Table III
Amount of Unreacted Carbon–Carbon Double Bonds Present in Some Polymers Made in Ethyl Acetate with Different Initial Monomer Concentrations Measured with Solid-State ^{13}C NMR Spectroscopy

initial monomer concn %	unreacted C=C bonds, %	initial monomer concn %	unreacted C=C bonds, %
5	4	25	12
10	10	35	16.5
15	14	40	18
20	15	50	20

solubility parameter toward higher values. Thus, at a certain conversion the solubility parameter has a value corresponding to the maximum swelling of the polymer. At this composition it can be assumed that the 20-Å pores are formed. The higher the monomer concentration, the more pronounced this effect will be. This is supported by the fact that the 20-Å peak is more pronounced at high TRIM concentrations.

Unreacted Carbon–Carbon Double Bonds. ^{13}C NMR analyses in the solid state (CP-MAS-DD) were carried out in order to determine the absolute amount of unreacted methacrylate groups. For polymers made in different solvents, the amount of unreacted carbon–carbon double bonds was found to have a minimum where the solubility parameters of the solvent and the polymer were the same (Table I). An explanation to this is that the polymer made in toluene[2] is more regular than the one polymerized in ethyl acetate. For polymers made in ethyl acetate, it was found that the amount of unreacted carbon–carbon double bonds increased with increasing monomer concentration as is shown in Table III. The amount of unreacted methacrylate groups in polymers made in ethyl acetate was higher than for those made in toluene.[2]

In conclusion, we have found that the polymerization of TRIM in different types of solvents gave macroporous polymers (high BET surface area) in which the amount of unreacted carbon–carbon double bonds and the BET surface areas varied with the difference in solubility parameter between the polymer and the solvent. The amount of unreacted double bonds passed through a minimum when the solubility parameter of the solvent was the same as that of the polymer. At this point the network has it most open structure, permitting more double bonds to participate in the polymerization reaction. Consequently, the polymer structure becomes more regular as $|\delta_{pol} - \delta_{solv}|$ approaches zero.

The pore size distribution of poly(TRIM) made in ethyl acetate was found to be different from that of poly(TRIM) made in toluene. Instead of only one peak at 20 Å as observed for toluene, three peaks were observed, one of which was the 20-Å peak. The lower the monomer concentration in the polymerization, the less pronounced was the 20-Å peak and the higher the 26- and 36-Å peaks. Throughout the series the large pores of poly(TRIM) made in ethyl acetate were larger than the ones obtained at corresponding concentrations in toluene.[2]

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Registry No. TRIM (homopolymer), 26426-04-0.

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Macroporous Gels. 3. Copolymerization of Trimethylolpropane Trimethacrylate and Methyl Methacrylate in Toluene or Ethyl Acetate

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ABSTRACT: Free-radical copolymerization of trimethylolpropane trimethacrylate (TRIM) with methyl methacrylate (MMA) was performed in two solvents, toluene and ethyl acetate. The resulting copolymers were found to be macroporous regardless of the TRIM-to-MMA ratio and of the solvent used in the interval studied. The pore size distributions of both small ($r < 50$ Å) and large ($r > 50$ Å) pores were found to change with the TRIM-to-MMA ratio. High-resolution solid-state ^{13}C NMR was used to determine the amount of unreacted carbon–carbon double bonds in the xerogels. They were found to decrease with an increasing MMA concentration in the monomer mixture.

Introduction

Macroporous polymers were first made by radical copolymerization of styrene and divinylbenzene, and most reports deal with this system. Many recent investigations have also been directed toward the control of the porous texture.[1,2] Macroporous polymers made from trimethylolpropane trimethacrylate (TRIM) have been shown to have some unexpected structural features.[3,4] Polymerization of TRIM in toluene yields polymers with two pore size distributions, one consisting of small pores ($r < 50$ Å) and one of large pores ($r > 50$ Å).[3] The small pores, which have a narrow pore size distribution, appear

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to be independent of the monomer-to-solvent ratio. The large pores, however, vary with this ratio. Polymerization in different solvents[4] will affect the pore size distribution of both the small and the large pores.

The aim of the present study is to see how copolymerization influences the porous structure. Here we shall report the results obtained from the copolymerization of TRIM and MMA in two different solvents (toluene and ethyl acetate).

