

# Preparation and Porous Structure Characterization of 4,4'-Diphenylmethane Dimethacrylate/Divinylbenzene Polymeric Particles

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Received 9 February 2004; accepted 21 July 2004

DOI 10.1002/app.21284

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Copolymers of isobutyl 4,4'-diphenylmethane dimethacrylate and divinylbenzene in the form of microspheres were obtained. For their preparation, the following techniques of heterogeneous polymerization were used: suspension polymerization, suspension-emulsion polymerization, and precipitation polymerization. Among the obtained microspheres, those synthesized by suspension-emulsion polymerization were of a size suitable for high-performance liquid chromatography, whereas the product of

suspension polymerization could be used as a packing material for gas chromatography. Their porous structure was studied in details. The influence of the polymerization technique on the particle size and morphology was examined. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 863–870, 2005

**Key words:** chromatography; copolymerization; crosslinking; structure

## INTRODUCTION

Macroporous poly(styrene-co-divinylbenzene) copolymers have been synthesized since the 1960s.<sup>1–3</sup> The growing interest in these materials for the last 30 years is due to their great number of applications as chromatographic packings, polymer-supported catalysts, polymer-immobilized extractants, and starting materials for the synthesis of ion-exchange resins. The specified applications of these copolymers are closely related to their porous structure and swelling properties. These copolymers are produced by suspension polymerization in the presence of pore-forming diluents. The morphology of the copolymers obtained by suspension polymerization is strongly influenced by the polymerization conditions: the monomers, diluent nature, dilution degree of the monomers, volume ratio of the diluents to monomers, reaction temperature, and so forth.<sup>4–6</sup>

Kun and Kunin<sup>7</sup> described the mechanism of pore formations as a three-stage process. In the first stage, a polymer with linear chains with pendant vinyl groups is formed. These reactive linear chains are called *globules*. As the polymerization continues, the pendant vinyl groups react intramolecularly, forming microgels and high-molecular-weight linear chains soluble in the diluent system. When the conversion increases,

polymer phase separation occurs. In this stage, microspheres are formed as a result of the agglomeration of polymeric microgels. In the second stage of porous structure formation, the microspheres aggregate and form larger agglomerates. In the third stage, the final product in the form of porous beads is obtained. The beads contain in their structure micropores, mesopores, and macropores as the spaces (volumes) fill with diluents.

This mechanism is generally accepted for styrene-divinylbenzene copolymers and is probably valid for other polymers synthesized by suspension polymerization.<sup>8–12</sup>

As with suspension polymerization products of broad particle size distributions have been obtained since the 1980s, an interesting modification of this method has been introduced.<sup>13–15</sup> This method is called *suspension-emulsion polymerization*.<sup>15</sup> In this technique, the monomers, initiators, and polymerization medium are the same as those in classic suspension polymerization. Only stabilizers of high molecular weights are replaced by anionic surfactants. The surfactant concentration should exceed the critical micelle concentration. As a result, beads of more uniform diameters are obtained than in conventional suspension polymerization. The mechanism of porous structure formation in this method is probably close to that proposed by Kun and Kunin.<sup>7</sup> Undoubtedly, diluents play an important role in porous structure formation.

In the 1990s, Stöver<sup>16</sup> described another polymerization method allowing the preparation of monodisperse materials. This method, called *precipitation poly-*

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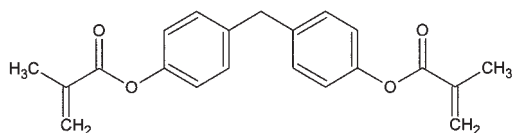


Figure 1 Chemical structure of DPMM.

merization, gives a product in the form of porous but irregular particles. The mechanism of this method is not well known.

In this article, the synthesis of 4,4'-diphenylmethane dimethacrylate/divinylbenzene (DPMM-DVB) copolymers in the form of beads is presented. For their preparation, suspension, suspension-emulsion, and precipitation polymerizations were used. The porous structure of the obtained beads was studied in detail.

## EXPERIMENTAL

### Materials

*p,p'*-Dihydroxydiphenylmethane was obtained by several crystallizations of commercially available Dian F (Organika-Sarzyna, Nowa Sarzyna, Poland). Divinylbenzene (DVB) from Merck (Darmstadt, Germany) was washed with a 5% aqueous solution of sodium hydroxide to remove inhibitors, whereas  $\alpha,\alpha'$ -azoisobutyronitrile (AIBN), sodium dodecyl sulfate, poly(vinyl pyrrolidone) (K 90), poly(vinyl alcohol) (PVA), 1-hexadecanol (cetyl alcohol), bis(2-ethylhexyl)sulfosuccinate sodium salt, methacryloyl chloride, chloroform, *n*-hexane, and acetonitrile, purchased from Fluka AG (Buchs, Switzerland), were used without purification. Toluene, dodecane, acetone, methanol, and ethanol (reagent-grade) were from POCH (Gliwice, Poland).

