

Synthesis of Highly Crosslinked Porous Copolymers of Methacrylic Ester of *p,p'*-Dihydroxydiphenylpropane Diglycidyl Ether and Divinylbenzene

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SYNOPSIS

Narrow disperse porous particles were formed by emulsion polymerization of two tetra-functional monomers in the presence of the diluent mixture: *n*-decanol and toluene. One monomer was divinylbenzene while the second was synthesized by the reaction between methacrylic acid and *p,p'*-dihydroxydiphenylpropane diglycidyl ether. In order to obtain chromatographic packings of different polarities copolymers of the following molar ratio of monomers, 0.2 : 0.8, 0.5 : 0.5, and 0.8 : 0.2, were synthesized. Porous structures of the obtained copolymers were studied by BET and EC methods. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polymeric microspheres with uniform size distribution have been described in the literature for over 25 years and are still a focus of attention of both scientists and producers.

Monodisperse, small latex particles with diameter of 0.5 μm may be successfully produced by emulsion polymerization whereas preparation of polymeric beads with diameter in the range of 10 μm for chromatographic purposes is not easy.

The conventional method of preparing polymeric packing materials is by suspension polymerization. Such method involve the addition of monomer or monomer mixtures and a monomer-soluble initiator to a stirred reactor containing water with a small amount of steric stabilizer. Typical result of this method is a broad particle-size distribution.¹⁻³

In order to obtain uniform particles several approaches were undertaken.⁴⁻⁶ Some of them are very interesting, for example, Almog and Levy⁷ reported the use of both suspending agents and surfactants in the preparation of small polystyrene particles while Li and Stover⁸ described the synthesis of monodisperse and highly crosslinked polystyrene-

divinylbenzene (PS-DVB) microspheres in the absence of any stabilizers or surfactants. Yamamoto et al.⁹ reported that nearly 10 μm PS spheres were produced in the mixed media of short-chain alcohol and 2-methoxy ethanol.

Undoubtedly the most promising is the two-stage swelling technique introduced by Ugelstad et al.^{10,11} This special process allows preparation of heretofore impossible size, namely 3–20 μm uniform spheres. After a routine initial polymerization step, a swelling agent is added which permits swelling of the sub-micron polymer particles by large volumes of monomer. Particles are additionally stabilized by molecules of surfactant, for example, sodium dodecyl sulfate.

Synthesis of porous particles required the presence of inert diluents, which lead to the formation of permanent pores in the material after removal of the diluents. The most important parameters responsible for porous structure are monomer type and reactivity, degree of crosslinking, amount of diluent, and diluent solvency for the copolymer (solvent-nonsolvent). Most of the porous particles produced for data are ST-DVB but acrylic and methacrylic are also mentioned.

The aim of this paper concerns the synthesis of methacrylic compounds from epoxy resins and their application in preparation of porous polymeric packings for high-performance liquid chromatography.

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Table I Polymerization Recipe

Monomers		Diluents		Aerosol OT (g)	AIBN (g)	Molar Ratio of Monomers	Volume Ratio of Diluents to Monomers
MEDDE	DVB	<i>n</i> -Decanol (mL)	Toluene (mL)				
7.470	7.530	19.1	3.4	2.2	0.2	0.2 : 0.8	1.5 : 1
11.981	3.019	19.1	3.4	2.2	0.2	0.5 : 0.5	1.5 : 1
14.111	0.889	19.1	3.4	2.2	0.2	0.8 : 0.2	1.5 : 1

EXPERIMENTAL

Monomers

Divinylbenzene was purchased from Merck while methacrylic ester of *p,p'*-dihydroxydiphenylpropane diglycidyl ether (MEDDE) was synthesized from *p,p'*-dihydroxydiphenylpropane diglycidyl ether (DDE).

Synthesis of MEDDE

DDE was isolated from commercial epoxy resin Ep-idian-6 (Chemical Plant Sarzyna, Poland) by vac-

uum distillation. A fraction boiled at 252–255°C under the pressure of 1.4 Torr was collected and crystallized from methanol. Melting point of the obtained compound was 37–38°C and its epoxide equivalent was equal to 0.58 eq/100 g.

