

Synthesis and Characterization of Methacrylate Polymeric Packings Based on Bisphenol-S

T. JABŁOŃSKA-PIKUS, W. CHARMAS, B. GAWDZIK

Department of Chemistry, MCS University, pl. Marii Curie-Skłodowskiej 3, 20-031 Lublin, Poland

Received 26 February 1999; accepted 2 June 1999

ABSTRACT: The synthesis of new porous copolymers for chromatography purposes is presented. They are formed during the suspension and emulsion polymerization of methacrylate derivatives of bisphenol-S with divinylbenzene in the presence of the pore-forming diluent. One type of the obtained copolymers contains sulfonyl functional groups in its skeleton and the second sulfonyl and more polar hydroxyl groups. Chemical and porous structures of the obtained polymeric packings were studied. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 142–148, 2000

Key words: porous copolymers; derivatives of bisphenol-S; 4,4-diphenyl sulfone dimethacrylate; 4-hydroxydiphenyl sulfone 4'-methacrylate; formation of porous structure

INTRODUCTION

In the last decade, polymeric packings for chromatography have become of increasing interest. The most popular styrene (ST)-divinylbenzene (DVB) packings are macroporous spherical beads of polystyrene crosslinked with DVB. Studies on new polymeric packings and methods of their modification make it possible to obtain materials of specific chromatographic properties. Polymeric sorbents based on phenyl acrylates or methacrylates are relatively new.^{1–3} In the synthesis of chromatographic materials, acrylic monomers with different substituents such as 4-nitro-, 4-benzoyl-, 4-carbomethoxy-, 2-formyl-, and 2,4,6-trichlorophenyl- were copolymerized with DVB in the aqueous suspensions.^{4–6} The main advantage of using these monomers is a possibility of inserting reactive groups into the copolymer skeleton or activating it before or after copolymerization.

To obtain chromatographic packings with good thermal and chemical stabilities special attention was paid to acrylic resins from bisphenol-S (bis 4,4'-dihydroxyphenyl sulfone).^{7,8} Mono- and dimethacrylic esters containing sulfonyl groups were crosslinked with DVB in the presence of the pore-forming diluent. Properties of the obtained porous polymeric sorbents were studied.

EXPERIMENTAL

Materials

Methacrylic acid, bisphenol-S, and α,α' -azoisobutyronitrile (Fluka, Buchs, Switzerland) were used without further purifications. DVB (Fluka) was washed with 3% aqueous sodium hydroxide solution before using. Reagent grade dichloromethane, acetone, hexane, ethyl acetate, chlorobenzene, chloroform, and methanol were from POCh (Gliwice, Poland).

Synthesis of Monomers

Methacryloyl chloride was prepared using the procedure of Rehberg et al.⁹ Then it was used for

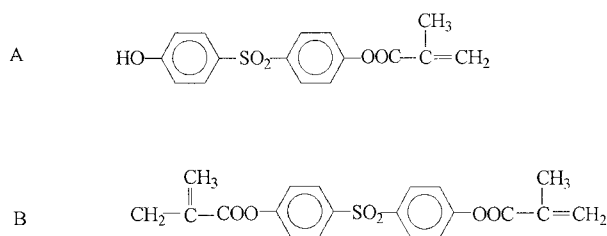
Correspondence to: B. Gawdzik.

Journal of Applied Polymer Science, Vol. 75, 142–148 (2000)
© 2000 John Wiley & Sons, Inc. CCC 0021-8995/00/010142-07

the syntheses of 4,4'-diphenyl sulfone dimethacrylate (DPS DM) and 4-hydroxydiphenyl sulfone 4'-methacrylate (DPS M) during the reactions with bisphenol-S (Fig. 1).¹⁰ Diester was purified by recrystallization from the mixture of dichloromethane and hexane (1 : 2; V/V/1 g with 5 mL of solvents), whereas DPS M was purified from chloroform (1 g with 3 mL of solvent).