Tetrahydrofuran [THF; high-performance liquid chromatography (HPLC) grade] was acquired from Merck. Alkylphenones and phthalates, used as probes in inverse exclusion chromatography experiments (laboratory-reagent-grade), were obtained from a number of sources, whereas polystyrene standards were obtained from Toyo Soda (Tokyo, Japan).

### Preparation of 4,4'-diphenylmethane dimethacrylate (DPMM)

To 20 g of *p,p'*-dihydroxydiphenylmethane placed in a reactor, a solution containing 10 g of NaOH in 300 mL of distilled water was added with stirring. When *p,p'*-dihydroxydiphenylmethane was completely dissolved, 300 mL of chloroform was added, and the concentration of the reactor was cooled to 10°C. At this temperature, 22 mL of methacryloyl chloride was dropped under stirring. Stirring was continued for 1 h at room temperature. Then, the organic layer was

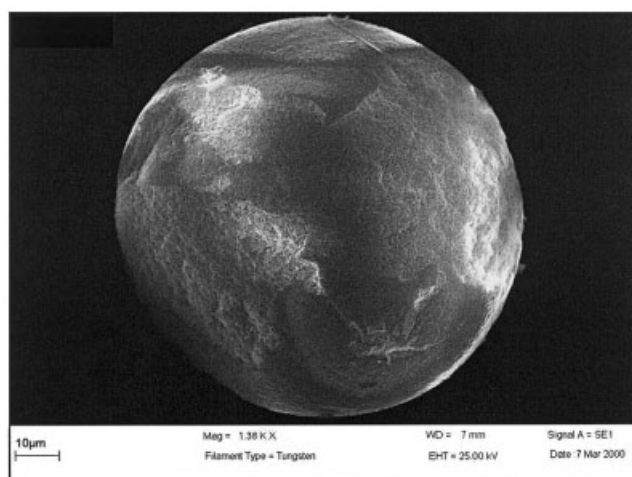
separated, washed several times with water, and dried. Chloroform was distilled off under reduced pressure. A solid product was crystallized from a mixture of chloroform and *n*-hexane (1:3 v/v).

The melting point of DPMM was 72°C. The chemical structure of this compound is presented in Figure 1.

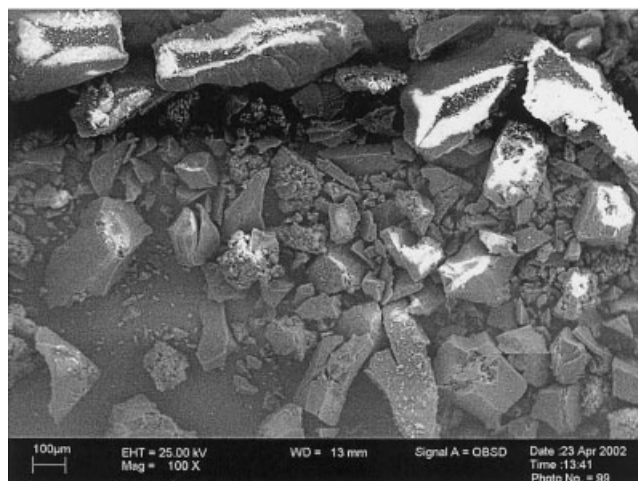
### Preparation of 4,4'-diphenylmethane dimethacrylate/divinylbenzene (DPMM-DVB) copolymers

#### Suspension polymerization

The copolymerization was performed in an aqueous suspension medium. In a typical experiment, 195 mL of distilled water and 6.5 g of PVA were stirred for 6 h at 80°C in a three-necked flask fitted with a stirrer, water condenser, and thermometer. Then, a solution



(a)



(b)

Figure 2 Scanning electron micrographs of the DPMM-DVB microspheres obtained by (a) suspension and (b) precipitation polymerization.