Addition of methacrylic acid to it was carried out in the temperature gradient. The mixture containing 200 g of DDE, 94.97 g of 95% methacrylic acid (Fluka), and 0.76 g of initiator, 2,4,6-tri(dimethylaminomethyl)phenol (Anchor Chem. Co.), was heated gradually at each of the temperatures, 80, 90, 100, 110, and 120°C, for 90 min. The product containing mainly methacrylic ester of *p,p'*-dihydroxydiphenylpropane diglycidyl ether

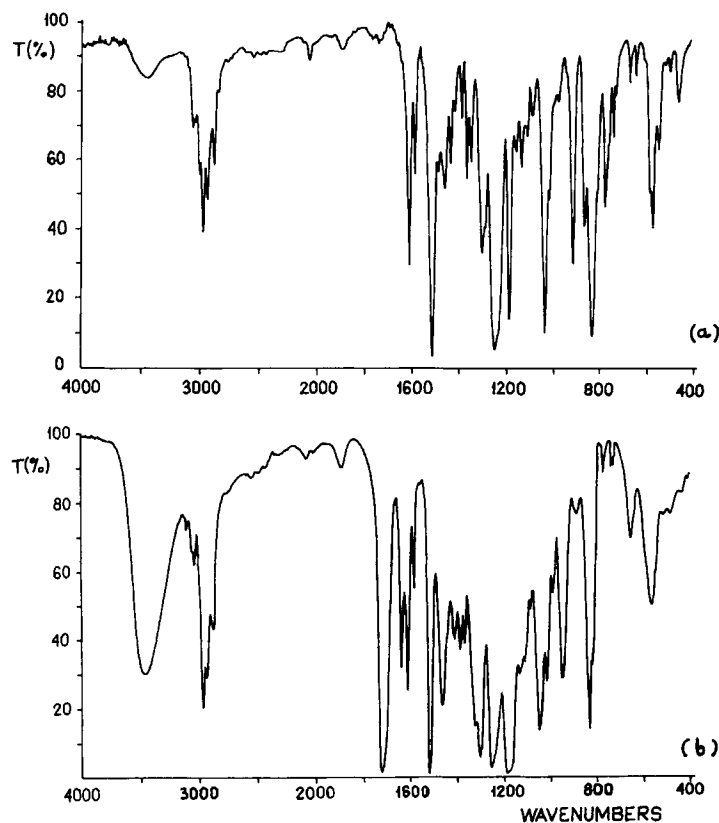


Figure 1 DRIFT spectra of the DDE (a) and MEDDE (b).

Table II Results of Elemental Analysis of the DDE and MEDDE

Substance	C (%)	H (%)
DDE	74.52	7.04
MEDDE	68.06	7.02

was used without further purifications. The acid value equal to 4.1 mg KOH/1 g MEDDE came from the free acids, which did not take part in the addition.

To control the efficiency of the reaction elemental analysis and FTIR spectra for DDE and MEDDE were made.

Other Chemicals and Solvents Used in Exclusion Chromatography Studies

Reagent grade toluene, methanol, acetone, *n*-decyl alcohol, sodium dodecyl sulfate (SDS), and dioctyl sodium sulfosuccinate (Aerosol OT-75) were from Merck. α, α' -Azobisisobutyronitrile (AIBN) was bought from Fluka. Tetrahydrofuran (HPLC grade) used as a mobile phase in the inverse exclusion chromatography (EC) studies was purchased from Merck. Polystyrene standards used in these measurements came from Merck and Toyo Soda.

Preparation of Porous Copolymers

Polymerizations were carried out in two parallel experiments in which SDS and Aerosol OT-75 were

used as surfactants. As the narrowest size distribution of particles was obtained when Aerosol OT-75 was used, this surfactant was applied in further experiments.

In these experiments three copolymers of different molar ratio of monomers were obtained (a detailed recipe used in this study is given in Table I). All polymerizations were performed in a 1-L glass kettle reactor in a thermostatted water bath equipped with a stirrer. The stirring speed was set at ca. 200 rpm.

For a typical polymerization procedure monomers—MEDDE (11.981 g) and DVB (3.019 g)—were diluted in the mixture of *n*-decanol (19.1 mL) and toluene (3.4 mL) while heating. Homogeneous solution with AIBN (0.200 g) was immediately poured to the water solution of Aerosol OT-75 (2.200 g). Polymerization was carried out at 80°C for 24 h.

