD curves of the co-

TABLE IV
Porous Structure of the Studied Polymers in a Swollen State

Polymer	Pore volume (cm^3/g)	Contribution of micropores (cm^3/g)	Swelling propensity (SP factor)
Modified emulsion polymerization	1.169	0.024	0.90
Multistep swelling polymerization	1.072	0.084	0.87

were determined (Table IV). According to Nevejans and Verzele,[31] the term microporosity defines the pores with a diameter smaller than 20 Å. In the studies presented here, differences between the retention volumes of toluene having a molecule diameter $\phi = 9$ Å and the molecule of dinonyl phthalate ($\phi = 22$ Å) indicate the contribution of micropores to the internal structure of the copolymer (Fig. 7). The results from the inverse EC indicate that the pore volumes of both the studied copolymers are significantly larger than those obtained from the nitrogen-adsorption measurements. Both polymers contain micropores in their internal structure. The contribution of micropores in the structure of the polymer obtained by the multi-step swelling polymerization is significantly higher than that of the modified emulsion polymerization. Simultaneously, the swelling propensity for this copolymer is smaller, indicating that the polymer obtained by the multistep polymerization is porous in its whole structure. Its polystyrene cores are microporous but they are detectable after wetting with a good solvent. In consequence, these materials can have rather limited applications as column packings in HPLC. More suitable for this aim are microspheres obtained by modified emulsion polymerization.

References

1. Horák, D. Acta Polym 1996, 47, 20.
2. Emulsion Polymerization. Piirma, I., Ed.; Academic: New York, 1982.
3. Arshady, R. Colloid Polym Sci 1992, 270, 717.
4. Sajjadi, S. J Polym Sci Part A Polym Chem 2002, 40, 1652.
5. Chern, C. S.; Lee, C. J Polym Sci Part A Polym Chem 2002, 40, 1608.
6. Horák, D.; Shapoval, P. J Polym Sci Part A Polym Chem 1996, 34, 1857.
7. Horák, D. J Polym Sci Part A Polym Chem 1999, 37, 3785.
8. Lim, M. S.; Chen, H. J Polym Sci Part A Polym Chem 2000, 38, 1818.
9. Bourgealami, E.; Lang, J. Macromol Symp 2000, 151, 377.
10. Cao, K.; Li, B. F.; Huang, Y.; Li, B. G.; Pan, Z. R. Macromol Symp 2000, 150, 187.
11. Tseng, C. M.; Lu, N. Y.; El-Aasser, M. S.; Vanderhoff, J. W. J Polym Sci Part A Polym Chem 1986, 24, 2995.
12. Okubo, M.; Ikegami, K.; Yamamoto, Y. Colloid Polym Sci 1991, 269, 217.
13. Wang, D.; Dimonie, V. L.; Sudol, E. D.; El-Aasser, M. S. J Appl Polym Sci 2002, 84, 2692.
14. Wang, D.; Dimonie, V. L.; Sudol, E. D.; El-Aasser, M. S. J Appl Polym Sci 2002, 84, 2710.
15. Halasz, J.; Martin K.; Ber Busenges Phys Chem 1975, 79, 731.
16. Li, K.; Stöver, H. D. H. J Polym Sci Part A Polym Chem 1993, 31, 3257.
17. Frank, R. S.; Downey, J. S.; Stöver, H. D. H. J Polym Sci Part A Polym Chem 1998, 36, 2223.
18. Tuncel, A.; Piskin, E. J Appl Polym Sci 1996, 62, 789.
19. Kiatkamjornwong, S.; Traisaranapong, S.; Prasassarakich, P. J Porous Mater 1999, 6, 215.
20. Dowding, P. J.; Goodwin, J. W.; Vincent, B. Colloid Surf A 1998, 145, 263.
21. Okay, O. Prog Polym Sci 2000, 25, 711.
22. Polacco, G.; Basile, C.; Palla, M.; Semino, D. Polym J 2000, 32, 688.
23. Yuan, H. G.; Kalfas, G.; Ray, W. H. J Macromol Sci Rev Macromol Chem Phys C 1991, 31, 215.
24. Jegat, C.; Bois, A.; Camps, M. J Polym Sci Part B Polym Phys 2001, 39, 201.
25. Gawdzik, B.; Maciejewska, M. J Polym Sci Part A Polym Chem 2002, 40, 3079.
26. Ellingsen, T.; Aune, O.; Ugelstad, J.; Hagen, S. J Chromatogr 1990, 535, 147.
27. Hosoya, C. K.; Fréchet, J. M. J. J Polym Sci Part A Polym Chem 1993, 31, 2129.
28. Tuncel, A.; Tuncel, M.; Salih, B. J Appl Polym Sci 1999, 71, 2271.
29. Camli, T.; Tuncel, M.; Senel, S.; Tuncel, A. J Appl Polym Sci 2002, 84, 414.
30. Tuncel, A.; Tuncel, M.; Alagöz, C.; Bahar, T.; Ergun, B. Colloid Surf A 2002, 197, 79.
31. Nevejans, F.; Verzele, M. J Chromatogr 1985, 350, 145.