The resulting copolymers were studied by nitrogen adsorption–desorption techniques (pore volume, surface area (BET), and pore size distribution (BJH), mercury porosimetry, bed density measurements, high-resolution solid-state ^{13}C NMR, and scanning electron microscopy (SEM).

Experimental Section

Materials. Trimethylolpropane trimethacrylate (TRIM, technical quality containing more than 98% TRIM from Merck AG or Alfa Products) was copolymerized with methyl methacrylate (MMA, analytical grade) in the presence of a solvent (toluene or ethyl acetate, analytical grade) at 73 °C. The initiator used was azobis(isobutyronitrile) (AIBN, analytical grade).

Polymerization. A polymerization experiment was performed as follows. AIBN (20 mg) was weighed into a 50-mL Hypo-vial. The vial was sealed, evacuated, and filled with nitrogen. Then 20 mL of a solution containing the monomers (30%) and solvent (70%) was added. The monomer consisted of a mixture of MMA (% by volume) and TRIM (% by volume), giving 100% monomer. The vial was placed in a shaking bath at 73 °C. After about 10 min gelation started, and after 5 min more the entire reaction volume was occupied by a turbid, stiff gel. The vial was kept in the shaking bath for 8 h before cooling. The yield of polymer was 99.5% or higher throughout the series of experiments.

Posttreatment. The resulting polymer was ground, and the bed volume was measured both in the swollen state and as xerogels after drying at 60 °C in vacuum for at least 24 h.

Texture Determination. The surface areas were determined by adsorption of nitrogen according to the BET method.[5] The pore size distributions for small pores (radius (r) < 50 Å) were obtained from nitrogen adsorption–desorption measurements according to the BJH method.[6] The pore sizes, the surface areas, and the pore volumes were determined in pore volume analyzers (Micromeritics 2100 E or Micromeritics Digisorb 2600).

The pore structure of large pores (r > 50 Å) was examined by mercury porosimetry (Micromeritics 9300) and scanning electron microscopy (SEM). The SEM investigations were carried out at three levels of magnification, 20 000, 78 000, and 100 000 times in a Jeol JSM 35 microscope.

Determination of Unreacted Carbon–Carbon Double Bonds. The amount of unreacted methacrylate groups was determined by high-resolution solid-state ^{13}C NMR spectroscopy using cross-polarization (CP), magic-angle spinning (MAS), and high-power decoupling (DD) (Varian XL-200 with solid sample accessories). Carbonyl groups conjugated with a double bond have a lower chemical shift (166 ppm vs. Me_4Si) than the unconjugated, reacted ones (176 ppm vs. Me_4Si). The difference is large enough to almost completely resolve the two peaks. This together with nearly similar contact times made quantitative measurements possible.[3]

Results and Discussion

Trimethylolpropane trimethacrylate (TRIM) was copolymerized with methyl methacrylate (MMA) in two different solvents, toluene and ethyl acetate, using a conventional solution polymerization technique. Studies of the macroscopic structure as a function of the TRIM-to-MMA ratio were carried out in both solvents. The initial monomer concentration was held constant (30%), while the composition of the monomer mixture was varied from 0% to 40% by volume MMA in TRIM. The initial initiator concentration was constant (0.1% w/v) throughout the series of experiments.

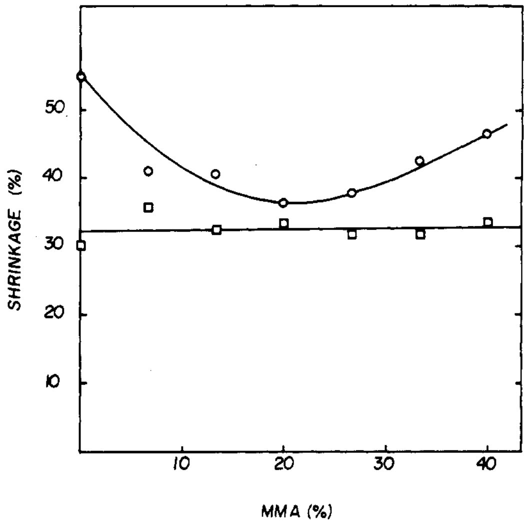

Figure 1. Dependence of shrinkage, caused by the removal of toluene (○) and ethyl acetate (□), on the initial MMA concentration in the monomer mixture.