After the polymerization the product was washed in hot water and extracted in a Soxhlet apparatus using acetone, methanol, and benzene. Uniform fractions of copolymers particles (5–15 μm) were isolated by sedimentation from methanol–acetone (90 : 10; v/v).

Characterization

Infrared Spectroscopy

Diffuse-reflectance, infrared, and Fourier transform (DRIFT) spectra were measured with a Perkin-Elmer model 1700 FTIR spectrometer. All samples

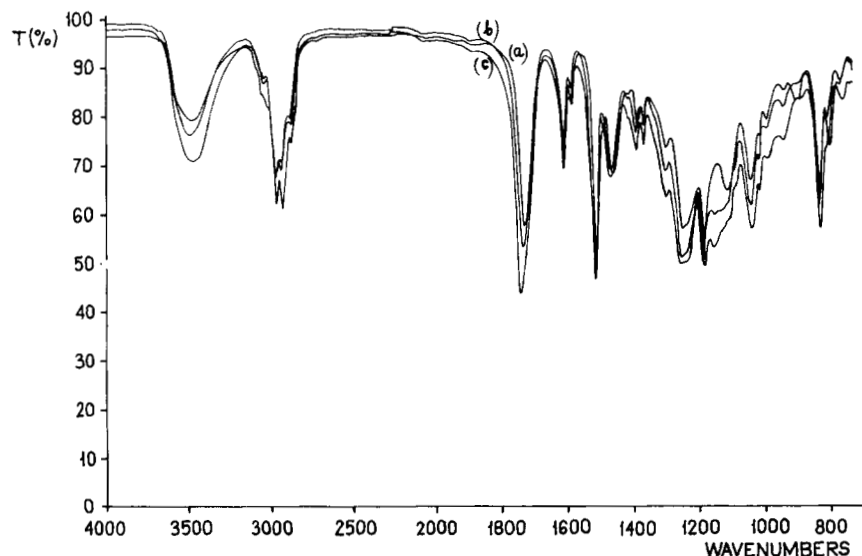


Figure 2 DRIFT spectra of the MEDDE–DVB copolymers of the following molar ratio of monomers: 0.2 : 0.8 (a), 0.5 : 0.5 (b), and 0.8 : 0.2 (c).

were measured as potassium discs. In order to make quantitative analysis for the samples of porous copolymers prepared from different molar ratio of monomers, 3 mg of each specimen was examined.

Elemental Analysis

Elemental analysis was made using a Hewlett-Packard model 185 CHN analyzer (Palo Alto, CA, USA).

Particle Size Distribution

For this purpose a MASTER M3.1 particle sizer (Malvern Instruments) was used. Particle size distributions were determined for the copolymers samples suspended in methanol-acetone (90 : 10; v/v).

SEM

The microspheres were imaged using a Tesla BS 301 (Czechoslovakia) scanning electron microscope (SEM). SEM specimens were prepared by redispersing the microspheres in methanol and placing a drop on a piece of cover glass. After solvent evaporation, particles were sputter-coated with a thin layer of gold.

Measurements of the Surface Properties of Copolymers

The specific surface areas and pore size distributions were measured on a Sorptomatic 1800 apparatus (Carlo Erba). The determination was 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 BET method, assuming that the area of a single nitrogen molecule is 16.2 \AA^2 .

Inverse Exclusion Chromatography Studies

Retention volumes of toluene, phthalates, and polystyrene standards were determined with an HPLC system consisting of a Hewlett-Packard HP-1050 gradient pump connected to a Rheodyne model 7125 injection valve equipped with a $20 \mu\text{L}$ sampling loop, a variable UV/vis detector (Labor, Hungary) operated at 254 nm, and a column packed with the MEDDE-DVB copolymers. Each substance was injected separately as a 0.1% solution in tetrahydrofuran (THF). THF of 0.5 mL/min was used as a mobile phase.