TABLE I  
Polymerization Recipe

Method of polymerization	Monomer (g)		Diluent (mL)		Specific surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Most probable pore diameter (Å)
	DPMM	DVB	Toluene	<i>n</i> -Dodecane			
Suspension polymerization	4.186	10.814	—	22.50	—	—	—
			3.40	19.10	21	0.023	520
			11.25	11.25	109	0.312	415
			19.10	3.40	143	0.345	55
Suspension-emulsion polymerization	4.186	10.814	22.50	—	7	0.009	24
			19.10	3.40	248	0.562	96
Precipitation polymerization	0.419	1.081	—	—	316	0.320	65

containing 15 g of the monomers and 0.075 g of AIBN in 22.5 mL of the diluents (toluene and *n*-dodecane) was prepared and added with stirring to the aqueous medium. The copolymerization was performed for 20 h at 80°C. Porous beads that 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 by sieving.

#### Suspension-emulsion polymerization

The suspension-emulsion copolymerization was nearly the same as the suspension polymerization, except that the stabilizer (PVA) was replaced by an emulsifier [2.2 g of bis(2-ethylhexyl)sulfosuccinate sodium salt].

#### Precipitation polymerization

Precipitation polymerization 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 (0.418 g of DPMM and 1.081 g of DVB). Then, the solution was added to the polymerization medium. The copolymerization was carried out for 20 h at 70°C.

#### Porous structure characterization

Parameters such as the specific surface areas, pore volumes, pore size distributions, and average pore diameters were determined via nitrogen adsorption on the surface of the studied stationary phases in a dry state. The specific surface areas were calculated with the Brunauer-Emmett-Teller (BET) method under the assumption that the area of a single nitrogen molecule was 16.2 Å<sup>2</sup>. These determinations were made with an ASAP 2405 adsorption analyzer (Micrometrics, Inc., Londonderry, NH). The measurements of the surface properties of the copolymers were preceded by the activation of the samples at 200°C for 2 h.

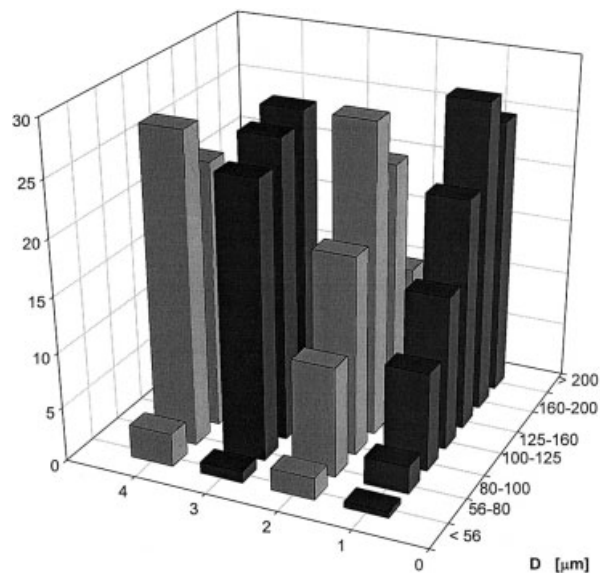
The beads were imaged with a Leo (Munich, Germany) 1430 VP numerical scanning electron microscope with a countershaft and an energy-dispersive X-ray detector.

In a swollen state, the beads were characterized with the inverse exclusion chromatography technique introduced by Halász and Martin.<sup>17</sup> The main assumption in this method is that in a good solvent chains of macromolecules form coils of a diameter corresponding to the polymer molecular weights. The diameter of the probe molecules ( $\Phi$ ; Å) was calculated as follows:<sup>18</sup>

$$\Phi = 0.63M_w^{0.59} \quad (1)$$

TABLE II  
Diameter and Retention Volume of the Probes on the Porous Copolymer Obtained by Suspension-Emulsion Polymerization

Probe	Molecular weight (g)	Diameter (Å)	Retention volume (mL)
1. Toluene	92.14	9.1	1.18
2. Acetophenone	120.15	10.6	1.20
3. Butyrophenone	148.20	12.1	1.18
4. Dimethyl phthalate	194.19	14.1	1.16
5. Diethyl phthalate	222.24	15.3	1.15
6. Dibutyl phthalate	278.35	17.4	1.12
7. Dipentyl phthalate	306.41	18.5	1.11
8. Dioctyl phthalate	390.57	21.3	1.10
9. Dinonyl phthalate	418.62	22.2	1.08
10. Didodecyl phthalate	502.78	24.7	1.06
11. Polystyrene	580	26.9	1.05
12. Polystyrene	2,450	62.9	1.00
13. Polystyrene	5,100	97.0	0.97
14. Polystyrene	11,600	157.5	0.91
15. Polystyrene	30,300	277.6	0.82
16. Polystyrene	68,000	447.1	0.71
17. Polystyrene	120,000	625.3	0.60
18. Polystyrene	390,000	1,253.3	0.60
19. Polystyrene	750,000	1,843.4	0.60
20. Polystyrene	1,260,000	2,503.6	0.60
21. Polystyrene	2,750,000	3,967.8	0.60



**Figure 3** Particle size distribution for the DPMM-DVB copolymer obtained by suspension polymerization in the presence of diluents containing different toluene concentrations: (1) 15, (2) 50, (3) 85, and (4) 100%.

where  $M_w$  is the molecular weight of the probe. The diameter of the probe molecule is associated with a pore diameter ( $\Phi$ ), which corresponds to the smallest pore allowing unhindered access for a probe of a given molecular weight.

