

On the Preparation of Porous Crosslinked Poly(ethylene dimethacrylate esters): Polymers and Copolymers

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SYNOPSIS

Macroreticular polymers and copolymers based on poly(ethylene glycol dimethacrylate esters) possessing a permanent porosity (white opaque beads, 40–60% porosity, 354 m²/g, the apparent density less than 1.060 g/mL, etc.) were prepared. The influence of the porogen thermodynamic quality and its weight fraction used in the polymerization mixture on the bead structure was also studied. The porous structure of the matrices was investigated and proved by SEM analyses, the N₂ adsorption (BET) method, etc. The thermal degradation mechanism of the macroreticular beads based on dimethacrylate esters shows that the thermal stability of samples depends on the monomer structure, i.e., the chain length between the two vinyl groups. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The study of porous crosslinked polymers and copolymers based on ethylene dimethacrylates with a well-defined porous structure, i.e., an optimal morphological structure for various application domains (catalysis, chromatographic materials, supports for the immobilization of enzymes) has been of great interest, because such networks have particular application in industrial and clinical fields.^{1–4} The synthesis of the porous networks is influenced by several parameters which have deep consequences on the chromatographic material efficiency.⁴ The porous structure of a network bead is influenced mainly by the percentage of dimethacrylate and the solvent–polymer solubility parameter, δ .^{5,6} The quality of a solvent used as a porogen (diluent, inert medium, etc.) depends on the thermodynamic quality (affinity), expressed as the relationship between the solvent and solute. Solubility occurs when the Gibbs free energy, ΔG , decreases or the chemical potential, μ_i , of each of the solution decreases. "Good solvents" for a polymer chain have high absolute values of ΔG and μ_i when they are mixed with the polymer.⁷ "Bad solvents" are those which, on mixing

with a polymer, give little changes in ΔG or μ_i . ΔG can be defined as $\Delta G = \Delta H - T\Delta S$ (1) where entropy, ΔS , always has a positive value for mixtures, and the ΔG sign is determined by the magnitude of the heat exchange for the mixture, ΔH . For relatively nonpolar porogens having no hydrogen bonds, ΔH is positive, considering it as a mixture of small molecules. Then, ΔH can be written as

$$\Delta H = v_1v_2(\delta_1 - \delta_2)^2$$

where v is molar fraction of solvent (1) and polymer (2); δ^2 = the cohesive energy density (C.E.D.), equivalent to the vaporization energy/volume unit for small molecules. In physical chemistry, the quantity δ is called the "solubility parameter" and is a very useful term to predict the solubility in polymer–solvent systems. If in the above expression ($\delta_1 - \delta_2$) = 0, then $\delta_1 = \delta_2$ and the two components are miscible.^{5,6} The polymer–solvent interaction in the mixture determines decisively the porous structure of the networks. Therefore, the formation of the structure can be explained in terms of differences between solvent and polymer interaction parameters.^{5,6}

It has to be mentioned that a few dimethacrylate adsorbents are commercialized under different trade names as follows: AMBERLITE XAD 7/8 (Rohm and Haass Co.)⁸ and the SPHERON/SEPARON

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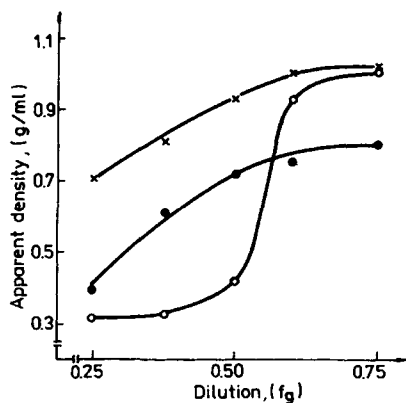


Figure 1 The variation of the apparent density values of PEDMA against the dilution of the monomer (i.e., $100 \times f_g$): (●) BuAc; (○) T; (x) CyOH.

series (Czechoslovakia).^{9,10} Copolymers of ethylene glycol dimethacrylate esters were first prepared by Wichterle and Lim¹¹ to be used in medicine. Copolymers of hydroxyalkyl methacrylate esters, glycidyl methacrylate, etc., crosslinked with ethylene glycol dimethacrylate esters offer many possibilities for the analogous polymer reactions,¹²⁻²³ particularly the networks based on glycidyl methacrylate.^{20,21}

This report deals with the preparation of poly(ethylene glycol dimethacrylate esters) and poly(methyl methacrylate-*co*-ethylene glycol dimethacrylate esters) via radical suspension polymerization and the study of the properties in function of the synthesis parameters.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA), ethylene glycol dimethacrylate (EDMA), diethylene glycol dimethacrylate (DEDMA), and triethylene glycol dimethacrylate (TEDMA), technical grades, were freed of inhibitor before use. The porogens (solvent used as inert media or diluents; toluene [T], *n*-butyl acetate [BuAc], and cyclohexanol [CyOH]), technical grades, were used as received.