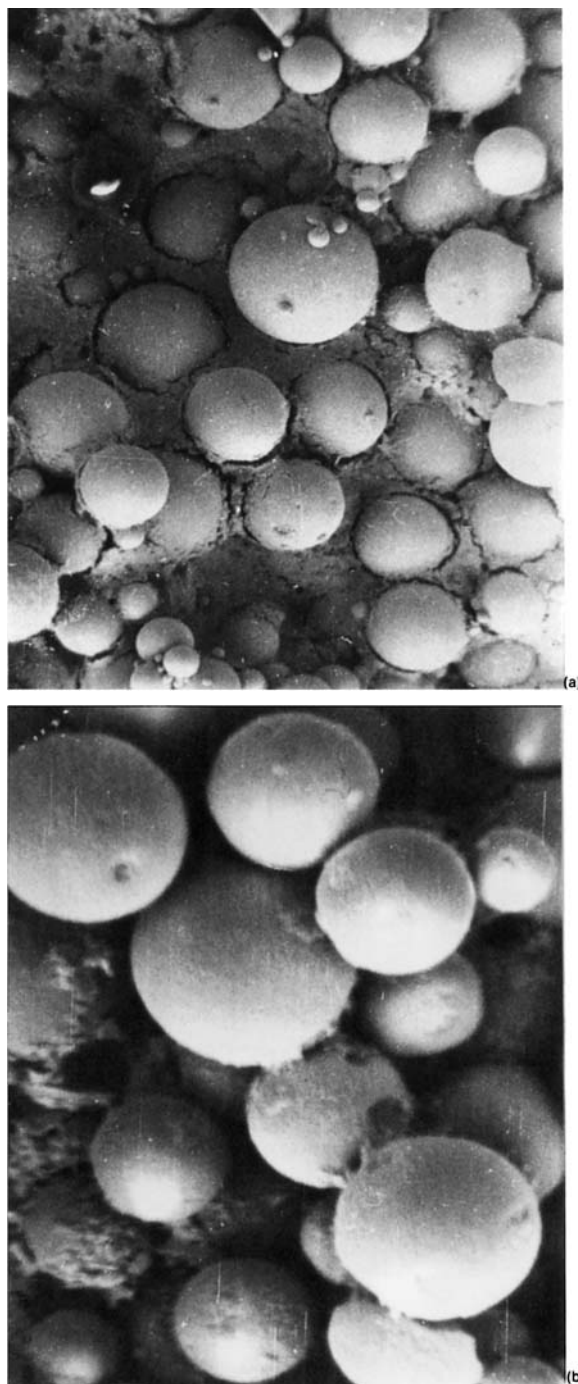


Figure 3 Scanning electron micrographs of the MEDDE-DVB copolymers obtained in the presence of SDS (a) and Aerosol OT-75 (b). Magnification $\times 3000$.

RESULTS AND DISCUSSION

As epoxy resins are characterized by interesting features such as good resistance to moisture, fire, and chemical agents they are the subject of many investigations. Beside pure epoxy resins different deriv-

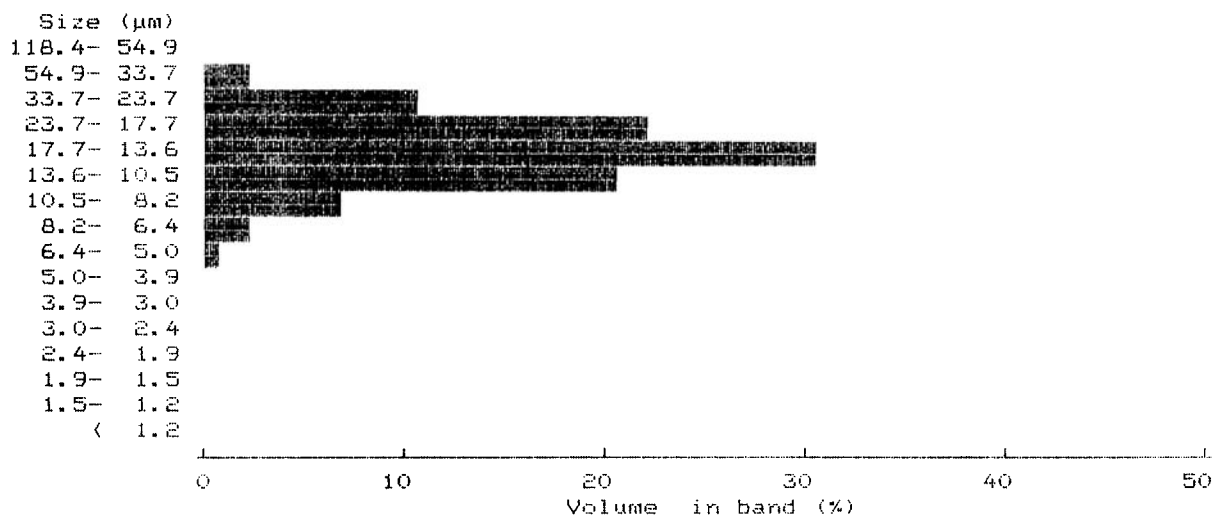


Figure 4 Size histogram of the MEDDE-DVB (0.2 : 0.8) porous beads obtained in the presence of Aerosol OT-75.

atives such as acrylic epoxy resins are also common. Recently, Boutevin et al.¹² discussed the influence of different amine catalysts on the reaction between epoxy groups and methacrylic acid.

