

Porous Bead Aliphatic-Aromatic Methacrylate Copolymers III. The Effect of Diluent on Porous Structure Formation of MMA-DMN Copolymers

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Synopsis

Porous bead copolymers of di(methacryloyloxymethyl)naphthalene and methyl methacrylate have been synthesized using a mixture of isooctane and toluene as a diluent of the monomer system. The copolymers obtained exhibit similar specific surface areas and enhanced specific pore volume as compared to those prepared in the presence of dodecane and toluene. Their submicroscopic structure is visualized as first-order organization of microglobules similarly to PPS-type styrene-divinylbenzene copolymers.

INTRODUCTION

As reported, microglobular structure is characteristic for copolymers prepared by heterogeneous crosslinking copolymerization where so-called macroporous polymers are obtained. Depending on the nature of the pore-forming agent and the monomer system as well as their concentration, macroporous polymers exhibit a broad range of porosity parameters, including gel type structures. In previous papers^{1,2} concerning the structure of MMA-DMN copolymers prepared using dodecane and toluene, rather low porosity parameters were found for which the strong precipitating activity of nonsolvent (dodecane) used was responsible. To extend the variation in surface areas and pores volumes, the use of a weaker precipitating agent has been proposed. In studies presented in this paper dodecane has been replaced by isooctane to examine the above prediction. Thus the influence of isooctane on the formation of porous structure of MMA-DMN copolymers is here checked by means of electron microscopy and sorptomatic data.

EXPERIMENTAL

The copolymers were prepared by radical suspension copolymerization of methyl methacrylate with di(methacryloyloxymethyl)naphthalene in the presence of a mixture of isooctane and toluene and 2,2-azobisisobutyronitrile as initiator. The composition of dispersed phases is given in Table I. A 2 wt % aqueous solution of the suspension stabilizer poly(vinyl alcohol) (Loba-Chemie, Wien-Fischamend, Austria) was used as the continuous phase in all cases. The polymerization was carried out at 80°C in a 1000-mL reactor for 10 h. After completing the synthesis, the obtained beads were washed with water and then extracted in soxhlet with acetone, benzene, and methanol. After drying (at 125°C in vacuum) the product was fractionated relative

TABLE I
Composition and Properties of MMA-DMN Copolymers

Sample no.	DMN (wt %)	Isooctane in diluent (vol %)	Diluent (mL)	S (m ² /g)	Capillary condensation of N ₂				V _p total (cm ³ /g)	True density (g/cm ³)
					Contributions of (%)					
					Micropores R < 40 Å	Mesopores 40 < R < 400 Å	Macropores R > 400 Å			
1	50	16.6	60	59.3	1.2	25.3	73.5	0.844	1.47	
2	50	14.3	70	52.5	4.5	89.6	6.6	0.581	1.48	
3	50	12.5	80	40.6	10	90	—	0.120	1.45	
4	50	25	80	3.4	3.8	43.3	52.9	0.263	1.40	
5	50	27.2	110	Unmeasurable ^a	—	—	—	—	1.37	
6	50	11.1	90	18	1.2	51.5	47.3	0.427	1.40	
7	50	22.2	90	7	8.8	49.5	51.7	0.225	1.49	
8	50	16.6	90	63.8	11.3	60.5	28.2	0.248	1.42	
9	52	12.5	80	67.7	11.7	88.3	—	0.28	1.44	
10	56.6	13.7	81	74	13.7	50	36.3	0.27	1.43	
11	60	21.5	51	118	11.7	83.2	5.1	0.400	1.47	
12	66.6	20	50	82	8.6	91.4	—	0.35	1.46	

^a Collapsed beads.