The porogen diluent quantity (f_g) used throughout the experiments is expressed by the relationship $f_g = \text{weight of monomers} / \text{weight of monomers} + \text{weight of porogen (g/g)}$. Hence, the monomer quantity (% C_m) contained by the organic phase (copolymerization mixture) might be calculated applying the relationship $C_m = 100 \times f_g$. Benzoyl peroxide used as an initiator was dissolved in the monomer mixture at 1.50% (w/w).

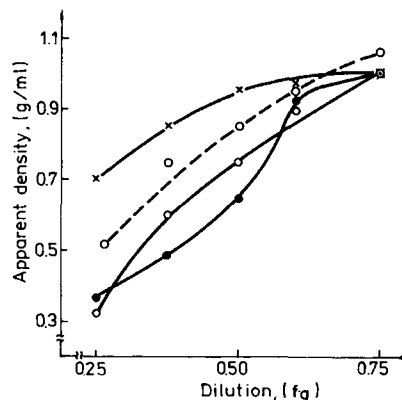


Figure 2 The variation of the apparent density values of PDEDMA against the dilution of the monomer (i.e., $100 \times f_g$): (●) BuAc; (○) T; (x) CyOH; (—) PTEDMA prepared with toluene.

The preparation of the macroporous crosslinked samples were performed as before.^{24,25} The beads of networks were sieved, (0.35–1.00 mm in diameter), washed with hot water, dried, and then extracted with $\text{ClCH}_2\text{CH}_2\text{Cl}$ in a Soxhlet apparatus.

Methods of Porous Structure Determination

All samples were vacuum-dried at 50°C for 48 h before being characterized. The porous networks were characterized measuring and calculating the following characteristics: the skeletal (ρ) and apparent densities (ρ_{ap}), porosity (% P), solvent-uptake coefficient, pore volume (PV), surface area (S), thermal stability, IR spectra, scanning electron microscopy, etc.

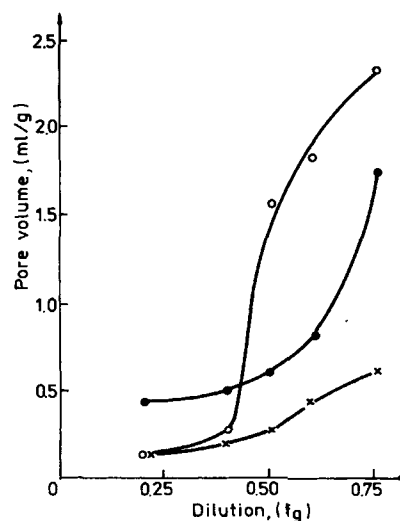


Figure 3 The pore volume of PEDMA vs. dilution of the monomer: (●) BuAc; (○) T; (x) CyOH.

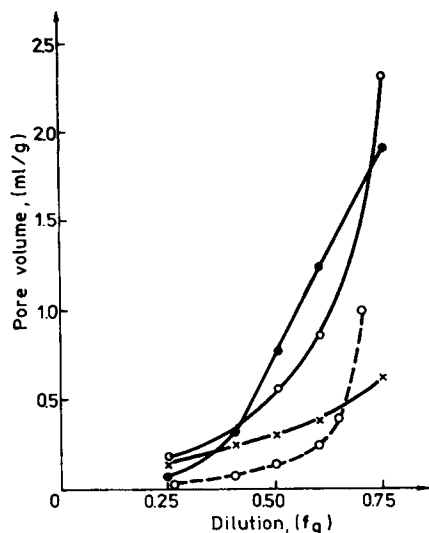


Figure 4 The pore-volume values of PDEDMA vs. dilution of the monomer: (●) BuAc; (○) T; (x) CyOH; (—) PTEDMA prepared with toluene.

The skeletal density (ρ) and the apparent density (ρ_{ap}) of polymer beads were measured by picnometry with *n*-heptane and mercury as the confining fluids. The beads were out-gassed in a picnometer and then were filled under vacuum with mercury at 20°C. The specific surface areas were measured by the N_2 -adsorption method²⁴ on a Ströhlein Area meter.

A few samples were characterized by thermogravimetric analysis. The measurements were performed on 20 mg powder sample, at heating rate of 12°C/min up to 900°C, in air on an Erdey-Paulik-Budapest Derivatograph. α - Al_2O_3 was used as the reference material.

The values of the pore volume (PV), the so-called macroporosity (Q), were calculated using the equation^{25,26}

$$PV = \frac{1}{\rho_{ap}} - \frac{1}{\rho} \quad (\text{mL/g}) \quad (1)$$

where ρ_{ap} is the apparent density (g/mL), and ρ , the skeletal density (g/mL) determined by the picnometric method in *n*-heptane.