As pore-size probes, toluene, alkylphenones, phthalates, and polystyrenes were used.<sup>19,20</sup>

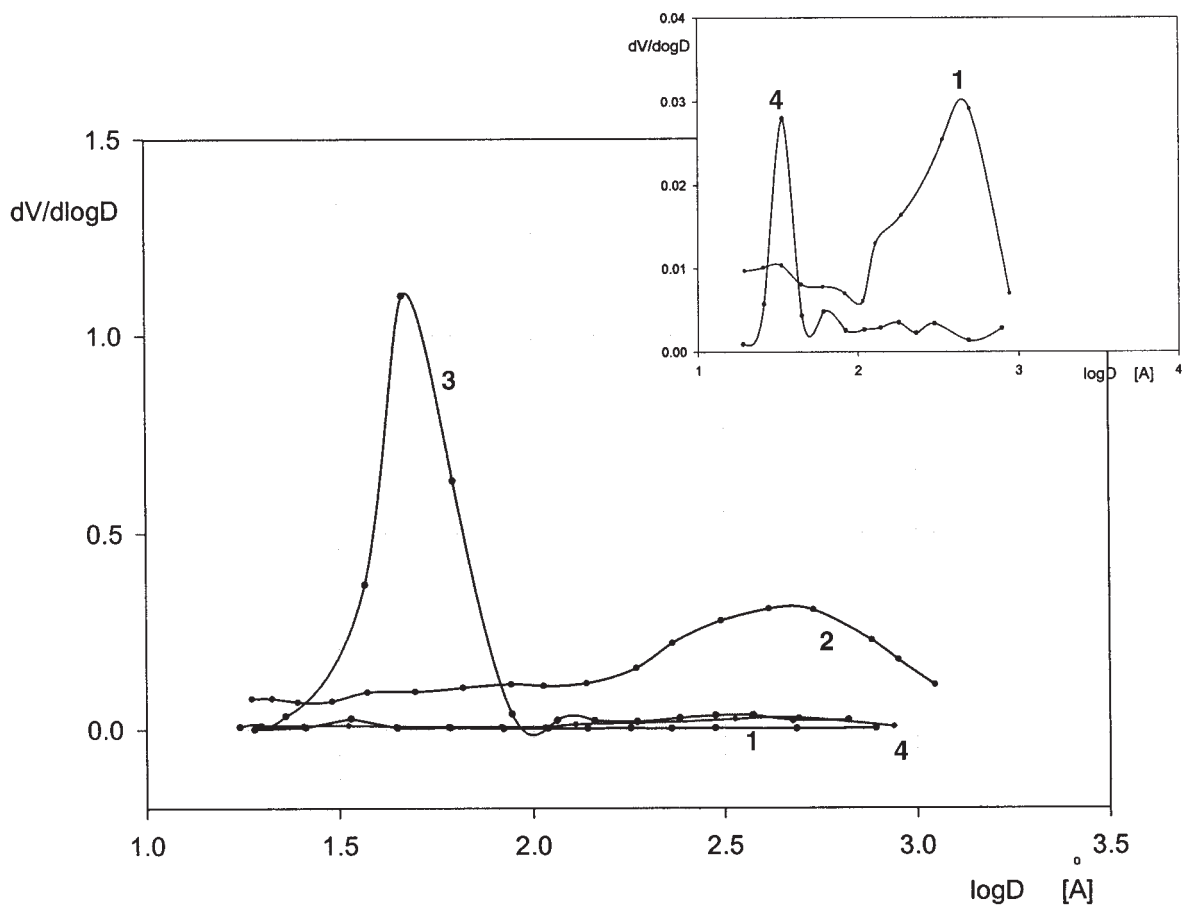
The cumulative pore size distribution was determined from a plot of  $1 - K_o(EC)$  versus  $\log \Phi$ , where  $K_o(EC)$  is the distribution constant in exclusion chromatography calculated as follows:<sup>18</sup>

$$K_o(EC) = \frac{V_R - V_o}{V_p} = \frac{V_R - V_o}{V_i - V_o} \quad (2)$$

where  $V_R$  is the retention volume of the probe,  $V_o$  is the interstitial volume equal to the retention volume of a totally excluded molecule,  $V_i$  is the retention volume of a totally included molecule, and  $V_p = V_i - V_o$  is the pore volume.