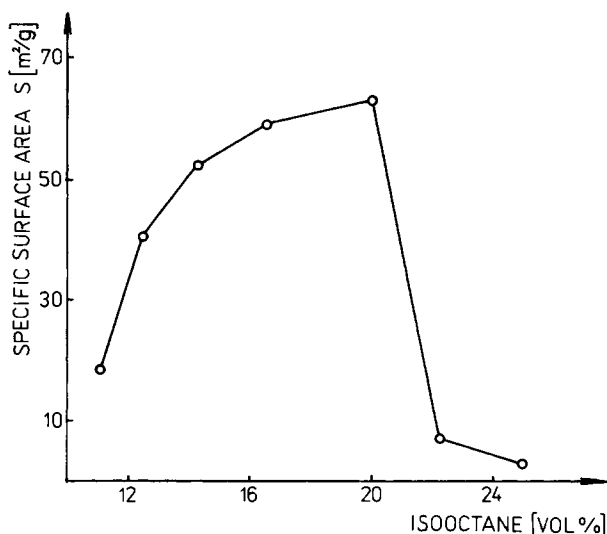


Fig. 1. Dependence of specific surface area on isooctane concentration in diluent.

to the size of grain. The fraction 0.15–0.2 mm of diameter was used in further operations.

Surface area Determinations

The surface area is obtained from nitrogen adsorption measurements according to the BET method. From nitrogen adsorption and desorption isotherms the pore size distribution is calculated according to Barret et al.³ and Wheeler.⁴ The apparatus used is a sorptomat 1800 (Carlo Erba, Milan, Italy). The specific pore volumes and the contribution of micropores, mesopores, and macropores are calculated from sorptomatic data as well. The true densities of copolymers are established by classical volumetric method using helium as a working gas. Scanning (Jeol apparatus) and transmission (Tesla BS, 613 Czechoslovakia) electron microscopy have been carried out for selected samples.

RESULTS AND DISCUSSION

The physical characteristics of MMA-DMN copolymers are listed in Table I. To get a well-developed surface, there were appropriately high concentrations of crosslinking agent used. Three main parameters of preparation have been varied: the DMN concentration in monomer mixture, the volume of diluent, and the concentration of isooctane in diluent.

Effect of Isooctane Concentration

For a fixed monomer composition (samples 1–8, Table I) the dependence between S_{BET} and isooctane concentration in diluent passes through a maximum (Fig. 1) so that there is a optimal concentration of isooctane developing maximal surface area. This effect is also reflected by the shapes of pore size distribution curves for samples 6–8 with fixed monomer and diluent

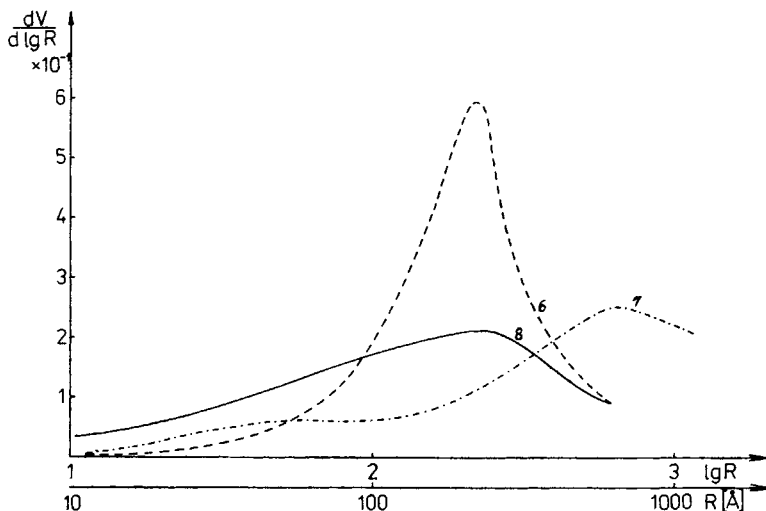


Fig. 2. Effect of isooctane concentration on the differential pore size distribution. Samples as in Table I.

amount (Table I, Fig. 2). For the smallest isooctane concentration the distribution is the narrowest one. For higher isooctane content, the distribution is wide and flat, and the positions of maxima correspond to larger pore size indicating an evolution of mesopores and their transition into macropores. For isooctane concentration higher than 25% surface area decreases down to values unmeasurable by a sorptomat (Sample 5, Table I), similarly to previously described samples prepared with the use of dodecane and toluene mixtures,² but here not such a drastic phase separation occurs (going outside the porous domain requires large amounts of isooctane than of dodecane).