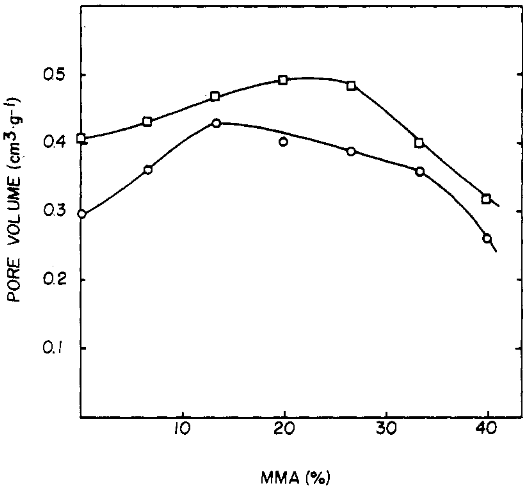

Figure 2. Dependence of pore volume on the initial MMA concentration in the monomer mixture: solvent = toluene (○), ethyl acetate (□); monomer:solvent = 30:70.

Removal of the solvent from the polymer caused shrinkage which varied with the TRIM-to-MMA ratio in the monomer mixture and the type of solvent used (Figure 1). Polymers made in toluene had a minimum at about 20% MMA in the monomer composition. However, with ethyl acetate the MMA content had little effect on the shrinkage. Throughout the experiments lower shrinkage was observed in ethyl acetate. The difference in behavior indicates structural dissimilarities between polymers made in the two solvents.

The influence of the MMA-to-TRIM ratio on the pore volume is shown in Figure 2. With toluene the pore volume had a maximum at about 10% MMA. Ethyl acetate caused the maximum to be displaced toward a higher MMA content (≈25%). Larger pore volumes were obtained for polymers made in ethyl acetate.

SEM investigations of the polymer xerogels indicated a basic structure made of small spheres (nodules) which had agglomerated to form large unshaped entities, irrespective of the solvent used (Figures 3 and 4). The agglomerated entities had diameters ranging from about 0.05 to 0.2 μm. For gels made in toluene, some of the unshaped entities were linked together by rodlike structures as is shown in Figure 3. Their diameters were about 0.05 μm. The SEM micrographs also show differences in structure between polymers made in the two solvents. Those made