The porosity (% P), the so-called void volume, was calculated according to eq. (2):

$$\% P = 100 \times (1 - \rho_{ap}/\rho) \quad (2)$$

and it represents the percentage of the pores (void volume) contained by the beads.

The average pore diameter was calculated according to relationship (3):

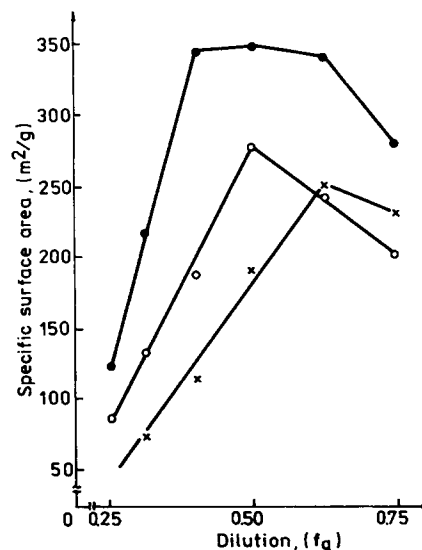


Figure 5 The specific surface area values of PEDMA vs. the dilution of the monomer: (●) BuAc; (○) T; (x) CyOH.

$$\bar{D} = - \frac{4VP}{S_{BET}} \times 10^3 \quad (\text{nm}) \quad (3)$$

where S_{BET} is the specific surface area (BET method)²⁴ (cylindrical model was assumed for the pore shape).

The scanning electron microscopy (SEM) studies were performed on the fractured bead which was fixed on a copper support and covered with a thin layer of gold. The investigations were carried out

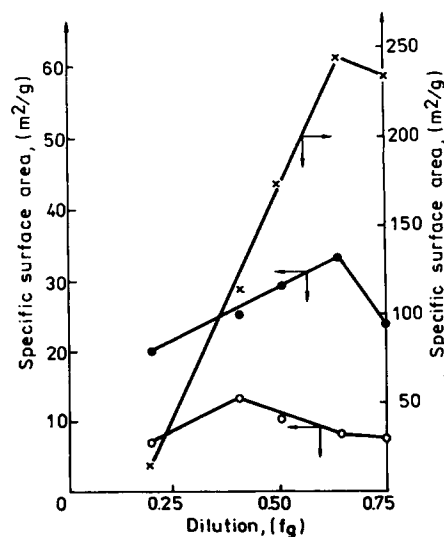


Figure 6 The specific surface area values of PDEDMA against the dilution of the monomer: (●) BuAc; (○) T; (x) CyOH.

Table I Some Features of Porous Poly(triethylene dimethacrylate) (Porogen: Toluene)

No.	f_g^a	Apparent Density (g/mL) ^b	Cyclohexane Regain (g/g)	Pore Volume (mL/g)	Porosity (P %)	Surface Area (m ² /g)	Mean Pore Diameter (nm)
1	0.30	0.5232	0.883	0.98	51.15	20.8	188.46
2	0.35	0.7492	0.400	0.40	30.04	17.3	92.48
3	0.40	0.8546	0.270	0.24	20.20	12.3	78.05
4	0.45	1.0914	0.093	0.17	—	—	—

^a Specific density, 1.071 g/mL.

^b f_g , weights of monomers/weights of monomers + porogen.

using a scanning electron microscope "Leitz SEM 1600 T" type.

RESULTS AND DISCUSSION

To investigate the influence of the porogen content, its solubility parameter value (δ) on the porous structure of the networks, several samples were synthesized. Also, the influence of the length and rigidity of the molecular chain between two double bonds in a molecule of the dimethacrylate ester on the porosity parameters was studied. Most of samples synthesized in the presence of a diluent have white milky beads whose apparent densities are less than 1.000 g/mL.

Figures 1 and 2 show the apparent densities vs. monomer concentration, and as expected, the higher the dilution of the monomers, the lower the apparent densities. The diluent quantity influences deeply the porous structure of each bead. That allows us to assume that both the diluent fraction and its solubility parameter (δ) determine the porous structure of the matrices.⁶

One can notice the differences concerning the structure of the methacrylate esters and the diluents on the polymerization process. The increase of monomer concentration leads to the decrease of the

porosity structure of the beads and, finally, it tends to the networks which possess more and more gel phase structure whose apparent density is closer, or identical, with the skeletal one.

It is to be noted that all the curve slopes change gradually with the monomer dilution (concentration % C_m) except the PEDMA samples prepared in the presence of toluene (Fig. 1). The curve slopes of the apparent densities change suddenly at $f_g = 0.5$ (Fig. 1), while the rest of the curve slopes develop smoothly (Figs. 1 and 2).

