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Macroporous Gels. 1. Polymerization of Trimethylolpropane Trimethacrylate in Toluene

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ABSTRACT: Free radical polymerization of trimethylolpropane trimethacrylate was performed in toluene solution. The resulting polymer was found to be macroporous with a narrow pore size distribution of small pores (radius <50 Å) and a pore size distribution of large pores (radius >50 Å) that varies with the monomer to solvent ratio. The amount of unreacted carbon–carbon double bonds in the polymer gels was found to be unexpectedly low. The polymers were studied with nitrogen adsorption–desorption techniques, mercury porosimetry, scanning electron microscopy, and solid-state ^{13}C NMR. An outline of a mechanism for polymerization is proposed which explains the experimental observations.

Introduction

Macroporous polymers for use as adsorption material and ion-exchange resins have traditionally been made by radical copolymerization of styrene and divinylbenzene (S–DVB). Most recent investigations have been directed towards the control of the porous texture by polymerization in several different types of porogens such as solvents, combinations of solvents and nonsolvents, or polymers.[1–5] Some attempts have also been made to explain the polymerization mechanism.[1,5,6]

Results from experiments with styrene–divinylbenzene systems are difficult to interpret because most authors have used divinylbenzene of technical quality which consists not only of meta and para isomers but also of the meta and para isomers of ethylvinylbenzene. Several of these monomers have different reactivities in radical polymerization.[5]

Our aim was to study the formation of macroporous polymers in a less complicated system. This led us to choose trimethylolpropane trimethacrylate (TRIM) as a model system since the reactivities of all methacrylate groups in this monomer are expected to be equal whether the groups have reacted or not.

The polymers are studied by surface area (BET) and pore size distribution (BJH) measurements, mercury porosimetry, bed density measurements, infrared spectroscopy (IR), scanning electron microscopy (SEM), and solid-state NMR (^{13}C CP-MAS-DD).

Experimental Part

Polymerization. Trimethylolpropane trimethacrylate (TRIM, technical qualities containing more than 98% TRIM from Merck AG, Norsolor Chimie, and Alfa Products) was polymerized in solution at 73 °C with toluene (analytical grade) as a diluent and azobis(isobutyronitrile) (AIBN, analytical grade) as initiator. A typical polymerization procedure was as follows: 20 mg of AIBN was weighed into a 50-mL hypovial. The vial was sealed, evacuated, and filled with nitrogen. Then 20 mL of a solution containing monomer (30%) and diluent (70%) was added. The vial was placed in a shaking bath at 73 °C. After 12–13 min gelation started and after an additional 5 min a turbid, stiff gel occupied the entire reaction volume. The vial was kept in the shaking bath for 8 h before cooling.

Posttreatment. After being ground, the bed volume of the resulting polymers was measured in the swollen state and as xerogels after drying at 60 °C under vacuum for at least 24 h.

Texture Determination. The pore structure at a pore radius larger than 50 Å was determined by mercury porosimetry (Micromeritics 9300). The surface area was obtained from adsorption measurements with nitrogen according to the BET method.[7] The pore size distributions were obtained from nitrogen adsorption–desorption isotherm measurements according to the BJH method.[8] The pore size and surface area measurements were carried out in two different pore volume analyzers (Micromeritics 2100 E and Micromeritics Digisorb 2600). Studies with a scanning electron microscope (JEOL JSM 35) were performed at two magnifications, 40 000 and 100 000 times.

Determination of Unreacted Carbon–Carbon Double Bonds. The amount of unreacted methacrylate groups was determined by solid-state ^{13}C NMR using cross-polarization (CP), magic-angle spinning (MAS), and high-power decoupling (DD) (Varian XL-200 with solid-sample accessories). Ground samples were compressed into KBr disks for FTIR spectrometry (Nicolet MX-10).

Results

TRIM was polymerized by solution polymerization in toluene. Most polymer gels were made as blocks and a few by conventional dispersion polymerization techniques. The monomer concentration was varied between 5 and 60% and was found to have a profound effect on the gel structure. The initiator concentration, on the other hand, did not influence the gel structure at all.

Shrinkage was observed upon removal of solvent, but all polymers were still macroporous as judged by the large surface areas (Figure 1). As could be expected the shrinkage of the polymer decreased with increasing monomer (TRIM) concentrations (Figure 2). From bed-volume and bed-weight measurements the bed density was calculated and a minimum was obtained at a monomer concentration of 15% (Figure 3).