In this paper we applied the products of the reaction between epoxy resins and methacrylic acid for preparation of polymeric packings for chromatography. To obtain the monomer MEDDE the reaction between DDE isolated from the commercial resin and methacrylic acid in the presence of 2,4,6-tri(dimethylaminomethyl)phenol was made. The reaction was controlled by FTIR and elemental analysis.

Figure 1 shows the spectra of DDE and MEDDE. The absorption band at 3450 cm^{-1} suggests that in the parent DDE traces of hydroxyl groups are present. For the MEDDE this band is more intensive because during the addition of methacrylic acid to the DDE hydroxyl groups are formed. At this spectrum an additional high intensity band at 1720 cm^{-1} appears. This band came from carbonyl groups typical for esters.

The results from elemental analysis presented in Table II also point to this reaction.

Effect of Monomer Molar Ratio

Ester and hydroxyl groups coming from the MEDDE probably have significant influence on the polarity of the studied copolymers. In order to determine the role of their concentration in the chromatographic process, three samples of porous polymers of the following molar ratio of the MEDDE-DVB mono-

mers—0.2 : 0.8, 0.5 : 0.5, and 0.8 : 0.2—were synthesized.

Different amounts of the polar monomer (MEDDE) in the copolymer skeleton were confirmed by quantitative FTIR analysis (Fig. 2). With the increase of the amount of the MEDDE in the copolymer the bands characteristic for it on FTIR spectra became more intensive.

Effect of Surfactant

Use of SDS in polymerization leads to the formation of polymeric beads, but with very broad particle size distribution (see Fig. 3). In the case of Aerosol OT-75 polymeric particles were rather uniform independently of the molar ratio of the monomers used. Figure 3 shows SEM micrographs of the copolymers synthesized in SDS and Aerosol OT-75 emulsions. Figure 4 presents the example of particle size distribution of the MEDDE-DVB microspheres measured by a particle sizer.

Porous Structure

Porous structure of the MEDDE-DVB copolymers was measured for dry samples based on the BET method and for the copolymers in a wet state using EC measurements.¹³

In EC studies toluene, phthalates, and polystyrene standards were used as the pore-size probes. The diameter of the probe molecules (Φ in Å) was calculated from the equation given by Halasz and Martin:^{14,15}