Suspension Copolymerization

Copolymerizations of DPS DM with DVB and DPS M with DVB were performed in an aqueous suspension medium. In a typical experiment, 300 mL of distilled water and 2.2 g of poly(vinyl alcohol) were stirred for 3 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 monomer, 3 g of DVB, 0.3 g of α,α' -azoisobutyronitrile in 30 mL of chlorobenzene was prepared and added while stirring to the aqueous medium. Copolymerization was performed for 18 h at 80°C. After that, the suspension mixture was taken into water to sediment. To remove stabilizers, unreacted monomers, residues of soluble copolymers, the obtained beads were washed with hot water, acetone, and methanol. Finally, they were dried in a vacuum at room temperature (Table I).



DPS M mp 154-155 °C

¹H-NMR (CDCl₃): δ 2.05 (-CH₃), δ 3.65 - 3.86 (-OH), δ 5.82, 6.36 (=CH₂), δ 6.86, 7.25, 7.85 (Φ) ppm.

DPS DM mp 146-147 °C

¹H-NMR (CDCl₃): δ 2.04 (-CH₃), δ 5.82, 6.36 (=CH₂), δ 7.25, 7.34, 7.94, 8.03 (Φ) ppm.

Figure 1 Chemical structures of DPS M (A) and DPS DM (B).

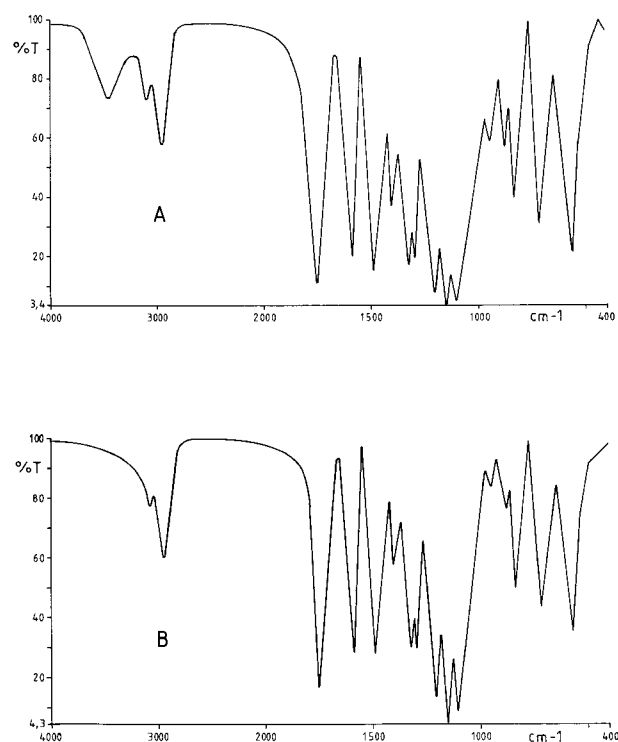


Figure 2 FTIR spectra of the porous copolymers: DPS DM/DPS M-DVB (A), and DPS DM-DVB (B).

Emulsion Copolymerization

Emulsion copolymerization was performed similar to a suspension. Only poly(vinyl alcohol) was replaced by anionic surfactant: sodium salt of dioctyl sulfosuccinate.¹¹ The obtained copolymeric beads were purified as described previously (Table II).

Measurements

The Fourier transform infrared (FTIR) spectra of monomers and copolymers were run on a Perkin-Elmer model 1725 using KBr pallets. ¹H nuclear magnetic resonance (NMR) spectra were recorded on an NMR model BS 567 A (Tesla, Czechoslovakia) operating at the ¹H resonance frequency of 100 MHz. Chemical shifts were referenced to tetramethylsilane serving as an internal standard. The ¹³C-CP/MAS-NMR was conducted on a Bruker 300 MSL CP/MAS instrument operating at 75.47 MHz. The spectra were run with fine powders of glassy beads at room temperature and the Kel-F rotor was used for MAS. The samples were rotated with a spectral width of 25,000 Hz, the CP time was 22 ms, and the number of scans

