

## The effect of mixed diluent on the porous structure of crosslinked PMMA beads\*

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### Summary

In this work copolymer beads, based on MMA (methyl methacrylate) and EGDM (ethylene glycol dimethacrylate), were prepared by suspension polymerization. A mixed solvent, composed of two different solvents, namely toluene and cyclohexane, was used as the diluent in the polymerization medium. The porous structure of the beads was found to be affected by the solvent composition used to dissolve the monomers initially. It was observed that the porosity and pore size increased gradually with the increase of cyclohexane content of the solvent composition. It was also detected that the pore radii changed from 2-10 nm to 700-1000 nm as the cyclohexane content of the diluent changed from nil to 100 % (v/v) respectively. These results indicate that pore size of the copolymer beads is a function of solvent composition.

### Introduction

Porous polymers have been used widely in the separation and purification processes. Polymeric adsorbents have been used widely as starting materials for ion exchangers, polymeric supports in chromatography and more recently as catalysts (1-4). Porous polymeric adsorbents possess a wide range of particle size porosity and pore size distribution, high capacity and superior regeneration efficiency and big surface area as compared to that of the conventional adsorbents. Since bead and pore size distribution and homogeneity of the beads highly affect the efficiency and repeatability of any separation, experimental conditions during the preparation of the polymeric beads became important (5-6).

In general polymeric microspheres within the size range of 50 nm to 2 nm are produced by either suspension, emulsion or dispersion polymerization. On the other hand porous polymeric beads are usually obtained by suspension polymerization. Formation of porous structure usually depends on the type of the solvent used in the polymerization medium. To obtain porous structure, a wide variety of inert compounds which can help to form pores were used up today (7-9).

Another way of obtaining porosity is to use diluents for the monomers (10-13). If the diluent is a bad solvent for the cross-linked polymer, a two-phase heterogeneous structure, consisting of the polymer and the diluent, is formed. In this technique pores are formed as the diluent leaves the medium. Thus the pore size distribution in the matrix structure can be controlled by changing the good solvent/bad solvent ratio of the diluent.

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Investigations on the pore formation mechanism in styrene-divinylbenzene (S-DVB) copolymerization were reported in many papers. However only a limited number of literature can be found for other comonomer systems such as 2-vinyl pyridine -DVB (14-15), 2-hydroxypropyl methacrylate-oligo(ethylene glycol) dimethacrylates (16), and methylmethacrylate-DVB (17).

This work deals with the effect of mixed diluents on the porosity and pore size distribution of cross-linked PMMA/EGDM beads. During the polymerization various mixtures of toluene and cyclohexane, which were determined as good and bad solvents respectively for the MMA-EGDM copolymers, were used as the diluent. Toluene/cyclohexane ratio was varied and the effect of composition of the diluent, on the pore size and pore size distribution of polymer beads, was determined by mercury porosimeter and SEM techniques.

The results indicated that the pore size and pore size distribution can be controlled by the composition of the diluent used in the polymerization medium.

### ***Experimental***

MMA and EGDM(Merck) were freed from inhibitor by extracting with 5 % aqueous KOH solution, then washing with water, and drying over  $\text{Na}_2\text{SO}_4$  and distilling under reduced pressure. Dibenzoyl peroxide(Merck), toluene(Merck) and cyclohexane(Merck) were used without further purification,

MMA-EGDM copolymer beads were obtained by suspension polymerization. A four necked reactor equipped with a stirrer, a thermometer, a gas inlet and a condenser was used during the experiments. 200 ml distilled water, containing 0.8 g NaCl, 0.4 g poly(vinyl alcohol) and 0.3 g starch was charged into the reactor and the temperature was raised to 80 °C by means of a thermostatic water bath. To this solution, 40 ml of monomer- diluent mixture was added dropwise under constant rate of stirring (400 rpm). Organic phase contained 32 g MMA, 8 g EGDM, 40 g diluent (cyclohexane-toluene mixture in varying ratio) and dibenzoyl peroxide 1 % by weight of the monomer. The reaction was allowed to continue for 4 h at 80 °C, under nitrogen atmosphere. At the end of the polymerization, the copolymer beads, 0.3 - 1.2 mm in diameter, were washed with water, then with acetone for 24 h in a soxhlet extractor and finally dried in vacuum.

The swelling behavior of the polymer beads was investigated in toluene at room temperature. To determine the weight swelling ratio  $q_w$ , copolymer beads were immersed in toluene for one week until reaching equilibrium. After drying by a filter paper, they were then weighed in the swollen state, and finally dried in vacuum till no weight loss could be observed.  $q_w$  was calculated as the ratio of the weight of a certain amount of bead in the swollen and dry state. The volumetric swelling  $q_v$  of the copolymer beads was determined as the ratio of the volume of swelled beads in toluene to the initial dry volume of approximately 1 g of copolymer beads. Experiments were done in a graduated cylinder of 10 mm diameter.