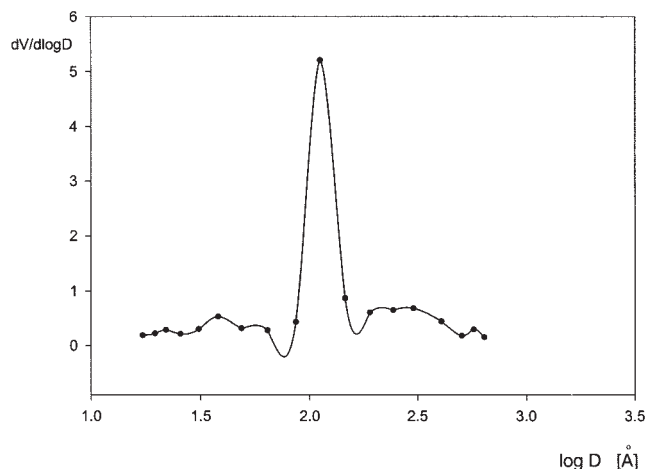
#### Chromatography measurements

The retention volumes of toluene, alkylphenones, phthalates, and polystyrene standards were deter-



**Figure 4** Differential pore size distribution, obtained with the BET method, as a function of the logarithm of the pore diameter ( $D$ ) for the studied copolymers.





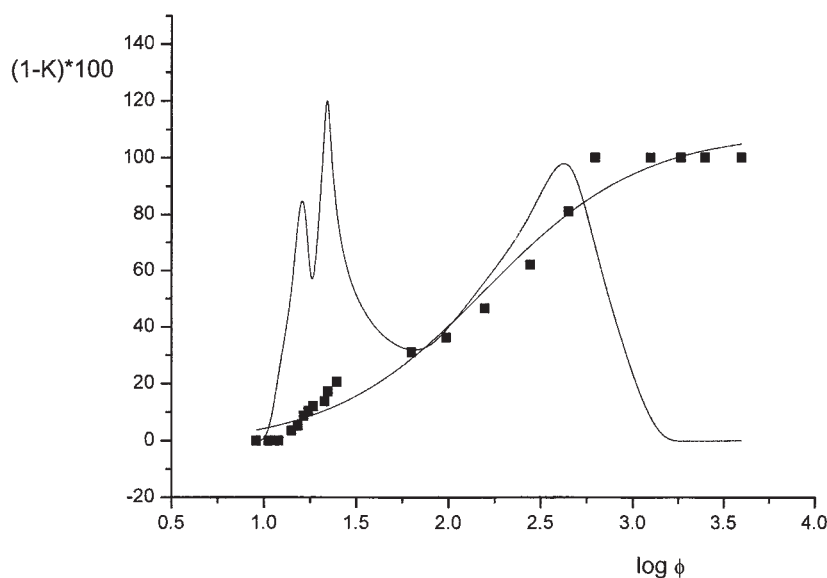
**Figure 5** Pore size distribution, obtained with the BET method, for the copolymer synthesized by suspension-emulsion polymerization.

mined with a Hewlett-Packard HP-1050 liquid chromatograph equipped with a diode-array UV detector, a Rheodyne 7125 injection valve with a 20- $\mu$ L sample loop, and columns packed with the DPMM copolymer. Each substance was injected separately as a 0.1% solution in THF. The columns were thermostated at 30°C.

To determine the swelling propensity (SP) factors, we used twice distilled water at the same flow rate as the mobile phase.

The SP factors of the copolymers were calculated according to Nevejans and Verzele:<sup>18</sup>

$$SP = \frac{p(\text{THF}) - p(\text{H}_2\text{O})}{p(\text{H}_2\text{O})} \quad (3)$$



**Figure 6** Pore size distribution, obtained from exclusion chromatography measurements, for the copolymer synthesized by suspension-emulsion polymerization.

where  $p = P/\eta$  is the pressure with respect to the mobile phase viscosity ( $\eta$ ) and the column inlet pressure ( $P$ ) when THF and water are used as the mobile phases.