The thermodynamic quality of the used porogens expressed as "cohesive energy density" has the following values: *n*-Butyl acetate (BuAc), 17.32×10^{-3} (J/m³)^{1/2}; toluene (T), 18.20×10^{-3} (J/m³)^{1/2}; and cyclo-hexanol (CyOH), 23.30×10^3 (J/m³)^{1/2}.

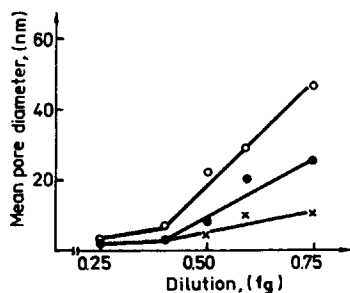


Figure 7 The mean pore-size values of PEDMA vs. the monomer dilution: (●) BuAc; (○) T; (x) CyOH.

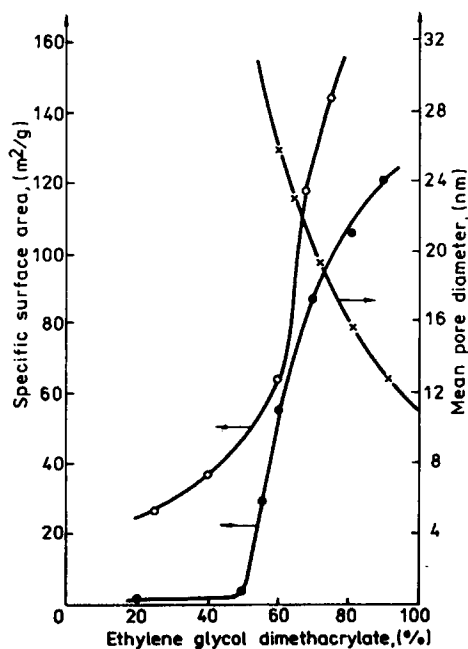


Figure 8 The specific surface area and the mean pore-size values of P(MMA-co-EDMA) against the percent of (●) EDMA; (x) CyOH; (○) BuAc.

Table II Main Characteristics of Porous Copolymers Prepared in the Presence of the Inert Solvent

No.	Dimethacrylate Ester (%)	f_g	Apparent ^a Density (g/mL)	Cyclohexane Regain (g/g)	Porosity (%)	Pore Volume (mL/g)	Specific Surface (m ² /g)	Mean Pore Diameter (nm)	Porogen
I. Poly(methyl methacrylate-co-ethylene dimethacrylate ester)									
1	50.0	0.33	1.0299	0.12	17.67	0.172	3.44	201.30	CyOH
2	70.0	0.33	0.8300	0.58	33.65	0.405	85.93	18.87	
3	90.0	0.33	0.6700	0.65	46.54	0.693	120.75	22.96	
4	70.0	0.25	0.8413	0.69	32.75	0.723	76.61	45.09	
5	70.0	0.40	0.8495	0.80	32.09	0.378	223.64	44.50	
6	70.0	0.50	0.8212	0.82	34.30	0.417	136.00	12.22	
II. Poly(methyl methacrylate-co-diethylene dimethacrylate ester)									
7	50.0	0.25	0.6284	0.77	50.05	0.801	71.40	44.88	BuAc
8	50.0	0.35	0.6207	0.76	50.38	0.812	63.66	51.00	
9	50.0	0.45	0.8420	0.34	32.69	0.388	38.24	40.61	
10	50.0	0.55	0.7027	0.65	29.73	0.625	86.18	28.96	
11	25.0	0.35	0.9210	1.16	26.38	0.286	26.08	23.93	
12	75.0	0.35	0.5715	0.79	54.32	0.950	144.68	26.28	
13	25.0	0.35	1.1780	0.10	5.83	—	—	—	T
14	50.0	0.25	0.5812	0.83	53.54	0.921	70.89	51.98	
15	50.0	0.35	0.7227	0.59	42.23	0.584	74.50	31.36	
16	50.0	0.45	0.6021	0.77	51.87	0.816	43.27	79.64	
17	50.0	0.55	0.87388	0.31	30.15	0.345	32.17	42.90	
18	75.0	0.75	0.4725	0.91	62.23	1.317	19.95	264.07	
III. Poly(methyl methacrylate-co-triethylene dimethacrylate ester)									
19	20.0	0.33	1.1305	0.10	—	0.085	1.90	179.38	BuAc
20	40.0	0.33	0.9070	0.25	27.49	0.303	3.94	307.79	
21	40.0	0.25	0.9833	0.23	21.40	0.218	2.25	386.88	
22	40.0	0.40	1.0725	0.11	14.27	0.133	0.87	611.49	
23	70.0	0.40	1.1007	0.10	12.01	0.109	4.96	880.26	

^a The specific density of copolymers; 1.251 g/mL.

