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Effect of diluents on the porous structure of crosslinked poly(methyl methacrylate) beads

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Summary

Copolymer beads based on methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDM) were prepared by suspension polymerization technique. Two different solvents, namely toluene and cyclohexane, were used as the diluents in the polymerization system. It was found that toluene produces pores of radii 2 to 10 nm corresponding to the interstices between the nuclei. In the case of cyclohexane as the diluent, formation of large pores with a broad size distribution from 10 to 1000 nm were observed. These sizes correspond to the spaces between the microspheres and the aggregates forming the copolymer beads. The results indicate that, as in porous styrene - divinylbenzene copolymers, the solvating power of the diluent present during the network formation is mainly responsible for the structural characteristics of porous MMA / EGDM copolymer beads.

Introduction

Heterogeneous (porous) polymer networks are widely used as starting materials for ion exchangers and as specific sorbents, and therefore, have been the subject of a large number of studies (1,2). Porous polymer networks have been prepared from the monomers in the presence of an inert (non-polymerizable) diluent. In the past three decades, pore structure formation in free-radical crosslinking copolymerization of vinyl / divinyl monomers has been reported repeatedly (1-14). The results indicate that a phase separation during the copolymerization and crosslinking reactions is responsible for the formation of porous structures. The degree of phase separation is dependent on the concentration of the crosslinking agent, concentration and the type of the diluent, and the reaction temperature. Incipient phase separation during the reactions can occur above or below the gel point, depending on the degree of crosslinking and the polymer solvent interaction parameter χ.

The study of the pore structure formation in styrene - divinylbenzene (S - DVB) copolymerization has been reported in many papers. However, only a few studies appeared in the literature for other comonomer systems such as the 2-vinylpyridine - DVB (16,17), 2-hydroxypropyl methacrylate - oligo(ethylene glycol) dimethacrylates (18), and methyl methacrylate - DVB systems (19). The present study deals with the synthesis and formation mechanism of porous methyl methacrylate - ethylene glycol dimethacrylate (MMA / EGDM) copolymer beads. The formation of porous structures was induced by using two different diluents, namely toluene and cyclohexane. The pore structure of the copolymers was examined as a function of the EGDM concentration and of the type of the diluent. The

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results allowed us to describe the conditions of the porosity formation in MMA/EGDM copolymers.

Experimental

The monomers MMA and EGDM were freed from the inhibitor by shaking with a 10 % aqueous KOH solution, washing with water, and drying over Na_2SO_4. They were then distilled under reduced pressure. All the other materials were used without further purification, including dibenzoyl peroxide (Merck), toluene (Merck), and cyclohexane (Merck).

The MMA - EGDM copolymer beads were obtained by the suspension polymerization method. Dibenzoyl peroxide as the initiator (1 wt % in relation to the monomers) was dissolved in the selected monomer-diluent mixture of 40 mL volume and this was then added to a solution of NaCl (0.8 g), poly(vinyl alcohol) (0.16 g), and starch (0.14 g) in 200 mL water at 80°C and 500 rpm. The reaction was allowed to proceed for 5h under nitrogen atmosphere. After polymerization, the copolymer beads of 0.3 - 1.1 mm in diameter were washed with water, extracted with acetone for 24h, and finally dried in vacuum at 60°C. Measurements showed that the pores in all of the networks are stable, i.e., they do not collapse on drying in the swollen state.

The swelling measurements of the networks were carried out in toluene at room temperature. The weight swelling ratio q_w was determined by immersing the copolymer beads in toluene for one week. They were then weighed in the swollen state and finally dried under vacuum to constant weight. q_w was calculated as the ratio of the weights of the gel in the swollen state and the dry state. The volume swelling ratio q_v was determined by placing the copolymer beads in a graduated cylinder and reading the volume. An excess of toluene was then added, and the volume was read at the swelling equilibrium. q_v was calculated as the ratio of final to initial volumes.

The surface morphology of the copolymer particles was characterized by an JEOL JXA-840A scanning electron microscope. Pore volume and pore size distribution were determined by mercury intrusion porosimetry on a Micromeritic AutoPore 9220 porosimeter. Cumulative pore volumes (V_p) were estimated from the intruded mercury volumes and the distribution function $\Delta V / \Delta \log r$ was used to express the pore size distribution, where ΔV is the pore volume change when the radius of a cylindrical pore was changed from r to $r-\Delta r$.