Effect of Toluene Volume

For a fixed monomer composition and isooctane amount in diluent (10 mL) an increase of toluene volume gives rise to a decrease of surface area and pore volume. It is connected with disappearing of macropores and slight increase of micropores participation (samples 1–3, Table I). This effect may be explained then as a decrease of internal surface availability with lowering of the pore size. From the pore size distribution it is visualized as lowering of the position of maxima and transition of wide distribution of big pores in two family of pores—bigger ones and smaller ones—and, finally, disappearing of macropores (Fig. 3).

Effect of Crosslinking Agent Concentration

There is an increase of S_{BET} with increasing of DMN concentration in feed but limited clearly for higher DMN content (compare samples 11 and 12, Table I).

Electron Microscopy

As the phase separation has a less drastic character than when dodecane was used^{1,2} the image should be more regular. This also means that the pores and the pore volume are expected to be smaller.⁵

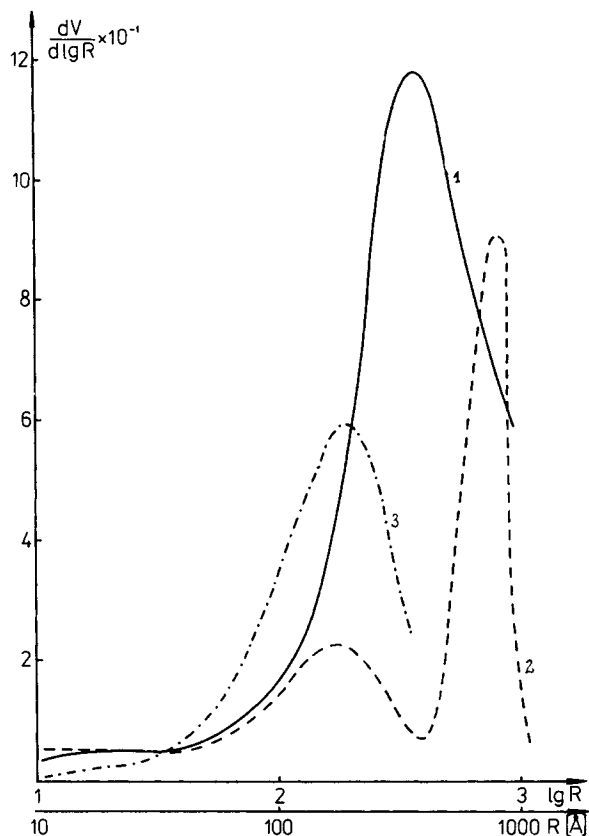


Fig. 3. Effect of toluene volume on the differential pore size distribution. Samples as in Table I.

The submicroscopic structure of the samples with measurable surface areas is microglobular (Fig. 4). Indeed the photographs show a regular