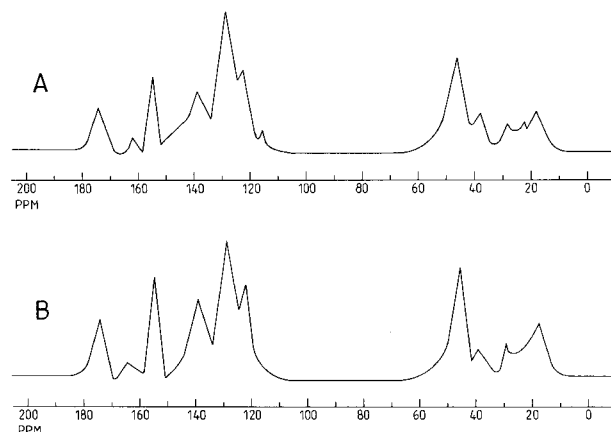


Figure 3 ^{13}C -CP/MAS NMR spectra of DPS DM/DPS M-DVB (A) and DPS DM-DVB (B) porous copolymers.

was in the range 150–750. Each sample was rotated with two different spin rates, and by comparing the results of spectra, the spinning side bands were eliminated.

Thermograms were run on a Paulik Erdey derivatograph (MOM, Budapest, Hungary). A laboratory mechanical sieve shaker was used for isolation of different sieve fractions of the beads. Characterization of porous structure was made by means of an adsorption analyser ASAP 2010 N (Micrometrics Inc., USA). Determinations were based on the measurements of adsorption and desorption of nitrogen on the surface of the studied sample while cooling it to liquid nitrogen. The specific surface areas were calculated by the Brunauer, Emmett, Teller (BET) method, assuming that the area of a single nitrogen molecule is 16.2 \AA^2 . The beads were imaged using a Tesla BS 300 scanning electron microscope (SEM). SEM specimens were prepared by redispersing the polymeric particles in

methanol and placing a drop on a piece of cover glass. After solvent evaporation, polymeric beads were sputter-coated with a thin layer of gold.

RESULTS AND DISCUSSION

Suspension and emulsion polymerizations were used to obtain porous copolymers of DPS DM-DVB and DPS M-DVB. During the suspension and emulsion polymerization of DPS M-DVB in different solvents, the beads were formed at once, but after 2 h they collapsed. Mechanically stable porous beads were formed during the copolymerization of DPS DM with DVB or when the mixture of DPS M and DPS DM (2 : 3; g/g) was copolymerized with DVB. The size of the particles obtained in the suspension polymerization was 56–200 μm , whereas those formed in the emulsion polymerization had diameters in the range of 5–25 μm . The latter were fractionated by sedimentation in acetone.

Infrared Spectroscopy

Infrared (IR) spectroscopy is the most widely used technique not only for the chemical reactions performed on crosslinked polymers but also for structure identification.¹² The FTIR spectra of DPS DM-DVB and DPS DM/DPS M-DVB are shown in Figure 2. C—H stretching vibrations of aromatic ring, backbone methylene, and methyl groups are observed at 3103, 3072, 2984, 2910 cm^{-1} for DPS DM-DVB and at 3103, 3070, 2990, 2937 cm^{-1} for the DPS DM/DPS M-DVB porous copolymer. The ester carbonyl group for both copolymers gave a sharp band at 1754 cm^{-1} . The aromatic skeletal absorption was observed at

Table I Experimental Parameters of Suspension Polymerization of DPS DM and DPS M with DVB

Copolymer	Monomer (g)	Crosslinking Agent (g)	Diluent ^a (mL)	Initiator ^b (g)	Water (mL)	Stabilizer ^c (g)
1. DPS DM-DVB	15.0 20.0	2.0	25.0	0.3	300.0	2.2
2. DPS DM/DPS M-DVB	(3 : 2; g/g)	3.0	40.0	0.4	300.0	2.2

^a Chlorobenzene.