The influence of the monomer concentration on pore volume is also shown in Figure 3. Excellent agreement was obtained in pore volume measurements by the mercury porosimetry and the BJH methods.

The surface area was found to be constant (330 m^2/g) within the accuracy of the measurements for monomer concentrations between 10 and 35% (Figure 1). Higher and lower TRIM concentrations tended to reduce the surface area.

Mercury porosimetry was used to measure the distribution of pores with a radius larger than 50 Å, which in the following will be designated large pores. A maximum between 50 and 200 Å was found in all samples. In Figure 4a the pore size distribution is plotted for four different monomer concentrations and in Figure 4b the maximum pore radius for each pore size distribution is plotted against the initial monomer concentration.

Pore size distribution measurements with respect to small pores (BJH method) gave very sharp maxima at a radius of 20 Å (Figure 5) in all experiments, independent of the monomer concentration (5–60%) in the polymerization.

SEM investigations of TRIM polymer xerogels show one basic structure, made of spheres which may agglomerate either in large unshaped entities or in rodlike textures. The "rods" have a diameter of 200–1000 Å and the holes vary

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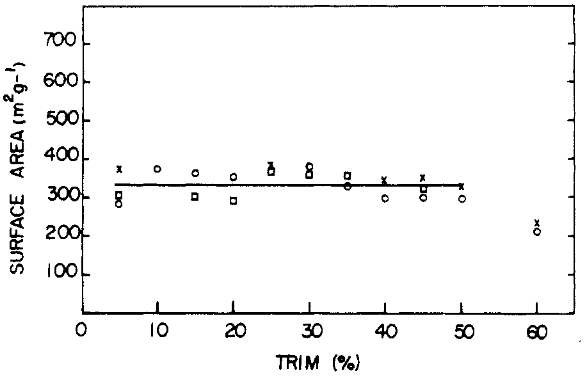

Figure 1. Dependence of BET surface area on the initial monomer concentration.

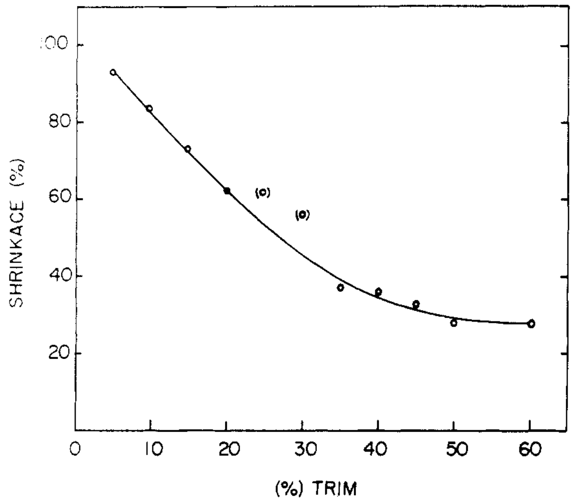

Figure 2. Dependence of shrinkage, caused by removal of toluene, on the initial monomer concentration in the polymerization.

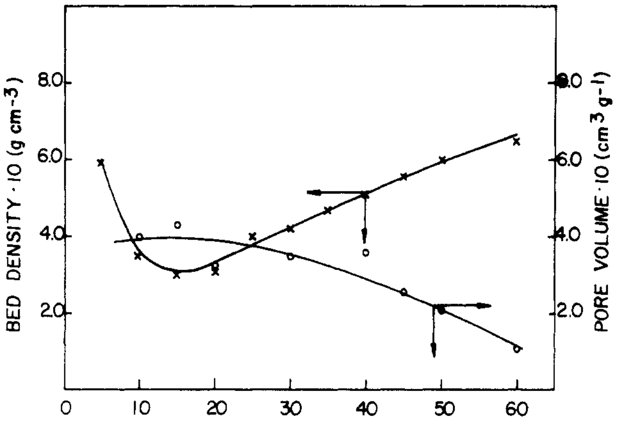

Figure 3. Dependence of bed density (×) and pore volume (○) on the initial monomer concentration.

between 0.1 and 0.8 μm (Figure 6). In Figure 6, bottom, typical junctions with several "rods" attached are shown. The number and size of the holes diminish with increasing monomer concentrations and structural details become more difficult to observe.

^{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. Carbonyl groups conjugated with a double bond have a lower chemical shift (166 ppm) than the unconjugated (reacted, 176 ppm) ones. The difference is large enough to completely resolve the two peaks (Figure 7). This together with nearly similar contact times (800 μs) make quantitative measurements possible.