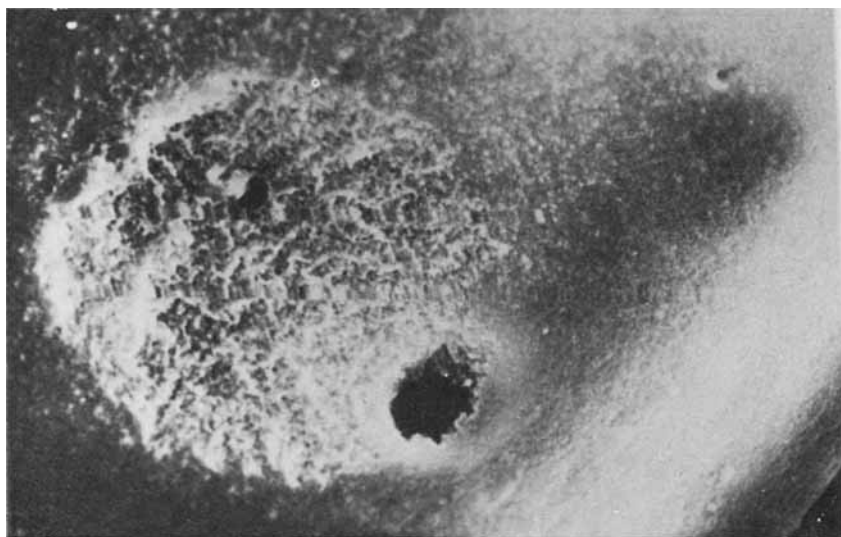


Fig. 4. SEM photograph of sample 2 (magnification $\times 1600$).

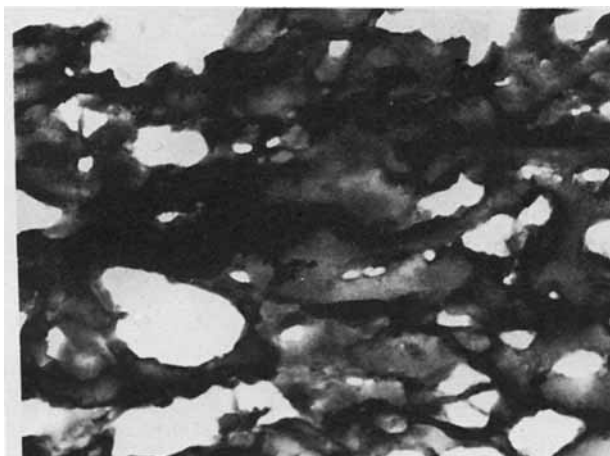


Fig. 5. TEM photograph of crosssection through the bead. Sample 3 (magnification $\times 32,000$).

formation of microglobules within the beads. Internal structure is visualized as first-order organization of microglobules associated with the presence of large spaces (Figs. 4-6). Almost all samples are characterized by macropores, creation of which is clearly caused by the presence of isooctane. All structures seem to be more permeable and loose compared to the copolymers prepared with the use of dodecane.² There are quite large globules individually located at the bead surface, which seem to be not porous at all (Fig. 7). They are probably compact, internally crosslinked gel particles, linked through their peripheric double bonds to their surface.

CONCLUSIONS

The porous structure of the MMA-DMN copolymers may be visualized schematically as it is shown in Figure 8. The shell consists of a monolayer of microglobules more tightly packed than the interior of the beads.

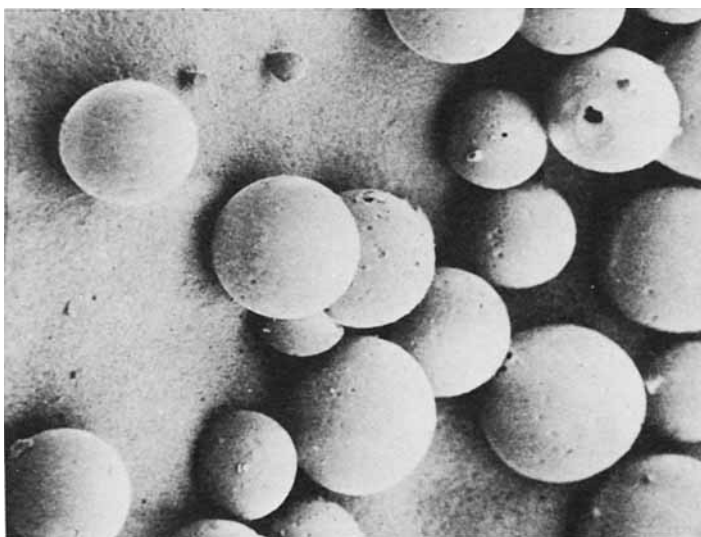


Fig. 6. SEM photograph of sample 1 (magnification $\times 120$).