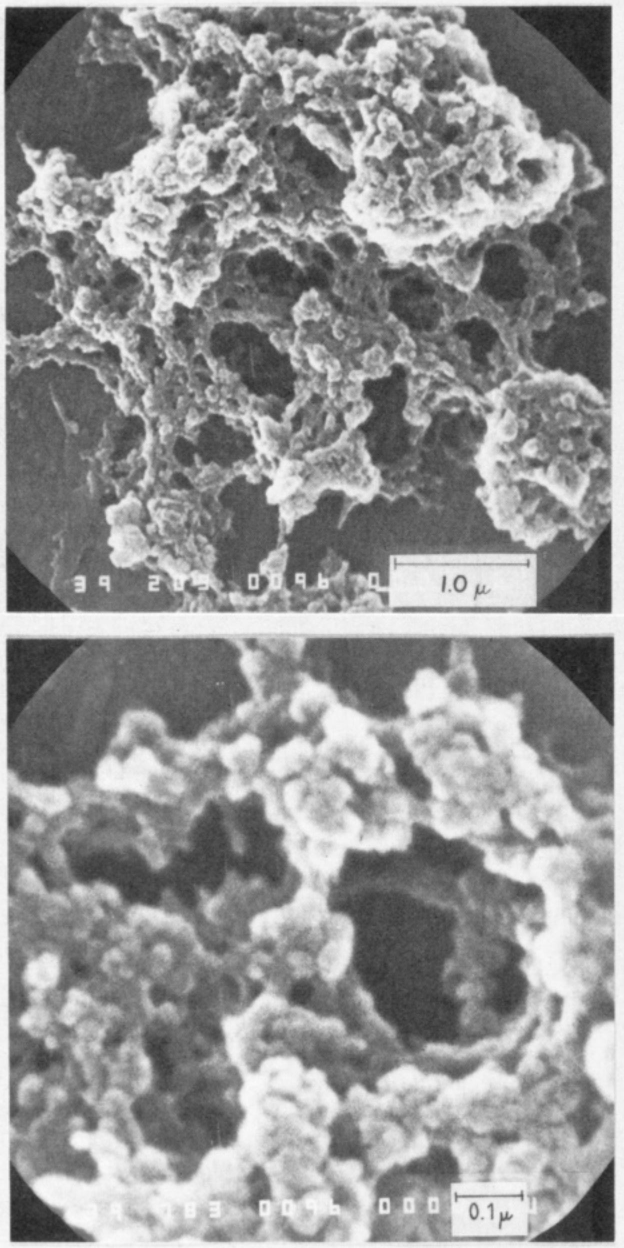

Figure 3. Scanning electron micrograph of a ground poly(TRIM-*co*-MMA) bead: MMA concentration = 33.3%; solvent = toluene; monomer:solvent = 30:70. Magnification levels: (a, top) ×16 000, (b, bottom) ×62 000.

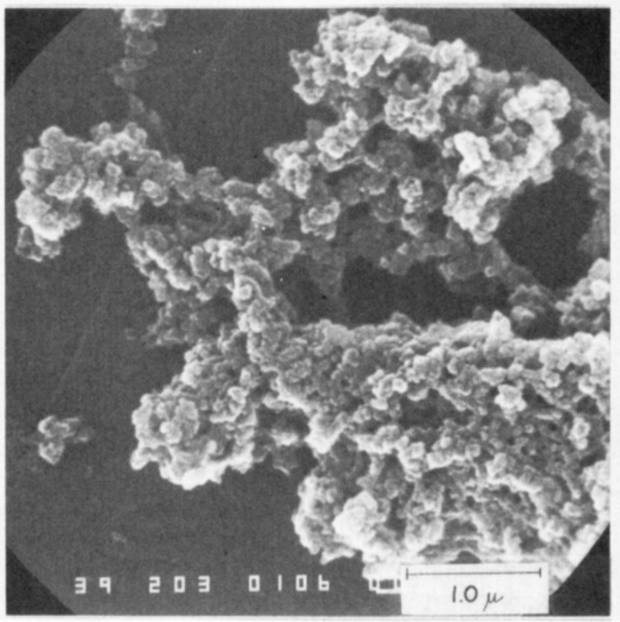

Figure 4. Scanning electron micrograph of a ground poly(TRIM-*co*-MMA) bead: MMA concentration = 33.3%; solvent = ethyl acetate; monomer:solvent = 30:70; magnification level, ×20 000.

in toluene had a more uniform appearance.

Large Pores. Mercury porosimetry was used to determine the pore size distribution of large pores ($r > 50$ Å). Results for some polymer xerogels made in the presence of toluene are shown in Figure 5a. The distributions represent four different monomer compositions. Changing the composition resulted in changes in the size of the larger pores. A low MMA content displaced the pore size distributions toward larger pore sizes compared to pure poly(TRIM) (Figure 5a). A maximum in pore size was obtained at a MMA concentration of about 25%.

For polymers made in toluene, the pore volume increased when the MMA content in the monomer mixture was increased from 0% to 15%. This was probably due to an enlargement of the large pores (Figure 5a) and to the formation of a more stable network as is indicated by a corresponding decrease in the shrinkage (Figure 1). Increasing the MMA content above 15% resulted in a decrease in the pore volume. This was probably due to a partial collapse of the large pores as is indicated by the increasing shrinkage (Figure 1). At the same time, the maximum of the pore size distribution was displaced toward larger pore sizes (Figure 5a). A further increase in the MMA concentration lead to a progressive collapse of large pores which was reflected in a displacement of the distribution toward smaller pore sizes (Figure 5a).

Changing the solvent from toluene to ethyl acetate affected the size distribution of the large pores. At low MMA concentrations it was found to be broader than in toluene and also displaced toward larger pore sizes. This is shown in the pore size distribution curve for 13.3% MMA in Figure 5b. Increasing the MMA content lead to a more narrow distribution as is shown in the curve for 26.7% MMA in Figure 5b. The maxima in pore radii were independent of the monomer composition in contrast to what was observed for polymers made in toluene.