Results and discussion

The initial volume fraction of the monomers in the organic phase was taken to be constant at 0.5 throughout the present study, and only the EGDM concentration was varied. Figures 1A and 1B show the pore size distribution curves of MMA - EGDM copolymers formed in the presence of toluene and cyclohexane as inert diluents, respectively. For the sake of clarity, only three curves for each series are illustrated in the Figures. The results indicate that increasing cross-linker content increases the amount of pores. At 50 % EGDM, the pore volume reaches to 0.3 and 1.1 mL/g with toluene and cyclohexane as the diluents, respectively. Thus, cyclohexane as an inert diluent induces higher porosities than toluene. Figures 1A and 1B also show that toluene produces pores of radii 2 - 10 nm. However, in the presence of cyclohexane, large pores with a broad size distribution in the range 10 - 1000 nm were obtained.

The difference in the pore structure depending on the type of the diluent is also illustrated in Figures 2A and 2B. Here, the pore size distribution curves are shown for fixed

EGDM contents (20 and 40 wt %, respectively) but for different type of diluents.

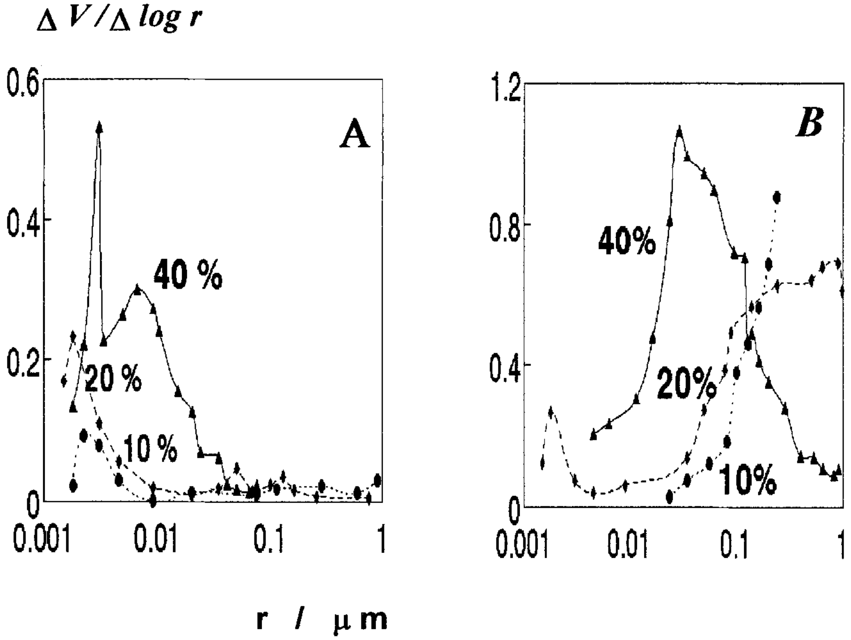

Fig. 1. Pore size distribution curves of MMA/EGDM copolymer beads obtained using toluene (A) and cyclohexane (B) as inert diluents. The EGDM concentrations are shown in the Figures. Diluent / monomer volume ratio = 1/1.

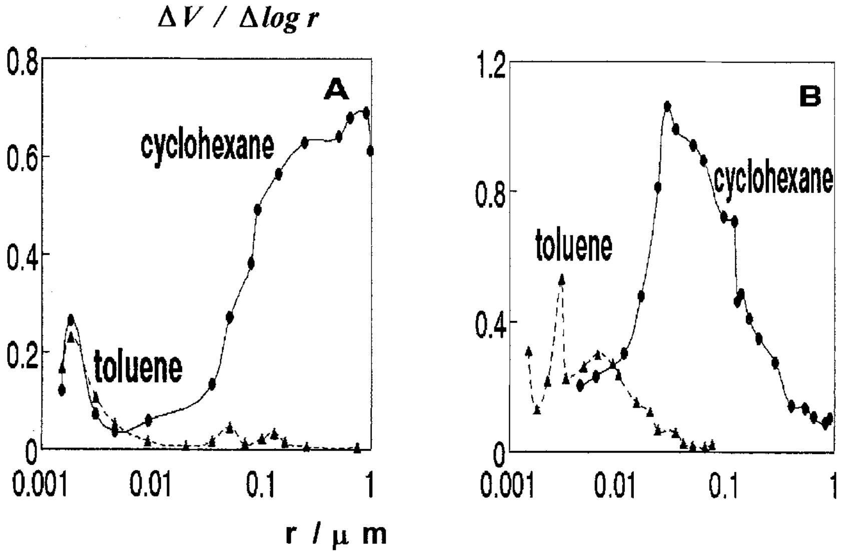

Fig. 2. Pore size distribution curves of MMA/EGDM copolymer beads with 20 (A) and 40 wt % EGDM (B). Diluent / monomer volume ratio = 1/1. The diluents used are shown in the Figures.

In toluene as a diluent, 70 to 90 % of the pores have radii less than 10 nm. In cyclohexane, this fraction is very small and increases up to 20 % with increasing EGDM content. The results clearly indicate different behavior of toluene and cyclohexane as a pore-forming agent. The effect of the type of the diluent on the network structure can also be seen in the SEM micrographs (Figure 3). As with previous results, the network structure formed in cyclohexane consists of agglomerates of different sizes. However, pores with less than 100 nm dominate the surface structure of polymers formed in toluene.