^b α, α' -Azobisisobutyronitrile.

^c Poly(vinyl alcohol).

Table II Experimental Parameters of Emulsion Polymerization of DPS DM and DPS M with DVB

Copolymer	Monomer (g)	Crosslinking Agent (g)	Diluent ^a (mL)	Initiator ^b (g)	Water (mL)	Stabilizer ^c (g)
3. DPS DM–DVB	20.0	3.0	30.0	0.4	500.0	1.8
4. DPS DM/DPS M–DVB	20.0 (3 : 2; g/g)	3.0	40.0	0.4	500.0	1.8

^{a,b} See Table I.^c Sodium salt of dioctyl sulfosuccinate.

1590 cm⁻¹. The bending vibration of methyl groups is visible at 1491 cm⁻¹. The —SO₂ groups gave intensive bands at 1115 and 1297 cm⁻¹. For DPS DM/DPS M–DVB porous copolymer, a sharp band at 3310 cm⁻¹ characteristic for hydroxyl groups is also observed. IR spectra of monomers showed characteristic valency vibrations of the molecule fragments at 3070 cm⁻¹ and deformation vibrations of benzene ring at 1600 cm⁻¹. There are also valency and deformation vibrations of —SO₂ groups at 1115 and 1300 cm⁻¹ and bending and oscillatory vibrations at 550 and 580 cm⁻¹.

It should be noted that on ¹H NMR spectra of DPS DM and DPS M, multiplet separation corresponding to aromatic protons is observed which suggests the twist aromatic ring planes by —SO₂ groups.

¹³C-CP/MAS-NMR Spectroscopy

In recent years, high-resolution solid-state NMR also known as ¹³C-CP/MAS–NMR has been used for characterization of crosslinked insoluble resins.^{13–15} Figure 3 shows the ¹³C-CP/MAS NMR spectra of DPS DM–DVB and DPS DM/DPS M–DVB porous copolymers. The spectra showed eight resolved signals at 174.2, 154.4, 138.8, 128.4, 122.3, 46.1, 38.0, and 18.0 ppm for the DPS DM/DPS M–DVB and at 174.2, 154.4, 138.8, 128.5, 122.3, 45.9, 39.4, and 17.7 ppm for the DPS DM–DVB.

The α-methyl groups appear as broad peaks at 18.0 (DPS DM/DPS M–DVB) and 17.7 ppm (DPS DM–DVB). The backbone —CH₂ groups are visible at 46.1 and 45.9 ppm as the intensive peaks, whereas tertiary carbon appears at 38.0 ppm for the DPS DM/DPS M–DVB and 39.4 ppm for the DPS DM–DVB. The ester carbonyl groups for both copolymers are observed as an intensive signal at 174.2 ppm. The ⁴C—O of the

phenyl ring for the copolymer DPS DM–DVB gave a sharp line at 154.4 ppm. The other carbon atoms of the phenyl ring gave peaks not well resolved at 138.8 ppm (¹C); 128.4 ppm (²C/⁶C), and 122.3 ppm (³C/⁵C). A similar spectrum of phenyl ring is observed for the copolymer DPS DM/DPS M–DVB.

Porous Structure Characterization

The specific surface areas, pore volume, and mean pore diameters for the studied copolymers are presented in Table III. From these data one can see that specific surface area of the DPS DM–DVB porous copolymer is significantly larger than that of DPS DM/DPS M–DVB. Consequently, the mean pore diameter is smaller for this copolymer. Only the pore volume is nearly the same. The values of porous structure parameters suggest application as chromatographic packings.