Small Pores. In spite of the shrinkage, a large BET surface area was observed in the polymer gels as is shown in Figure 6. The surface area appears to have a maximum at about 10% MMA concentration in the monomer mixture when ethyl acetate was used as the solvent. The corresponding concentration in toluene was about 5% MMA. The gels made in ethyl acetate had in all cases larger BET surface areas than those made in toluene.

BJH pore size distribution measurements of small pores of gels made in toluene gave at low MMA concentrations a pronounced maximum at a radius of 20 Å. Two less pronounced peaks at radii of 25–27 and 36–38 Å were also observed (Figure 7a). An increase in the MMA concentration (Figure 7b) resulted in a decrease in the amount of pores with 20-Å radii and an increase of the pores with 23-Å radii. The pores at 25–27 and 36–38 Å were displaced toward larger pore sizes, 32–33 and 42–43 Å.

One hundred percent TRIM in ethyl acetate gave xerogels with three peaks. When a small amount (6.7%) of MMA was added, the peaks could still be observed. Greater percentages of MMA produced broader distributions without distinct peaks as are shown in Figure 8 for 13.3% MMA.

The different types of BJH pore size distributions obtained indicate that copolymers made in toluene have more regular structures than those made in ethyl acetate. This

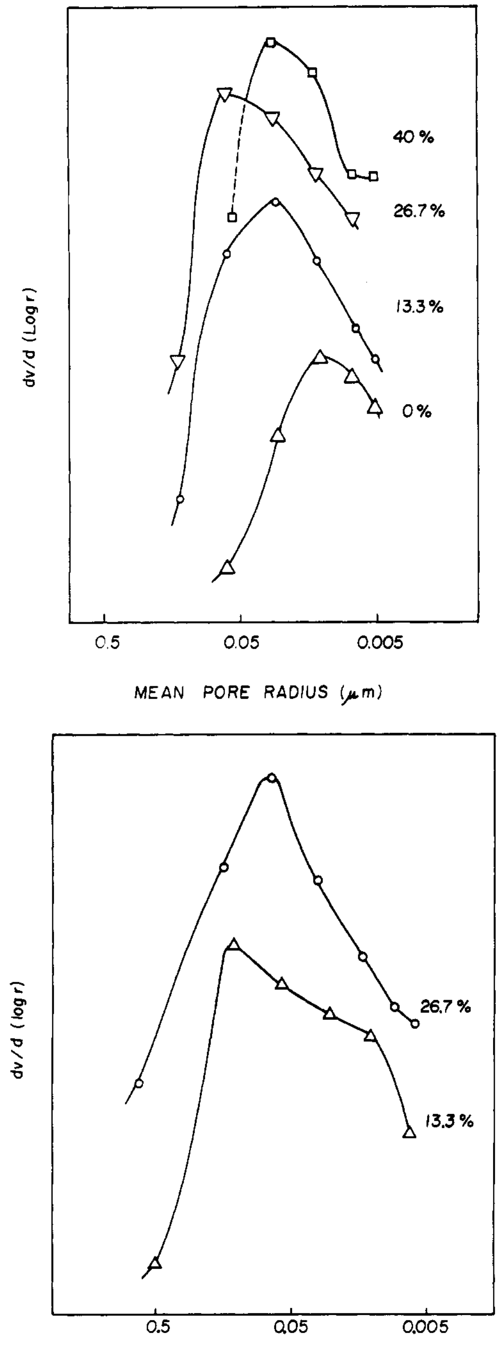

Figure 5. Pore size distribution, measured with mercury porosimetry, for (a, top) four and (b, bottom) two polymers made with different MMA concentrations in the initial monomer mixture: solvent = (a) toluene, (b) ethyl acetate; monomer:solvent = 30:70; interfacial contact angle = 130°; mercury surface tension = 485 dyn/cm.

is also supported by the observations made in ref 3 and 4. Kinetic measurements made with NMR also show that during the copolymerization of MMA and TRIM in toluene, the rates of addition of monomers are the same, while in ethyl acetate they differ.[8] The different behavior was probably due to percipitation of nodules in ethyl acetate. In toluene the network was more expanded, thus facilitating "template" polymerization and the formation of a regular structure with uniform pores.