The solvent-polymer solubility (δ) of the cross-linked polymers have been calculated applying the "Small's molar attraction constants,"^{27,28} and the following values have been obtained: poly(ethylene glycol dimethacrylate) (PEDMA), 18.80×10^{-3} (J/m³)^{1/2}; poly(diethylene glycol dimethacrylate)

(PDEDMA), 19.12×10^{-3} (J/m³)^{1/2}; and poly-(triethylene glycol dimethacrylate) (PTEDMA), 19.40×10^{-3} (J/m³)^{1/2}. These values are quite close and large differences concerning the bead structure would not be expected when BuAc and T were used as diluents. Significant modifications in the porous

Table III Physical Features of Poly(ethylene dimethacrylate) Prepared in the Presence of Toluene

Polymer	f_g	Apparent Density (g/mL)	Porosity (%)	Pore Volume (L/g)	Pore Diameter (nm)	Specific Area (m ² /g)
PEDM	0.5	0.4218	66.30	1.57	22.74	276.20
PDEDM	0.5	0.8050	35.60	0.44	39.55	44.50
PTEDM	0.35	0.7492	30.04	0.40	92.48	17.30

Table IV Thermogravimetric Features of Poly(ethylene dimethacrylate esters)

Polymer	First Stage		Second Stage		Third Stage		Fourth Stage	
	T ($^{\circ}\text{C}$)	W (%) ^a	T ($^{\circ}\text{C}$)	W (%)	T ($^{\circ}\text{C}$)	W (%)	T ($^{\circ}\text{C}$)	W (%)
PEDM	40–60	2	220–450	98	—	—	—	—
PDEDM	40–110	3	220–400	87	400–525	10	—	—
PTEDM	40–110	3	210–310	46	310–455	47	455–550	4

^a W , weight given in percentages.

structure might be noticed in the case of CyOH used as porogen because $\delta_{\text{cyclo}} > \delta_{\text{polym}}$.

The mechanical strength decreases appreciably resulting in friable beads when larger quantities of the diluent are used (for f_g less than 0.30). This observation was also recorded during the synthesis of poly(styrene-*co*-divinylbenzene) samples in the presence of large quantities of *n*-heptane or other porogens which are nonsolvents for the polystyrene chains.²⁹

The dilution of the polymerization mixture influences the pore volume (PV) of PEDMA, i.e., the increasing of the diluent quantity favors the formation of PEDMA beads with permanent porosity (Figs. 3 and 4).

Figure 3 shows the diluent influence on the pore volume of PEDMA samples, and one can notice that toluene seems to be the most adequate porogen because the largest pore volume beads can be obtained. Beads with the lowest pore volume were obtained when CyOH was used as the inert diluent (Fig. 3). For instance, the bead pore volume corresponding to the weight fraction $f_g = 0.75$ had the following

magnitude: 2.13 mL/g (T), 1.75 mL/g (BuAc), and 0.65 mL/g (CyOH). Hence, the porogens might easily be ordered from the viewpoint of the thermodynamic quality influence on porous structure³⁰ of polymers as $T > \text{BuAc} > \text{CyOH}$.

Also, the beads of PDEDMA had the largest pore volumes when T and BuAc were used as porogens. But not the same behavior was recorded in the case of PTEDMA prepared in the presence of toluene (Fig. 4); dotted line). This means that the porous structure of the polymers is determined not only by the crosslinked density. Therefore, the influence of the monomer structure on the matrix pore volume recorded in this study might suggest the following sequence of dimethacrylate esters: EDMA > DEDMA > TEDMA.

The mechanism of the polymerization process is rather complex because the monomer/diluent ratio changes continuously due to the monomer consumption (the concentration of monomer decreases in the favor of the polymer formation). Therefore, the pore structure of the beads is quite heterogeneous and it becomes more disperse when a "bad solvent" is used as the diluent. The above assumptions might be seen in Figures 5 and 6 where the specific surface areas were plotted vs. the weight fraction of monomer.

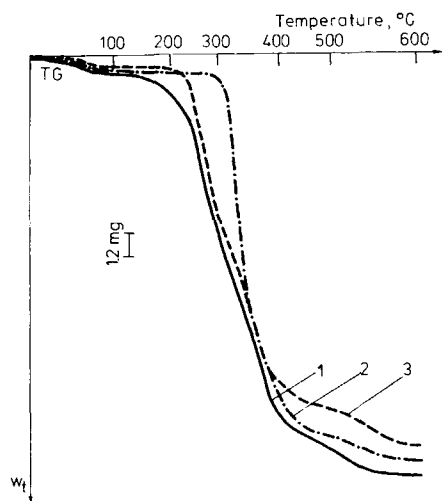


Figure 9 Curves of losses in air of (1) PEDM, (2) PDEDMA, and (3) PTEDMA.