The surface morphology, of the copolymer particles, was characterized by an JEOL JXA840A scanning electron microscope. Pore volume and pore size distribution were determined by mercury intrusion porosimetry by a Micromeritic Auto Pore 9220 porosimeter. Cumulative pore volume ( $V_p$ ) was determined from the intruded mercury volume and the distribution function  $\Delta V/\Delta V \log r$  which was used to express the pore size distribution, where  $\Delta V$  is the pore volume change when the radius of spherical pore was changed from  $r$  to  $r+\Delta r$ .

## Results and Discussion

In a previous study (8) the porous structure of MMA-EGDM copolymers was examined as the function of EGDM concentration. During this study it was observed that the type of the diluent used in the polymerization medium had a pronounced effect on the porosity of the copolymer beads.

Taking in mind the above result it was aimed in this work to investigate the effect of diluent composition on the porosity of the copolymer beads. Figures 1A and 1B show the porosity and density changes of MMA-EGDM copolymer beads, which were formed in the presence of cyclohexane-toluene mixture, as the function of diluent composition. The results indicate that the porosity decreased while the density of the copolymer beads

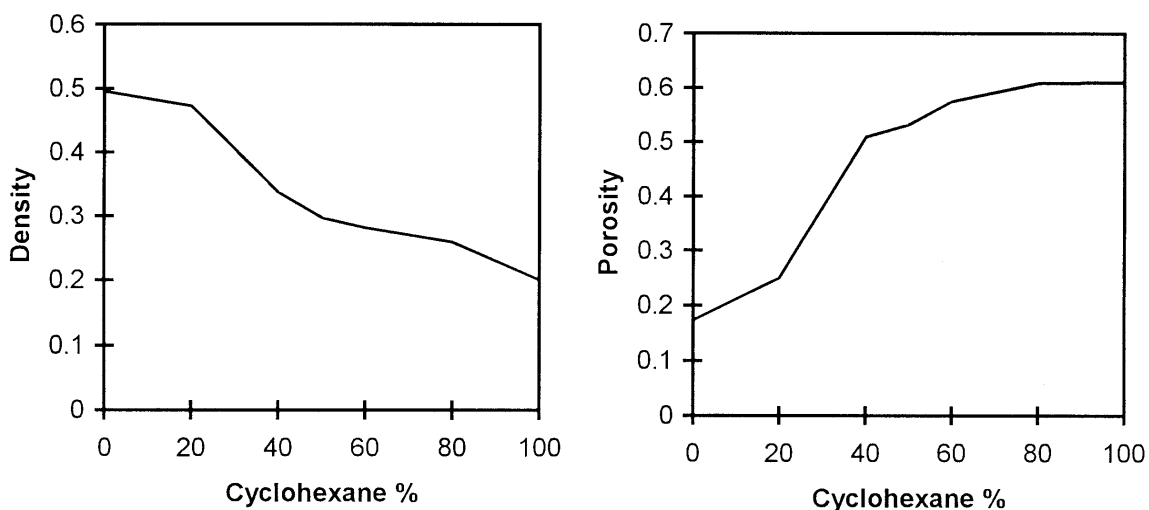
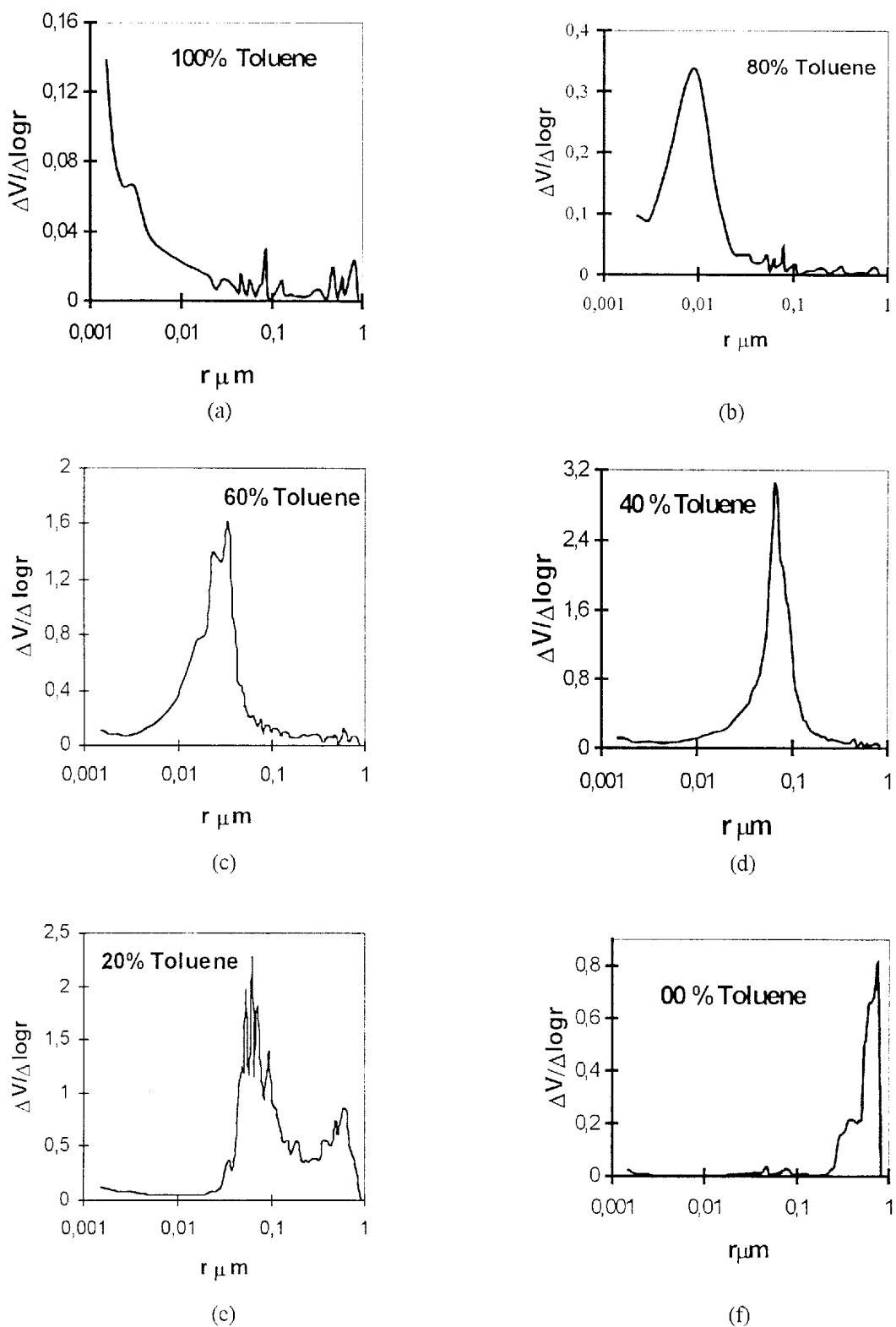