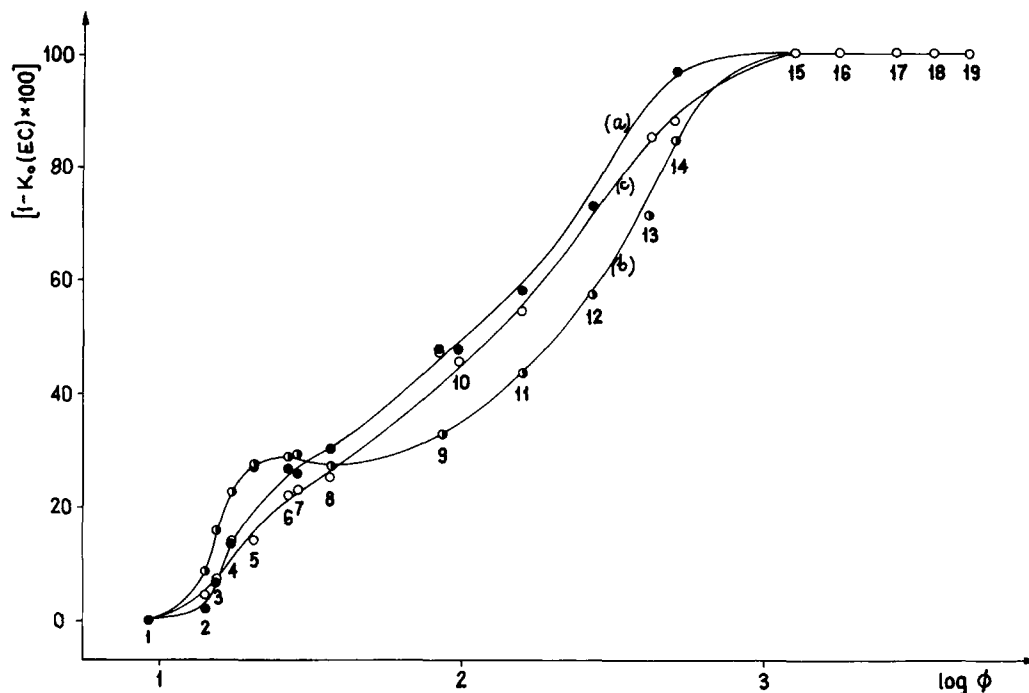


Figure 5 Course of cumulative curves for the MEDDE-DVB copolymers: 0.2 : 0.8 (a), 0.5 : 0.5 (b), and 0.8 : 0.2 (c). 1, toluene; 2, dimethyl phthalate; 3, diethyl phthalate; 4, dibutyl phthalate; 5, dinonyl phthalate; 6-19, polystyrenes (580, 666, 1,050, 4,000, 5,100, 11,600, 30,300, 68,000, 83,000, 390,000, 750,000, 1,460,000, 2,610,000, and 3,840,000).

$$\Phi = 0.62 M_w^{0.59}$$

where M_w is the molecular weight of the probe (g).

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.

The cumulative pore size distribution was determined from the plot $1 - K_0(\text{EC})$ versus $\log \Phi$, where $K_0(\text{EC})$, the distribution constant in exclusion chromatography, was calculated from the following equation:¹⁶

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

where

V_R = 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

$V_p = V_i - V_0$ = the pore volume

In the inverse EC measurements reported here, V_i is equal to the retention volume of toluene.

The data presented in Table III show that the results obtained for dry and wet copolymers are different. Pore volumes calculated as a difference between retention volumes of totally included and excluded molecules and the weights of the packings in the column are significantly larger than those obtained from BET isotherms. The same effect is observed for the micropores contribution. In the BET method, volumes of micropores are very small, independent of the copolymers composition. In EC measurements, micropores contributions measured

Table III Characterization of the Porous Structure of the Copolymers Studied

Molar Ratio of Monomers	Specific Surface Area (m ² /g)	Pore Volume of the Copolymer (cm ³ /g)		Volume of Pores with Diameters Smaller than 20 Å (cm ³ /g)	
		EC	BET	EC	BET
0.2 : 0.8	132	1.246	1.184	0.178	0.001
0.5 : 0.5	55	1.027	0.536	0.197	0.001
0.8 : 0.2	15	0.924	0.214	0.022	0.001

as a difference between the retention volume of toluene having molecule diameter $\Phi = 9 \text{ \AA}$ and of molecules of dinonyl phthalate ($\Phi = 22 \text{ \AA}$) are different for different copolymers. These differences are especially visible in Figure 5, in which the cumulative pore size distribution curves are presented. From their courses one can see that for all studied copolymers the maximum pore diameter is equal to ca. 1200 \AA , corresponding to an exclusion limit for PS 390,000. Independently of the molar composition of copolymers, the most probable are pores with diameter of ca. 150–300 \AA . For copolymers containing 0.2 and 0.5 mol fractions of the MEDDE, pores with diameter of ca. 22 \AA are highly probable, which means that these copolymers have two dispersive structures. The most regular pore size distribution curve for copolymer containing 0.8 mol fraction of the MEDDE makes this copolymer the most useful for packing for HPLC columns.

CONCLUSIONS

The new porous polymer formed from two cross-linking agents is presented. It is synthesized from methacrylic ester of *p,p'*-dihydroxydiphenylpropane diglycidyl ether and divinylbenzene. The particles obtained have diameters in the range of 3–30 μm with spherical particle shapes that allow them to be used in HPLC as packing materials. Because this material possesses polar groups in the structure, three copolymers of the following molar ratio of the MEDDE–DVB monomers, 0.2 : 0.8, 0.5 : 0.5, and 0.8 : 0.2, were synthesized. Porous structure and especially contribution of micropores in the internal structure of these copolymers were studied. Results from EC measurements indicate that microporosity is strictly associated with the chemical composition of the obtained copolymers.

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