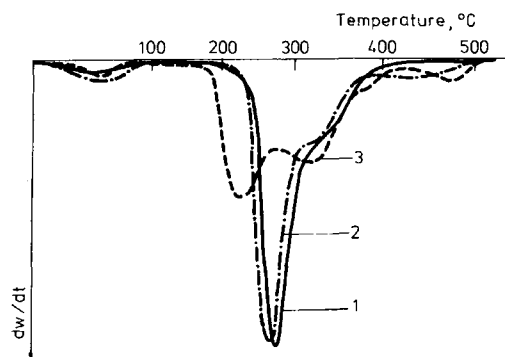


Figure 10 DTG curves for decomposition in air of (1) PEDMA, (2) PDEDMA, and (3) PTEDMA.

Table V Kinetic and Thermogravimetric Features of Poly(ethylene dimethacrylate esters)

Polymer	Kinetic Features		T_m (°C)
	n^a	E_a (kJ/mol)	
PEDM	4	212	310
PDEDM	4	206	280
PTEDM	4	164	270

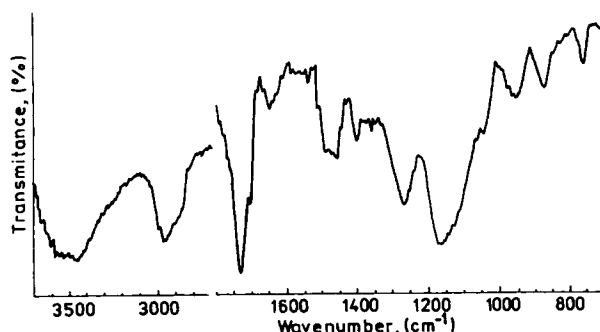
^a Reaction order.

Figure 5 shows the variations of the specific surface area for PEDMA prepared in the presence of the three porogens. As a general observation, it can be seen that the highest value of the specific surface area (354.0 m²/g; $f_g = 0.40$) was yielded when BuAc was used as the porogen and this maximum moved toward a higher concentration of the monomer for T and CyOH, respectively (Fig. 5). Figure 5 shows evidently the relationship between the thermodynamic quality (i.e., the cohesive energy density) and the maximum values of the specific surface areas recorded for TEDMA. The specific surface areas of PEDMA decrease with the increase of the weight fraction of the monomer and the value of the solvent-polymer solubility parameter (Fig. 5). The investigations extended on PDEDMA showed a strange behavior of the three porogens, where the highest values recorded for the specific surface areas were noticed when CyOH was used as the diluent (Fig. 6). We assumed that the monomer structure might determine the reversal behavior of the porogens which at lower weight fraction of diluent yielded samples with high specific surface areas (Fig. 6).

Several features of PTEDMA samples carried out in the presence of toluene are listed in Table I. Table I shows that macroreticular samples, with large pores, are quite friable (which indicates a weak mechanical strength even for moderate dilution) and yield when TEDMA is polymerized in the presence of T, at various porogen weight fractions (Table I).

The mean pore diameters (nm) of PEDMA macroreticular samples vary conversely with the polymerization mixture dilution (Fig. 7). One can notice that during this linear variation of the mean pore diameter the slope of the curves alter at about $f_g = 0.40$. The mean pore diameter variation is correct because a high percentage of the diluent weight fraction favors the formation of large pores, while small dilutions leads to samples having narrower mean pore diameters.

Poly(methyl methacrylate-*co*-ethylene glycol dimethacrylate) (P(MMA-*co*-EDMA) samples were

**Figure 11** IR spectra of PEDMA networks.

prepared in the presence of BuAc and CyOH, resulting in networks whose specific surface areas are 120.75 and 144.68 m²/g, respectively (Fig. 8). Spectacular changes of the specific surface area were observed at 60.0% EDMA contained by the polymerization mixture (Fig. 8). The macroreticular samples of P(MMA-*co*-EDMA) prepared in the presence of CyOH possess mean pore diameters between 10 and 30 nm, which depend on the EDMA percentage of the copolymers (Fig. 8).

Some features of the macroreticular copolymer samples based on EDMA, DEDMA, and TEDMA, prepared in the presence of T, BuAc, and CyOH, are listed in Table II. Table II shows that several conclusions might be pointed out: The copolymer features depend on dimethacrylate structure, the solvent thermodynamic quality (δ), and, of course, the weight fraction ratios of monomers and porogens.

The specific surface areas of the copolymer samples depend on the distance between the two vinyl groups. Therefore, the macroreticular samples crosslinked with TEDMA¹⁹⁻²³ possess the largest values of the mean pore diameters (386.88–880.26 nm) (Table II).