Fig. 1. The porosity (A) and density (B) curves of PMMA-EGDM copolymers obtained using a mixed solvent of cyclohexane and toluene, as the inert diluent.

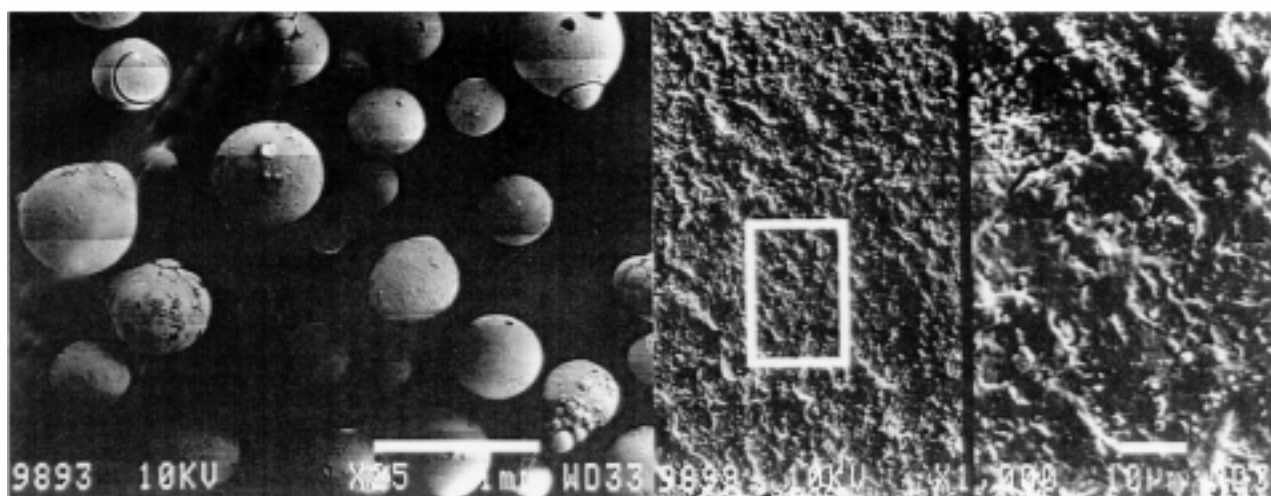
increased as the toluene content in the diluent increased.