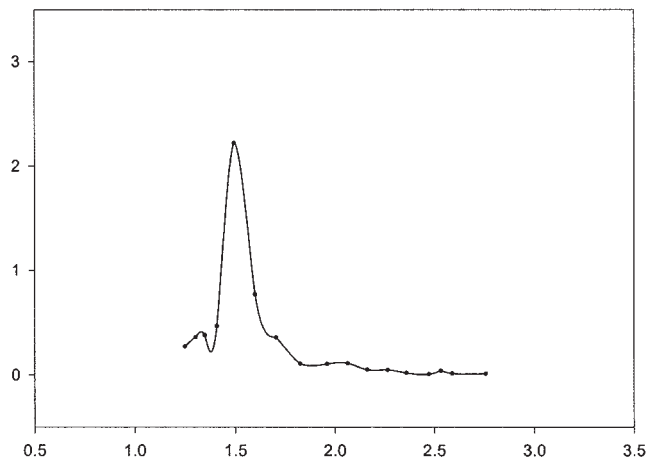
Gas chromatography (GC) measurements were carried out on a Dani (Monzese, Italy) GC 1000 gas chromatograph equipped with a thermal conductivity detector, stainless steel columns (100 cm  $\times$  1.6-mm i.d.), and helium as carrier gas at a flow rate of 50 mL/min.

The separation of the test mixture containing acetonitrile, 2-propanol, triethylamine, 1,2-dichloroethane, and octane was carried out at 200°C.<sup>21</sup> Compounds from homologous series (*n*-alkanes, alcohols, and keton-2-ones) were also separated at 200°C.

The samples were injected with a 1- $\mu$ L syringe (SGE, North Melbourne, Australia).

## RESULTS AND DISCUSSION

Porous DPMM-DVB copolymers were prepared by three heterogeneous polymerization techniques: suspension, suspension-emulsion, and precipitation. In Table I, the polymerization recipes are presented. The copolymers obtained in suspension and suspension-emulsion polymerizations were in the form of microspheres, whereas the product of precipitation polymerization was irregular particles (Fig. 2). In the suspension and suspension-emulsion polymerizations, toluene and *n*-dodecane were used as pore-forming diluents. These two copolymers were obtained in the presence of exactly the same concentration of diluents. For the copolymers obtained by the suspension and suspension-emulsion polymerizations, the influence of the pore-forming diluent on the particle size and

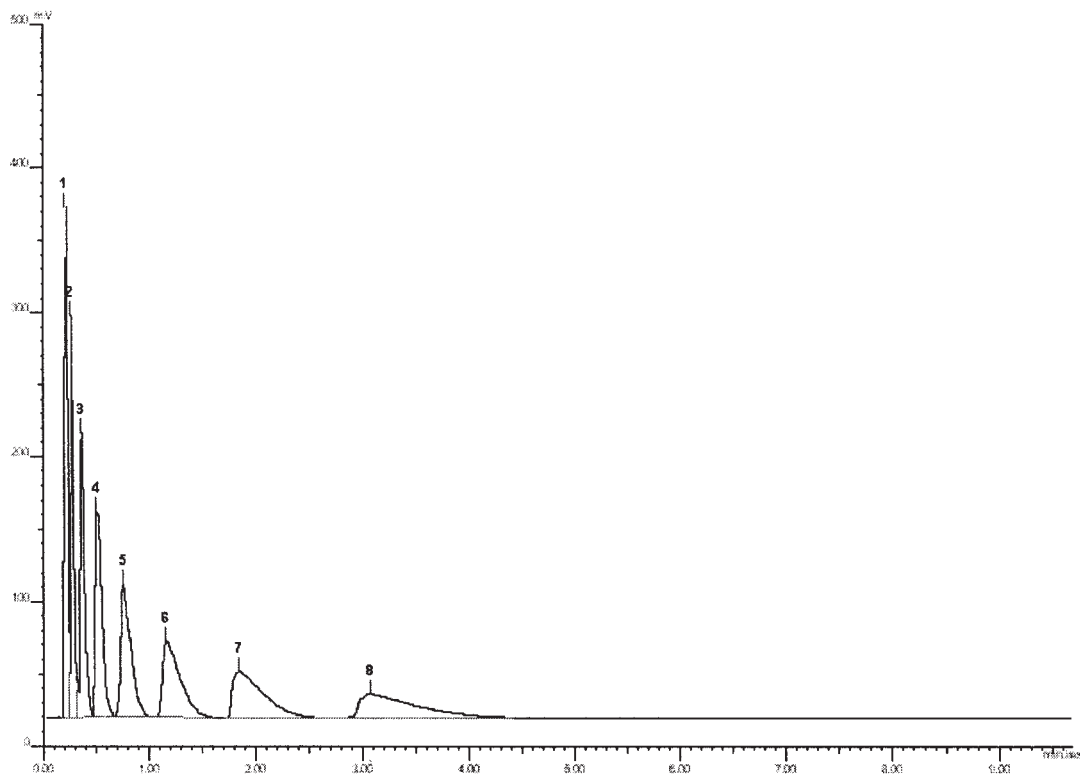


**Figure 7** Pore size distribution, obtained with the BET method, for the copolymer synthesized by precipitation polymerization.