Unreacted Carbon–Carbon Double Bonds. Solid-state ^{13}C NMR analyses (CP-MAS-DD) were carried out in order to determine the amount of unreacted carbon–carbon double bonds in the polymer xerogels. All unreacted double bonds in the polymer originates from unreacted pendant methacrylate groups. These groups can be related to the reacted methacrylate groups of TRIM or to all reacted methacrylate groups in the polymer. In Tables I and II, the amount of unreacted methacrylate groups is shown for some copolymers together with their monomer composition. In Table I the solvent was toluene and in Table II ethyl acetate. The amount of unreacted methacrylate groups appeared to have maximum for about 13% MMA when toluene was used as the solvent (Table

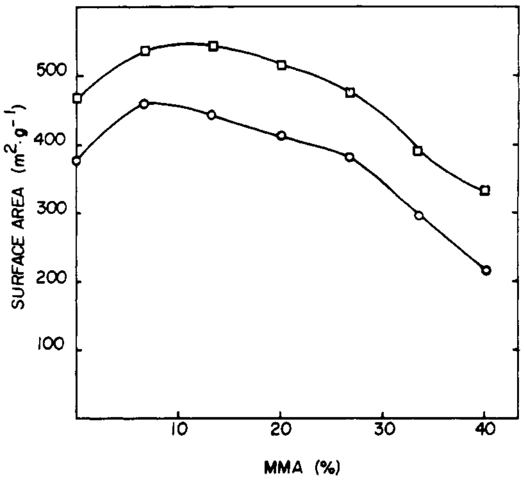

Figure 6. Dependence of the BET surface area on the initial MMA concentration in the monomer mixture: solvent = toluene (○), ethyl acetate (□); monomer:solvent = 30:70.

Table I
Amount of Unreacted Carbon–Carbon Double Bonds Present in Some Different Copolymers, Related to the Total Amount of Methacrylate Groups Present in the Polymer or the Methacrylate Groups Coming from TRIM, Made with Various Monomer Compositions[a]

TRIM, vol %	MMA, vol %	MMA, mol %	C=C/total,[b] mol %	C=C/ TRIM,[c] mol %
100	0	0	9.0	9.0
93.3	6.7	19.5	10.9	11.7
86.7	13.3	33.9	11.2	13.1
80.0	20.0	45.8	8.2	10.5
73.3	26.7	55.1	4.4	6.2
66.7	33.3	62.5	3.3	5.1
60.0	40.0	69.2	2.0	3.6

[a] The initial monomer concentration was constant at 30% and the polymerization was performed in the presence of toluene. [b] Total amount of methacrylate groups in the polymer. [c] The amount of TRIM methacrylate groups.

Table II
Amount of Unreacted Carbon–Carbon Double Bonds Present in Some Different Copolymers, Related to the Total Amount of Methacrylate Groups Present in the Polymer or the Methacrylate Groups Coming from TRIM, Made with Various Monomer Compositions[a]

TRIM, vol %	MMA, vol %	MMA, mol %	C=C/total,[b] mol %	C=C/ TRIM,[c] mol %
100	0	0	16.7	16.7
93.3	6.7	19.5	14.3	15.3
80.0	20.0	45.8	9.3	11.6
73.3	26.7	55.1	7.1	9.7
66.7	33.3	62.5	4.9	7.3
60.0	40.0	69.2	4.8	8.0

[a] The initial monomer concentration was constant at 30% and the polymerization was performed in presence of ethyl acetate. [b] Total amount of methacrylate groups in the polymer. [c] The amount of TRIM methacrylate groups.