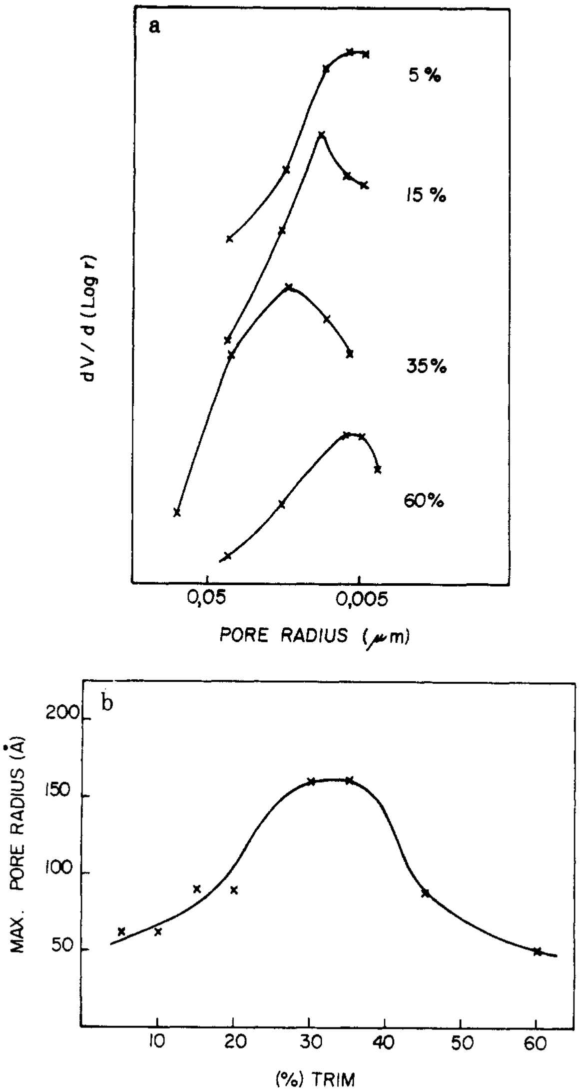

Figure 4. (a) Pore size distributions, measured with mercury porosimetry, for four polymers made with different monomer concentrations (interfacial contact angle = 140°, mercury surface tension = 485 dyn/cm). (b) Dependence of maximum pore radius of large pores (>50 Å) on initial monomer concentration, measured by mercury porosimetry (interfacial contact angle = 140°, mercury surface tension = 485 dyn/cm).

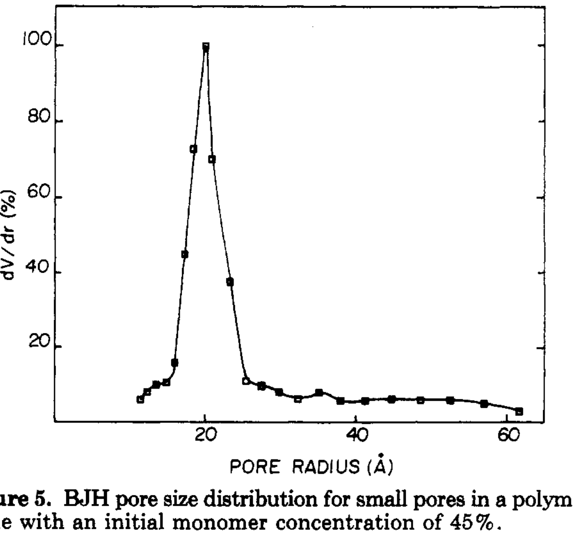

Figure 5. BJH pore size distribution for small pores in a polymer made with an initial monomer concentration of 45%.

In Figure 8 the experimentally determined signal intensity is plotted against contact time. The amount of unreacted double bonds was found to increase with increasing initial