The radii of copolymer beads which were prepared in pure toluene or in pure cyclohexane were found to vary between 2 - 10 nm and 700 - 1000 nm respectively. The effect of the composition of diluent on the pore radii can be seen in Figure 2. It is seen that as the cyclohexane content of the diluent increased from nil to 100 % (v/v), pore radii increased from 2-10 nm to 700-1000 nm.

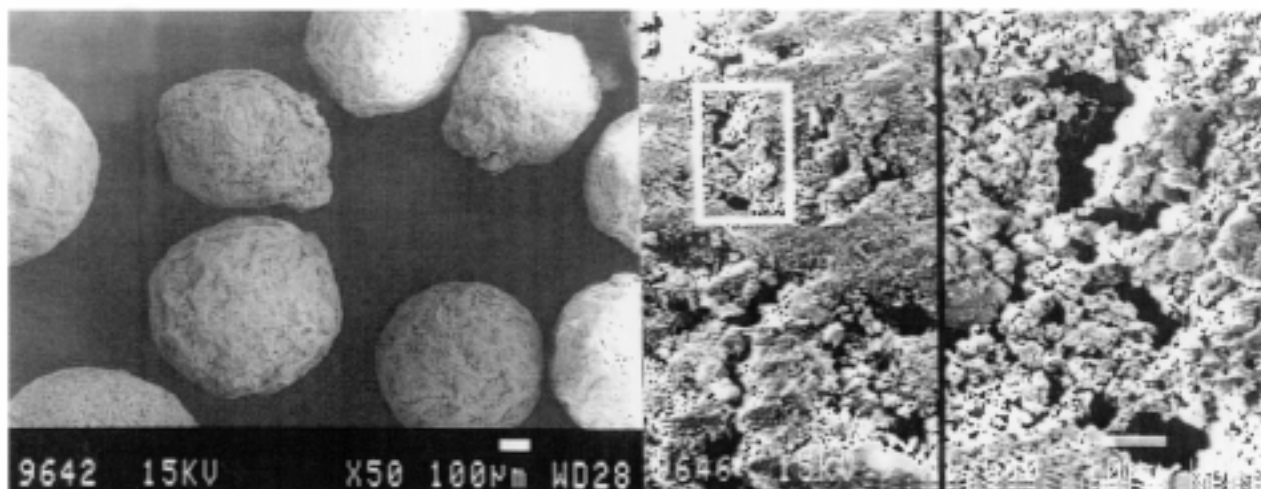
The effect of the composition of the diluent on the network structure can also be seen in the SEM micrographs (Fig. 3). Increasing the amount of cyclohexane, the bad solvent for copolymer, in the polymerization medium caused to form greater pores due to the phase separation between the copolymer and the diluent.



**Fig. 2.** Pore size distribution curves of MMA-EGDM copolymer beads. (a. 2-10 nm; b. 5-40 nm; c. 30-70 nm; d. 80-100nm, e. 60-1000nm, f. 700-1000 nm)



(A)



(B)

**Fig. 3.** SEM micrographs of MMA/EGDM copolymers obtained from 80 % toluene (A) and 20 % toluene (B).

As the amount of the good solvent present in the polymerization medium increased phase separation delayed and did not occur prior to gel point. However beyond the gel point, as the cross-linking density of the copolymer increases with increasing conversion, its swelling capacity will decrease and the phase separation will occur in anyway. Thereafter, since the gel cannot contain solvent more than its capacity, it will separate into two phases. The diluent which is used as a bad solvent for the copolymer acts as a precipitating agent and causes the system to separate into two phases prior to the gel point due to the polymer-solvent incompatibility. After the removal of the diluent from the beads, porosity is formed. The extraction method of the solvent from the beads also affects the pore structure. If the solvent used to extract the residual monomer and diluent from the pores is a good solvent for the copolymer it may cause the walls of the pore to collapse and thus causing some of the pores to be blocked.

The swelling characteristics of the PMAA-EGDM copolymer beads which were prepared in mixed diluents are collected in Table 1.

**Table 1.** Swelling characteristics of MMA-EGDM copolymers

Toluen %	100	60	40	20
$Q_w$	1.289	1.4030	1.4060	1.4368
$Q_v$	2.100	1.5715	1.3993	1.2050

It was expected and found that the weight swelling ratio, which is depended on porosity of the copolymer beads, should increase with the porosity. Since the crosslinker ratio was kept constant, volume swelling ratio was expected to be unaffected by the porosity. Contrarily as we can not explain it was found that the volume swelling ratio was also depended on the porosity somehow.

The figures of pore size distribution showed that porosity and pore size increased gradually with the percentage of cyclohexane in the diluent composition. These results indicated that the pore size and the porosity of the MMA-EGDM copolymer beads can be controlled. This fact gives a possibility to produce adsorbents with desired properties.

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