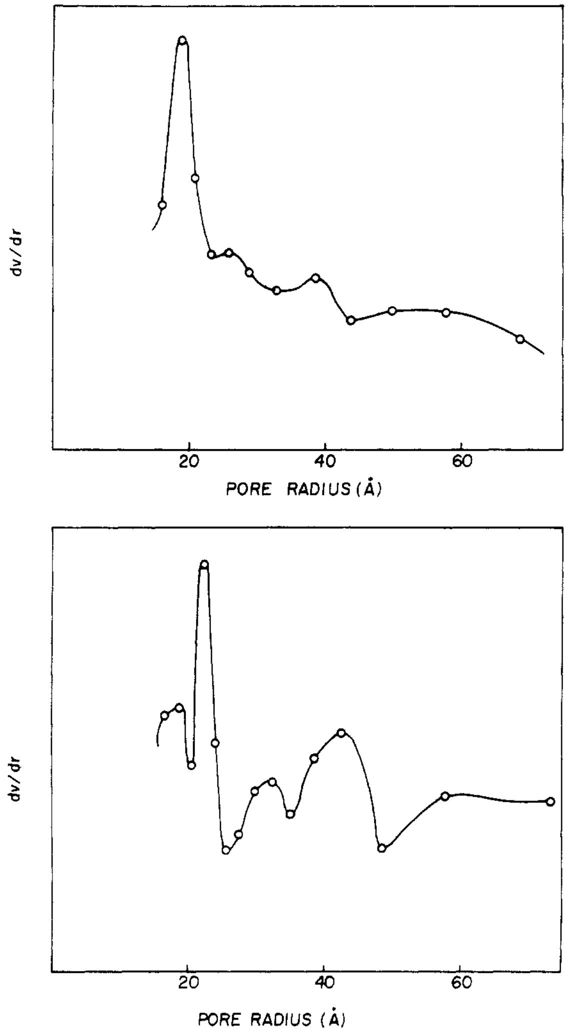

Figure 7. BJH pore size distribution for small pores ($r < 50$ Å) in a copolymer made with initial MMA concentrations of (a, top) 6.7% and (b, bottom) 33.3% in the monomer mixture: solvent = toluene; monomer:solvent = 30:70.

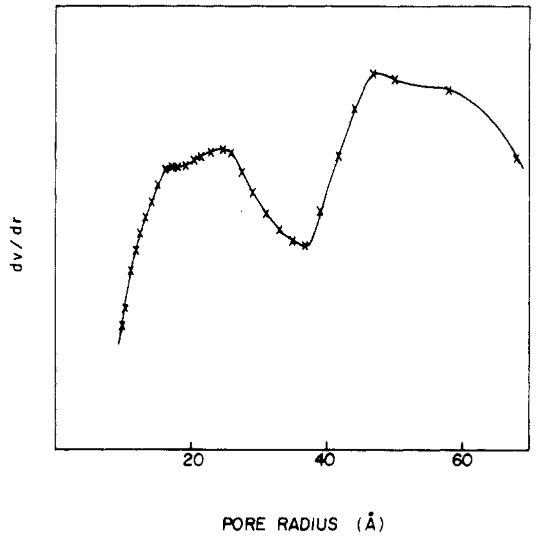

Figure 8. BJH pore size distribution for small pores ($r < 50$ Å) in a copolymer made with an initial MMA concentration of 13.3% in the monomer mixture: solvent = ethyl acetate; monomer: solvent = 30:70.

I). For polymers made in ethyl acetate the amount of unreacted methacrylate groups decreased when the MMA content increased. The absolute amount of unreacted double bonds was lower for toluene than for ethyl acetate. A probable reason for this is that a more open structure is obtained when toluene is used as the solvent. This causes a larger amount of the pendant double bonds to participate in the polymerization reaction.

In conclusion, we have found that the copolymerization of TRIM with MMA (up to 50% (v/v) MMA concentration) in the presence of toluene or ethyl acetate gives a macroporous polymer. The small pores were observed to vary in size with the MMA concentration.

For polymers made in toluene, the typical 20-Å peak[1] became smaller, and new peaks appeared at larger pore radii when the MMA concentration was increased. The same behavior was observed for polymers made in ethyl acetate at low MMA concentrations. Increasing the MMA concentration, however, resulted in a broad size distribution in which no distinct peaks were observable. An increase in the MMA concentration was also found to cause a decrease in the number of unreacted methacrylate groups in the xerogels, independent of the solvent used.

For polymers made in toluene, the large pores were found to vary in size according to the TRIM-to-MMA ratio. The polymers made in ethyl acetate did not show this behavior. This investigation showed that it is possible to change the pore size distributions occurring in poly(TRIM) via copolymerization with MMA.

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Registry No. (MMA)(TRIM) (copolymer), 107711-84-2.

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