SEM

The scanning electron micrographs of the DPS DM–DVB and DPS DM/DPS M–DVB copolymers obtained during the emulsion polymerization are shown in Figure 4. The particles have a

Table III Characterization of the Copolymers Porous Structure

Copolymer No.	Specific Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Mean Pore Diameter (Å)
1	357.6	0.64	35.7
2	253.7	0.62	49.2
3	349.8	0.59	31.6
4	227.0	0.60	48.4

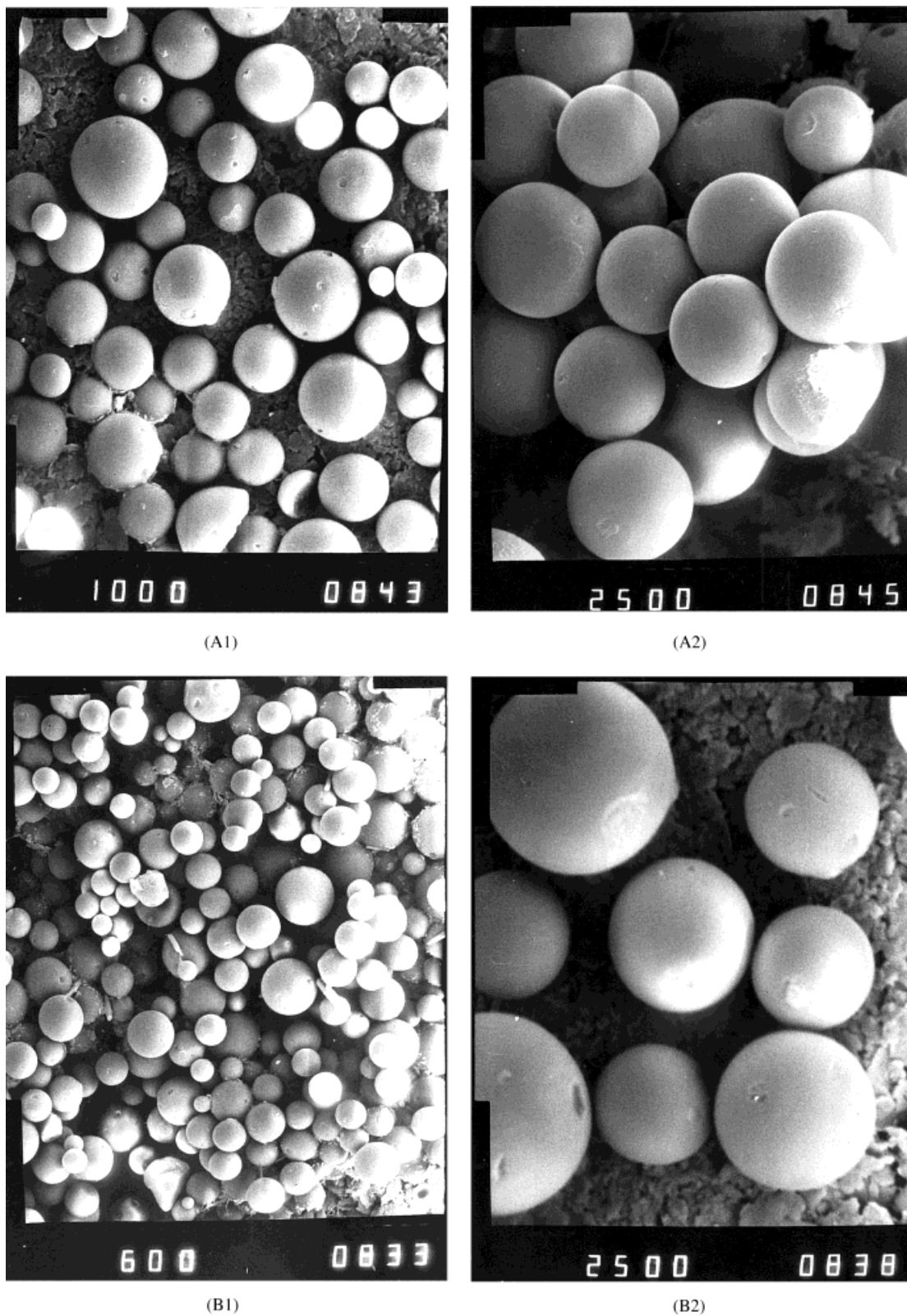


Figure 4 Scanning electron micrographs of the DPS DM/DPS M-DVB (A), original magnification $\times 1000$ (1), $\times 2500$ (2), and DPS DM-DVB (B), original magnification $\times 600$ (1), $\times 2500$ (2) porous copolymers.