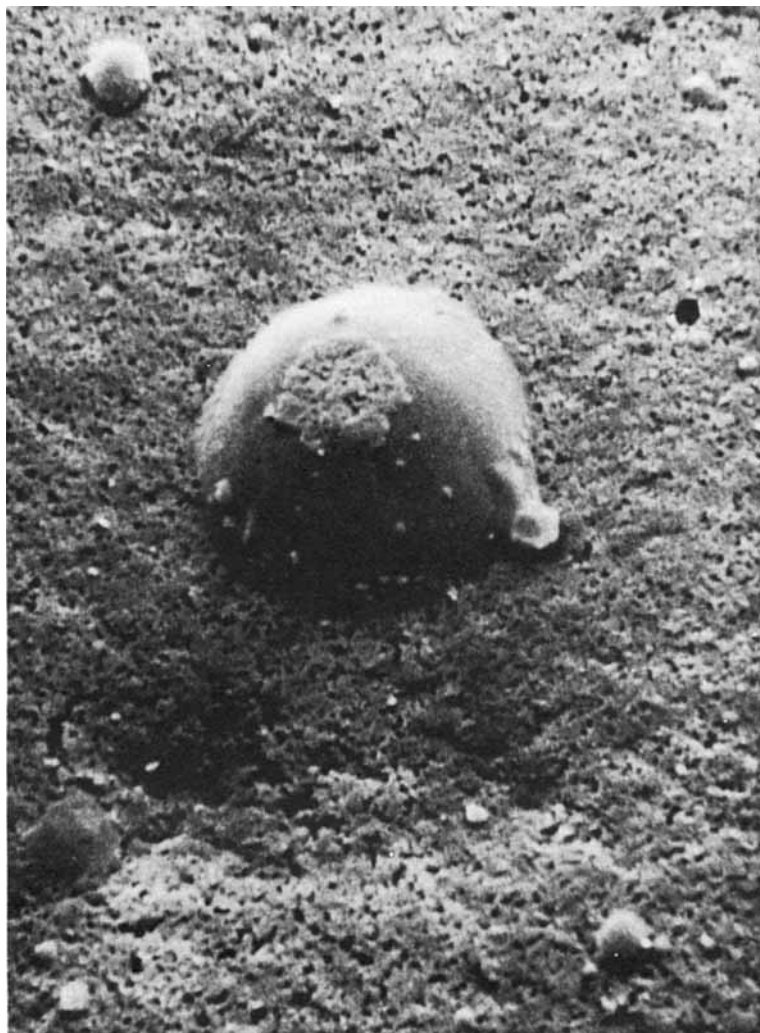


Fig. 7. Detail from Figure 6 (magnification $\times 5600$).

The fine structure is microglobule organization (more irregular in the presence of dodecane²). All sizes of detected pores are present in the region of fine structure. There are also large holes (spaces of diameter 10,000 Å and more) whose volume and size are connected with nonsolvent (dodecane

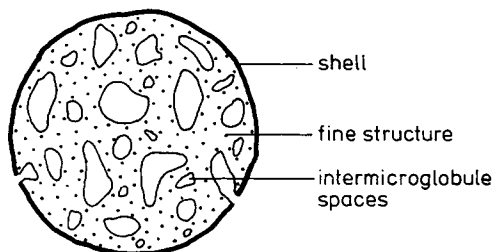


Fig. 8. Pattern of porosity construction of MMA-DMN copolymers prepared using a mixture of nonsolvent and solvent as a diluent.

or isooctane) concentrations. They are absent for weak dilution of the monomer system and grow in number with the increase of nonsolvent concentration in diluent, leading to empty or collapsed beads (with no measurable surface area) for sufficiently high concentration of nonsolvent.

A larger pore volume requires more nonsolvent whereas enhanced internal surfaces are obtained at its intermediate concentrations and low solvent (toluene) content coupled with sufficiently high DMN concentration.

A construction of that porous structure may be considered on the base of a three-stage process described recently by Chung et al.,⁶ where gelation, molecular overlap, and phase separation are the stages leading to the porous or gel-type structure, depending on the precipitating activity of the diluent used.

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