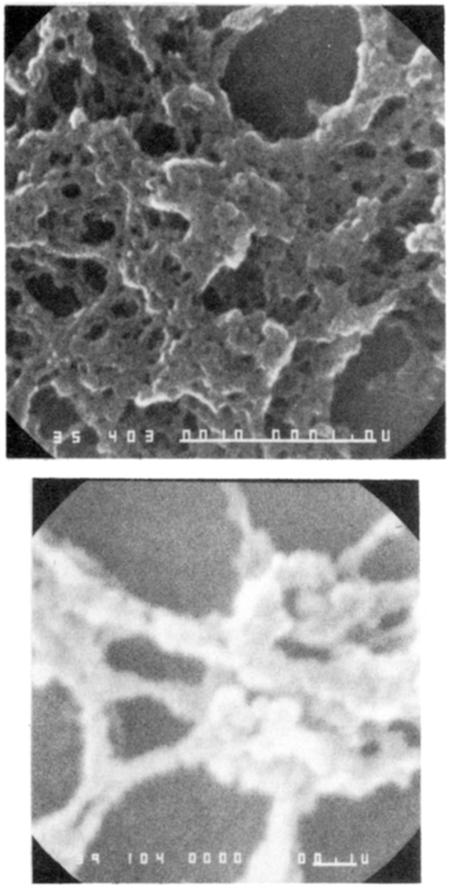

Figure 6. (Top) Scanning electron micrograph of a ground poly(TRIM) bead (initial monomer concentration 10%), 24 000×. (Bottom) Scanning electron micrograph of a ground poly(TRIM) bead (initial monomer concentration 30%), 60 000×.

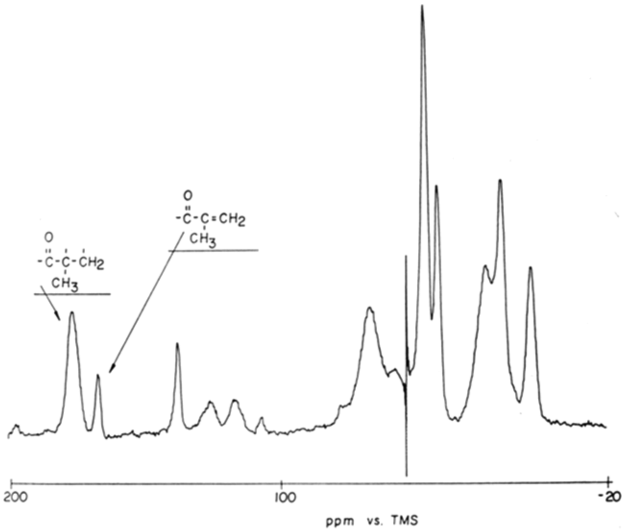

Figure 7. High-power, decoupled, magic-angle CP ^{13}C NMR spectra (50.3 MHz, spin rate 3 kHz, 54 000 transients, contact time 800 μs) of poly(TRIM) made with an initial monomer concentration of 60%.

monomer concentrations (Table I)

For routine measurements IR analyses are experimentally more convenient to perform than solid-state NMR analyses. For this purpose the NMR values were used to calibrate the IR measurements. Absorbancies at 1630, 1330, and 750 cm^{-1} were studied. The first two bands correspond to the carbon–carbon double bond and the last one to the methylene group in the polymer main chain.[9] The relative absorbancies at 1630 cm^{-1} are presented for some of our polymers in Table I together with the corresponding initial monomer concentrations.

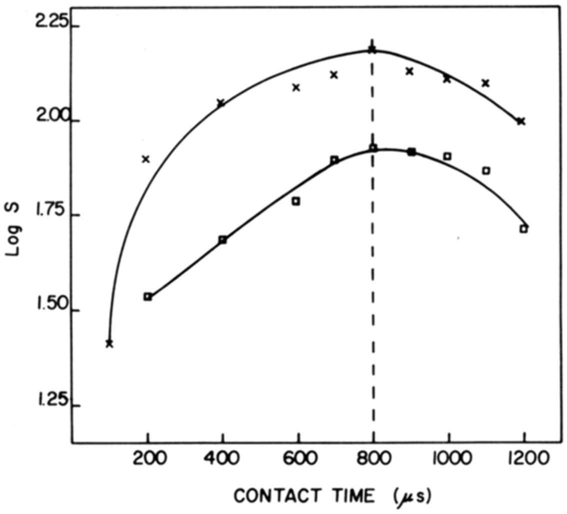

Figure 8. Plot of log (signal) vs. contact time for unconjugated carbonyl groups at 176 ppm (×) and conjugated carbonyl groups at 166 ppm (○).

Table I
Amount of Unreacted Double Bonds Present in Some Polymers Made with Different Initial Monomer Concentrations Measured by Solid-State ^{13}C NMR and the Corresponding Relative Absorbancies at 1630 cm^{-1}

% init monomer concn	NMR % unreacted C=C	FTIR (peak height[a])
5	4.3	
10	5.6	
20	6.4	15.0
25		17.0
30	9.0	18.8
35	9.6	
40	14.2	35.0
50	14.3	35.8
60	14.9	36.5

[a] Peak height over the base line normalized with the peak at 1140 cm^{-1}, ester group.