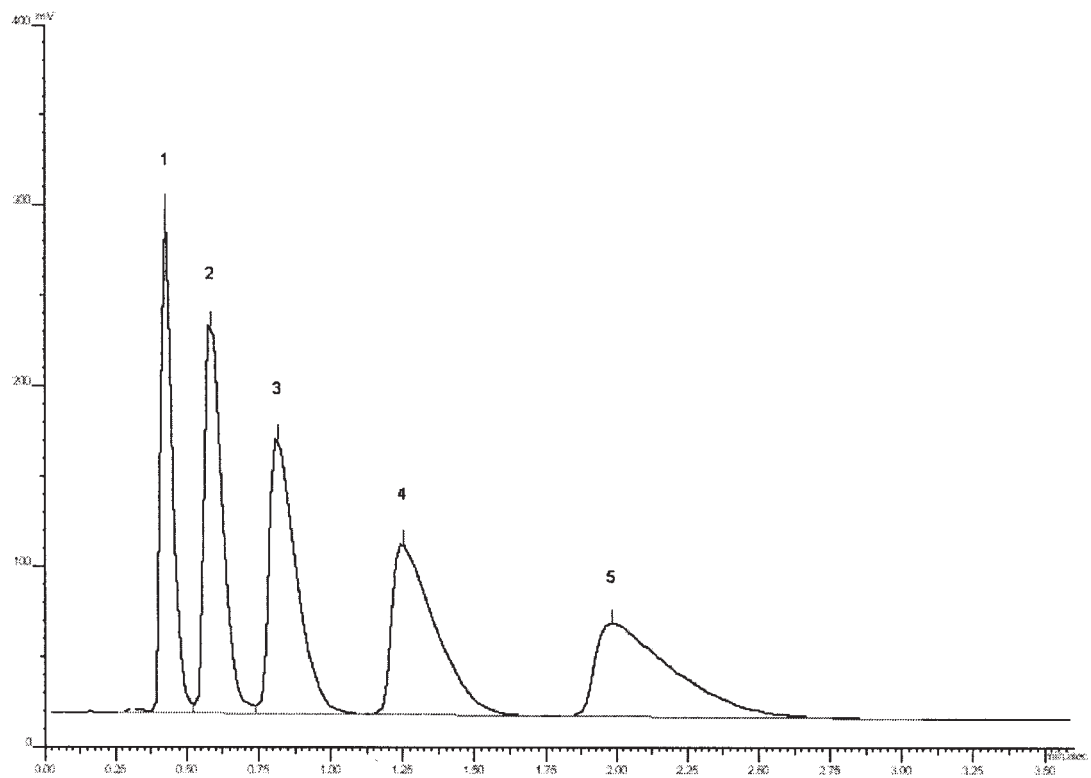
their porous structure was investigated. The results presented in Figure 3 show that independently of the composition of the pore-forming diluent, rather broad particle size distributions were obtained. Studies of the porous structure of the microspheres obtained by suspension polymerization indicated that the most uniform pore size distribution was for the polymer obtained in the presence of the diluent containing 19.1

mL (85%) of toluene and 3.4 mL (15%) of dodecane (Fig. 4). Their most probable pores had diameters of approximately 55 Å. Such a composition of diluents was used in the preparation of DPMM-DVB suspension-emulsion microspheres. Unexpectedly, the pore size distribution function for this copolymer was quite different (Fig. 5). In this case, the most probable pore diameters were around 100 Å. The specific surface area was approximately 100 m<sup>2</sup>/g larger. These results suggested different mechanisms of copolymerization. These pore size distributions were obtained for the samples in a dry state. As the microspheres obtained by suspension-emulsion polymerization had diameters suitable for HPLC, this material was packed into the column, and its porous structure in the wet state was studied. Diameters and retention volumes of used probes are listed in Table II. In contact with an organic solvent, the polymer swelled, and its porous structure changed (Fig. 6). From these data, we can see that the function of the pore size distribution had three maxima. This showed that there were not only mesopores but also micropores in the internal structure of the obtained copolymer. Thus, the results from inverse exclusion chromatography resembled the situation in a real HPLC column.