Table VI Main Features of Macroreticular Copolymer Samples Analyzed by SEM (60% dilution of monomers)

Porous Sample	Surface Area (m ² /g)	Average Pore Size (nm)	Porogen	
			δ^a	Type
PEDMA (a)	354.4	24.75	17.32	BuAc
PEDMA (b)	276.2	22.74	18.20	T
DEDMA (c)	28.2	171.45	17.32	BuAc
DEDMA (d)	7.8	433.67	18.20	T
TEDMA (e)	12.3	78.05	18.20	T

^a Solvent-polymer solubility parameter [$\times 10^{-3}$ (J/m³)^{1/2}].

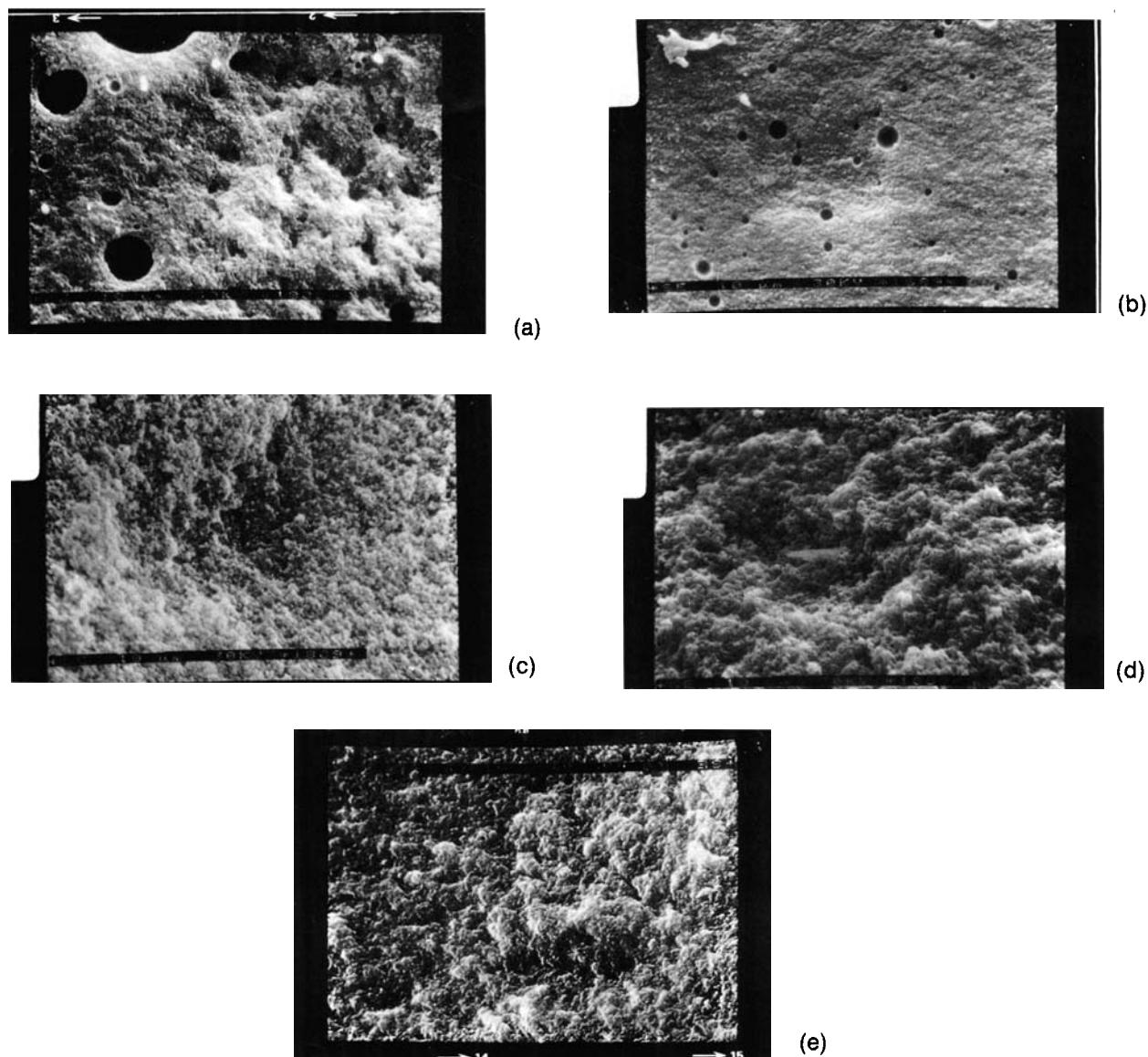


Figure 12 SEM photos of (a, b) PEDMA, (c, d) PDEDMA, and (e) TEDMA.