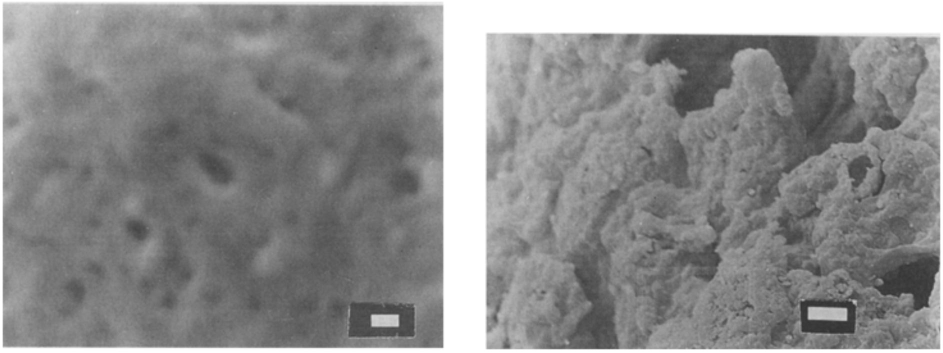
(A) (B)

Fig. 3. SEM micrographs of MMA/EGDM copolymers obtained with toluene (A) and cyclohexane (B) as the diluent. EGDM = 40 wt %. Diluent / monomer volume ratio = 1/1. The scaling bar corresponds to 100 nm (A) and 10,000 nm (B).

The cumulative pore volume and the swelling characteristics of the polymer samples with 20 and 40 % EGDM are collected in Table I. Although the volume swelling ratios are almost independent of the type of the diluent, the weight swelling ratio is a strong function of the diluent type. This is due to the fact that the volume swelling results from the change of the network volume, which only depends on the crosslink density. However, weight swelling in such highly crosslinked networks mainly results from the filling of the voids by the solvent and therefore is dependent on the porosity of the networks.

***Table I*:** Characteristics of MMA/EGDM copolymers formed in toluene and cyclohexane as the diluents

EGDM :	20 %		40 %	
Diluent:	Toluene	Cyclohexane	Toluene	Cyclohexane
Pore volume (mL/g):	0.11	1.05	0.34	1.13
Volume swelling ratio:	1.4	1.3	1.4	1.2
Weight swelling ratio:	1.4	4.1	1.8	3.2

The different behavior of the diluents toluene and cyclohexane as a pore-forming agent can be explained by their solvating powers for poly(MMA) chains. In Table II, the solubility parameters of the monomers, diluents and the polymer are collected. The difference between the solubility parameters of the solvent and of the polymer shown in the last column of Table II indicates that both the monomers and toluene are good solvents for the polymer so that they are solvating diluents for MMA / EGDM system. Thus, toluene cannot induce a phase separation prior to the gel point. However, beyond the gel point, as the crosslinking density of the gel increases with increasing conversion, its swelling capacity will decrease until it reaches to the degree of dilution of the gel in the reaction system. Thereafter, since the gel cannot contain solvent more than its capacity, it will separate into two phases. Thus, phase separation and formation of porous structures in toluene occurs by ν - induced syneresis (2).

Table II : Solubility parameter of the monomers, diluents and the polymer.

material	$\delta \ (cal/cm^3)^{0.5}$	$\Delta\delta$
MMA	8.8	0.5
EGDM	8.9	0.4
toluene	8.9	0.4
cyclohexane	7.8	1.5
poly(MMA)	9.0 - 9.5	-

According to Table II, cyclohexane is a bad solvent and should act as a precipitant in free-radical cross-linking copolymerization of MMA /EGDM comonomer system. Thus, cyclohexane causes the separation of the system into two phases prior to the gel point due to the polymer-solvent incompatibility (χ - induced syneresis) (2). As a result, cyclohexane produces higher porosities than toluene.

In analogy with the porous styrene - divinylbenzene networks, the pore structure of MMA - EGDM copolymers by using inert diluents may be considered as follows. The porous structure of these copolymers consists of agglomerates of various particles; the smallest particles of about 10 - 20 nm in diameter are the nuclei, and the aggregation of these nuclei results in the microspheres with diameters of 50 - 100 nm; the microspheres are aggregated again in particles of about 250 - 1000 nm in diameter. The pores are defined as the spaces between the nuclei, microspheres, and particles. According to the experimental data, toluene induces pores corresponding to the spaces between the nuclei. However, the pores formed using cyclohexane as the diluent correspond to the voids between the microspheres and the aggregates forming the copolymer beads.

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