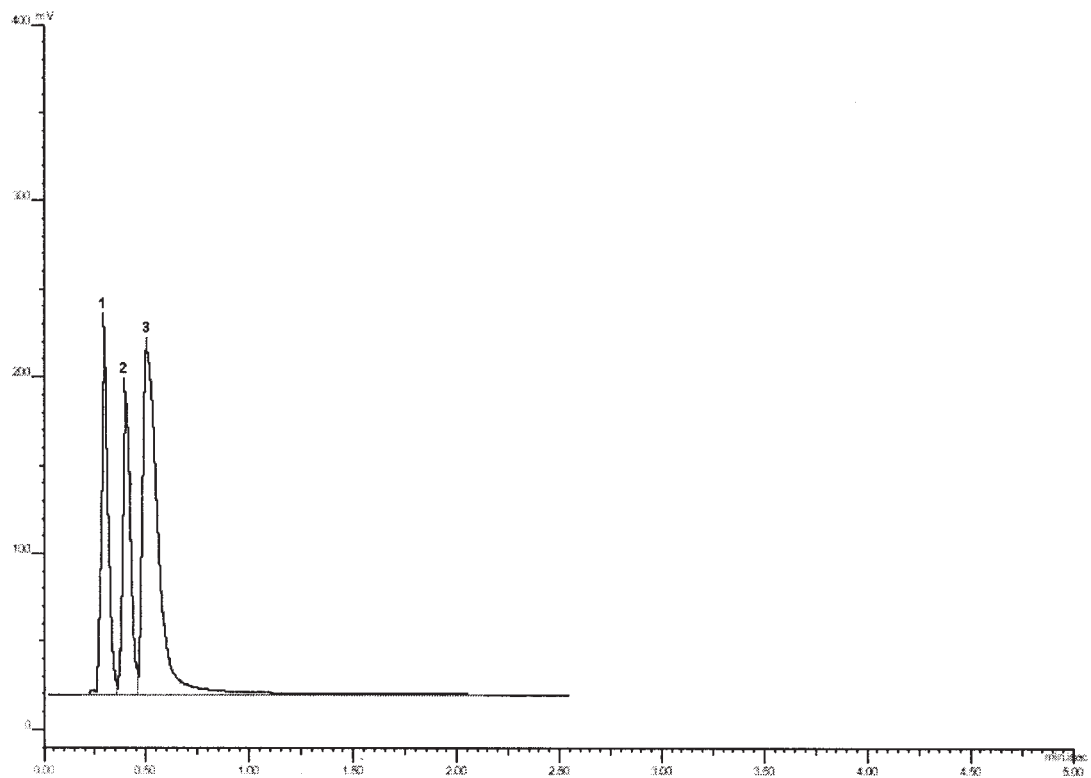
For precipitation, the reaction medium played the pore-forming role. The polymer obtained by this tech-



**Figure 8** Separation of the mixture of alkanes: (1) *n*-pentane, (2) *n*-hexane, (3) *n*-heptane, (4) *n*-octane, (5) *n*-nonane, (6) *n*-decane, (7) *n*-undecane, and (8) dodecane.



**Figure 9** Separation of the mixture of ketones: (1) 2-propanone, (2) 2-butanone, (3) 2-pentanone, (4) 2-hexanone, and (5) 2-heptanone.



**Figure 10** Separation of the test mixture: (1) acetonitrile and 2-propanol, (2) 1,2-dichloroethane, and (3) triethylamine and octane.

nique possessed the largest specific surface area and a narrow pore size distribution (Fig. 7). Unfortunately, the DPMM-DVB copolymer obtained by this technique was irregularly shaped and could not be used for any chromatographic purpose.

The microspheres obtained from suspension polymerization were used as GC packings. The chromatographic properties of the porous DPMM-DVB copolymers are presented in Figures 8–10. In such applications, the porosity of the particles and the presence of functional groups in the beads are key factors. The peaks of the compounds from different homologous series obtained from GC measurement were asymmetric. This asymmetry was observed for both polar (ketones) and nonpolar (*n*-alkanes) compounds. Figure 10 shows the separation of a test mixture containing a proton donor (2-propanol), a proton acceptor (triethylamine), a weak dipole (1,2-dichloroethane), a strong dipole (acetonitrile), and an octane with no polar functionality. Unfortunately, in this phase 2-propanol was coeluted with acetonitrile, whereas triethylamine was coeluted with octane. This means that copolymers of DPMM and DVB have rather limited applications in gas chromatography techniques as packing materials. On the other hand, the application of polymeric beads creates new possibilities. For example, the preparation of molecularly imprinted polymers can lead to packings suitable for the separation of isomers.

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