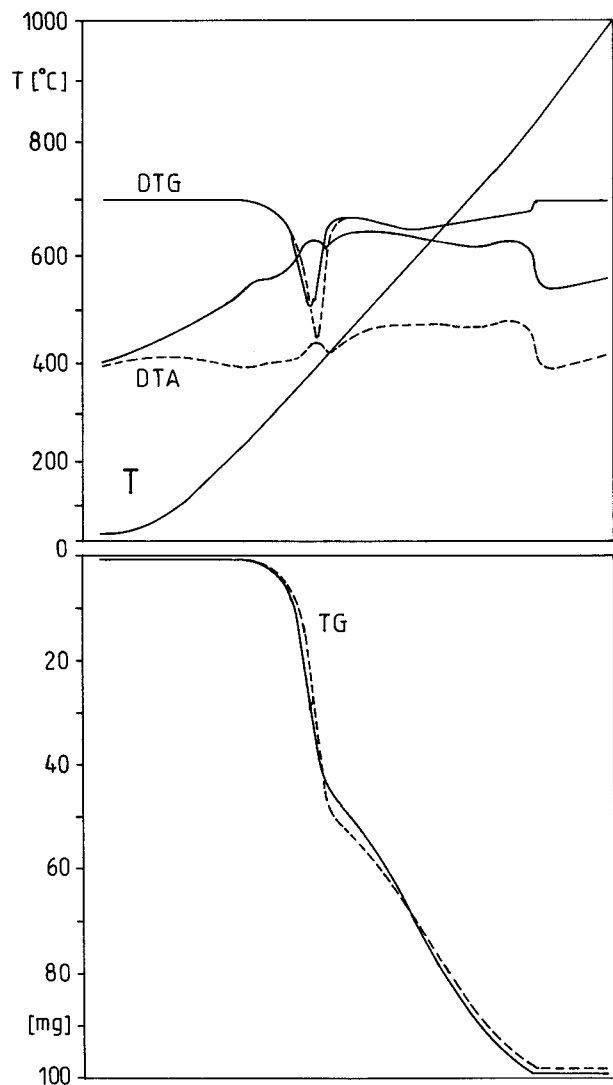


Figure 5 Thermogravimetric analysis of the copolymers studied: DPS DM/DPS M-DVB (solid line), and DPS DM-DVB (dashed line).

perfect spherical shape, but distributions of particle sizes are rather wide. It can be observed that the particles possess smooth surface which confirm the fact that the diluent used in the synthesis is a good solvent for the resins.

Thermogravimetric Analysis

Thermogravimetric curves of the crosslinked copolymers are shown in Figure 5. The initial decomposition temperature of the DPS DM-DVB is noted at 320°C, whereas the DPS DM/DPS M-DVB is 310°C. Final decomposition

temperatures are 800°C, and 780°C, respectively. The copolymers decompose in two stages. The first stage decomposition for the DPS DM-DVB was observed in the range 320–410°C, whereas for the DPS DM/DPS M-DVB it was between 310°C and 400°C. The second stage degradation takes place between 420°C and 800°C and 410°C and 780°C, respectively. The thermal resistances of both copolymers are similar and high.

Swelling Studies

Besides porous structure, chemical structure is the main deciding parameter for porous sorbents applications. In the studied polymers, sulfonyl groups are present. Additionally, the DPS DM/DPS M-DVB porous copolymer contains hydroxyl functional groups. The accessibility of functional groups in the skeleton of crosslinked copolymers is associated with swelling.¹⁶

To investigate the swelling behavior of copolymers, the samples were swollen in ethyl acetate, methanol, dichloromethane, and 1,4-dioxane for 1 h. The excess of solvent was removed by the centrifugal method.¹⁷ The results are expressed as the weight of the solvent absorbed per 1 g of the dry resin and change of volume after swelling (Table IV). From these data one can see that swelling of the beads in dichloromethane is the highest.