Discussion

It can be seen from the results that TRIM polymerized in solvent gives polymer beads of high porosity, which is consistent with previous observations.[10] The polymerization was made with toluene as pore-forming agent. It acts as a solvent for the monomer and as a swelling agent for the polymer. As is well-known from styrene–divinylbenzene systems the properties of the porogen are of great importance for the morphology of the polymer.[5]

The surface area measurements were almost identical for all polymers (Figure 1). This occurred in spite of considerable shrinkage upon removal of solvent from the polymer. Since the surface area is dominated by small pores an obvious explanation is that the shrinkage is caused by a collapse of large pores.

According to pore volume and bed density measurements there is an almost linear dependence of both pore volume and density on monomer concentrations above 15% (Figure 3). When the monomer concentrations decrease below 15% the bed density abruptly increases and the pore volume decreases. This is further evidence for a collapse of large pores since these methods are more sensitive to large pores than to small ones. The mercury porosimetry measurements, which show a dependence of maximum pore radius on initial monomer concentration

(Figure 4), also indicates that large pores collapse because the pore radius decreases with decreasing monomer concentrations below 15%.

BJH pore size distribution measurements of small pores (<50 Å) showed a very sharp peak at 20 Å (Figure 5). This sharp maximum was observed in all experiments. This indicates that the polymer has a very regular structure on the microlevel, which is probably caused by the specific nature of the monomer.

The two pore size distributions vary in different ways with respect to the monomer concentration. The micropores at 20 Å were found to be independent of TRIM and initiator concentrations while the large pores were independent of initiator and dependent on monomer concentration.

The TRIM molecule has a compact tetrahedral structure with double bonds at three of the four corners. If one of these corners is attached to a growing polymer chain, the next double bond added must belong to another molecule. This is evident from studies of molecular models. Intramolecular ring cyclization of small rings is unlikely to occur because of the rigid structure of the molecular arms and because the rings formed would consist of 9, 10, or 11 atoms, which is known to be unfavorable.[11] Furthermore, when a new molecule is added to a growing chain, it is subject to steric hindrance from the two last added monomer units. This makes a rigid structure probable, as has been shown for bulky side groups in vinyl polymers.[12,13]

It is convenient to discuss the structure of TRIM gels in terms of three levels of organization. The polymer chains first formed comprise the primary level. These polymer chains have pendant double bonds exposed to the solution and are quite rigid because of the bulkiness of the side groups. The second level may be formed by polymerization of pendant groups on neighboring monomer units or more probably by copolymerization of pendant groups with one of the double bonds in the TRIM monomer. Because of high local concentrations of double bonds it is highly probable that a newly formed radical will attach to a previously formed polymer molecule, with propagation along that chain. The new chain at the outside of the original one will also have pendant groups exposed toward the solution. In this way multilayer structures will be formed. The tertiary level comprises the macroscopic structure which is obtained when multilayer structures join to form a network. This event occurs early in the polymerization when a radical propagating on a primary or secondary structural unit reacts with a double bond belonging to another similar unit and so on until gelation occurs.

The proposed mechanism explains the fact that most of the carbon–carbon double bonds have reacted (Table I and Figure 7). As a comparison, investigations of the amount of unreacted double bonds in gels formed by polymerization of pure divinylbenzene show that about 40–50% of the double bonds are unreacted.[5,14]

In order to create such a narrow distribution of pore sizes in the microregion as we have obtained the polymerization should be made in a "solvent" for the polymer. Copolymerization with methyl methacrylate or the use of a nonsolvent causes a less regular structure to be formed, as is evident from pore size distribution measurements by the BJH method.[15] Polymerization in a nonsolvent also affects the morphology and the large pores in the polymer gel. These become larger and the minimum corresponding to that in Figure 3 is displaced toward lower monomer concentrations.[15] This shows that the type of solvent used is of great importance since it affects the pore structure.

In conclusion we have found that the polymerization of TRIM in a solvent gives a macroporous polymer with a narrow pore size distribution of small pores and a pore size distribution of large pores that varies with the monomer to solvent ratio. We have also found that the large pores at monomer concentrations below 15% collapse when the gels are dried and that the amount of unreacted double bonds in the polymer is relatively low. A mechanism for the formation of the primary, secondary, and tertiary structures has been proposed which explains the experimental observations.

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Registry No. TRIM (homopolymer), 26426-04-0; TRIM, 3290-92-4.

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