Several macroreticular polymers and copolymers are based on dimethacrylate esters as chromatographic supports.^{8,9} Therefore, a few samples, whose features are listed in Table III, were analyzed by TG, DTG, and DTA on a MOM Budapest Derivatograph, Paulik-Paulik-Erdey type.

The thermal stability of the macroreticular samples (Table IV) presents the involvement of a complex degradation mechanism, as evidenced by thermogravimetric study (Figs. 9 and 10). The slopes of TG and DTG curves suggest that the complexity of the thermal degradation mechanism increases in the following sequence: PEDMA, PDEDMA, PTEDMA, and a few thermogravimetric features are listed in Table IV.

It can be seen that there is a common stage between 40 and 110°C. The first stage might be assigned to the volatilization of undesirable components (low molecular compounds), which are present in the starting samples. But significant mass losses are observed during the second thermal degradation stage, particularly for PEDMA and PTEDMA samples. We assume that the second degradation stage, particularly for samples based on DEDMA and TEDMA, which is missing at PEDMA, is due to the chain segment length and structure which exists between the two vinyl groups of dimethacrylate esters. It has to be mentioned that PDEDMA and TEDMA contain ether bonds besides the ester ones, a fact which

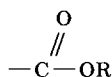
influences the particular thermal behavior of PDEDMA and PTEDMA.

The data listed in Table IV reveal that there is a third thermal degradation stage only for PTEDMA. The activation energies were estimated using the differential method of Freeman and Carroll,³¹ and the kinetic data for the three porous samples (E_a), reaction order (n), and the temperature corresponding to the medium decomposition rate (T_m) are listed in Table V. It can be seen that a certain sequence may be emphasized for the thermal stabilities: PEDMA, PDEDMA, PTEDMA.

The thermal stability of the porous samples decreases simultaneously with the increasing of the chain length between the double bonds of a crosslinker. The experimental results are in good agreement with the data previously reported by Asejeva and co-workers^{28,29,32} concerning the thermal behavior of some crosslinked polymers based on ethylene glycol unsaturated esters.

The high values of the reaction order " n " lead us to assume that the porous crosslinked samples decompose accordingly to a very complex degradation mechanism also involving chain reactions. To confirm the chemical structure of the beads, infrared spectroscopy was applied using the KBr disk technique, because the samples were insoluble in the usual solvents and the structure of the polymer had to be preserved. The best concentration was the 3.0 mg sample and 100 mg KBr. Spectra were recorded on a Perkin-Elmer 577 spectrophotometer.

IR analyses of poly(dimethacrylate esters) prove a complex structure. IR spectra contain adsorption bands at 1734, 1265, 1160, and 1060 cm^{-1} assigned to C=O and



groups; 2890 and 2855 cm^{-1} , vibrations attributed to *sym* $-\text{CH}_3$; and 2960 and 2930 cm^{-1} vibrations assigned to *asym* $-\text{CH}_3$ (Fig. 11).

The microscopic study (SEM) performed on several samples of macroreticular polymers, whose features are listed in Table VI, shows that the porous beads have a spongy structure with small and large pores. Figure 12(a)–(e) shows differences between the porous matrices in the function of the structures of the monomer and the inert diluent.

The structure of PEDMA prepared in the presence of T is composed of smaller agglomerations of particles and microspheres than in the case of PDEDMA or PTEDMA. Also, some differences can

be observed between the agglomeration sizes of PDEDMA performed in the presence of BuAc and T.

We assume that there is no difference between the two vinyl groups and the process of (co)polymerization can be described as (1) the production and agglomeration of highly crosslinked gel microspheres, and (2) the binding together of microspheres/agglomerates and the fixation of the matrix structure as a consequence; the bead porosity is the result of the phase separation which occurred during polymerization in the presence of the porogen.

CONCLUSIONS

By suspension polymerization of dimethacrylate esters, or their copolymerization with methyl methacrylate, in the presence of toluene, *n*-butyl acetate, and cyclohexanol results macroreticular crosslinked matrices (white opaque beads with a specific surface area of 354 m^2/g).

The porous structure of the matrices has also been proved by various measurements applied in this study, and several conclusions can be drawn, such as:

- The diluent thermodynamic quality (δ) and its weight fraction determine the characteristics of the macroreticular structure.
- The dimethacrylate ester structure (i.e., the chain length between the two double bonds) influences the main features of the porous beads and the following sequence is suggested: EDMA, DEDMA, TEDMA.
- The main features of macroreticular poly(methyl methacrylate-*co*-ethylene glycol dimethacrylate) samples depend on the dimethacrylate ester percentage, the diluent quantity, and its thermodynamic quality.
- The thermal stability of samples depends on the matrix chemical structure.

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