Possible Applications

The new porous copolymers DPS DM-DVB and DPS DM/DPS M-DVB may be used in gas and liquid chromatography as packings. DPS DM-DVB was successfully applied in gas chromatography. Its chromatographic properties were discussed previously.¹⁸ The results indicate that its selectivity is mainly governed by the existence of functional groups in the internal structure.

The DPS DM/DPS M-DVB copolymer exhibits stable porosity and thermal resistance. It can be considered a highly active polymeric intermediate. The free —OH groups present in the phenyl ring can be modified both with chiral and non-chiral reagents.

Table IV Swelling Studies

Solvent	Copolymer No.					
	1			2		
	<i>m</i> (g)	<i>V_o</i> (mL)	<i>V</i> (mL)	<i>m</i> (g)	<i>V_o</i> (mL)	<i>V</i> (mL)
Ethyl acetate	4.07	2.05	3.95	4.22	1.90	3.70
Methanol	3.05	2.04	4.10	3.61	1.87	3.90
Dichloromethane	6.81	2.04	4.25	7.00	1.88	4.00
1,4-Dioxane	4.60	2.04	3.90	4.68	1.90	3.85

m, Weight of the solvent absorbed per 1 g of a dry copolymer; *V_o*, volume of 1 g of dry copolymer; *V*, volume of 1 g of copolymer after swelling.

REFERENCES

- Gawdzik, B.; Matynia, T.; Osypiuk, J. *Chromatographia* 1998, 47, 509.
- Narasimhaswamy, T.; Reddy, B. S. R. *J Appl Polym Sci* 1991, 43, 1645.
- Narasimhaswamy, T.; Murthy, N. T.; Sumathi, S. C.; Reddy, B. S. R. *Angew Makromol Chem* 1993, 213, 21.
- Molan, G. E. *J Polym Sci, Part A* 1965, 3, 1267.
- Mansfield, M. L.; Guttman, C. M.; Dimarzio, E. A. *J Polym Lett Ed* 1986, 24, 565.
- Walsh, D. J.; Rostami, S. *Adr Polym Sci* 1985, 70, 119.
- Liaw, D. J.; Sheri, W. C. *Angew Makromol Chem* 1992, 199, 171.
- Liaw, D. J.; Sheri, W. C. *Angew Makromol Chem* 1992, 200, 137.
- Rehberg, C.; Dixon, M.; Fischer, C. J. *J Am Chem Soc* 1945, 67, 209.
- Liaw, D. J.; Teng, K. F. *Angew Makromol Chem* 1993, 207, 43.
- Ugestad, J.; Mørk, P. C.; Berge, A.; Ellingsen, T.; Khan, A. A. In *Emulsion Polymerization*; Piirma, I., Ed.; Academic Press: New York, 1982; Chapter 11.
- Letsinger, R. L.; Klaus, J. *J Am Chem Soc* 1964, 86, 3884.
- Resing, H. A.; Garroway, A. N.; Weber, D. C.; Ferrais, J.; Ellingsen, D. S. *J Am Chem Soc* 1983, 105, 6577.
- Andreis, M.; Koenig, J. L. *Adv Polym Sci* 1989, 89, 69.
- Laupretre, F. *Prog Polym Sci* 1990, 15, 425.
- Frechnet, J. M. J.; Farral, M. J. *The Chemistry and Properties of Crosslinked Polymers*; Labana, S. S., Ed.; Academic Press: New York, 1977.
- Propper, K. W.; Reichenberg, D.; Hale, D. K. *J Chem Soc* 1952, 3129.
- Matynia, T.; Gawdzik, B.; Jabłońska-Pikus, T. *Chem Anal (Warsaw)* 1998, 43, 935.