the use of the Chemistry Department Nicolet NT-300 NMR spectrometer supported by the instrument program of the NSF Chemistry Division.

Registry No. **2**, 96614-05-0; **3**, 20451-53-0; **3** (homopolymer), 87500-51-4; **3** (dimer), 102848-46-4; **3** (trimer), 102848-47-5.

References and Notes

(1) Lenz, R. W. *Organic Chemistry of Synthetic High Polymers*; Interscience: New York, 1967. Lenz, R. W.; Ciardelli, F. *Preparation and Properties of Stereoregular Polymers*; Reidel: Dordrecht, Netherlands, 1980.

(2) Cram, D. J.; Kopecky, K. R. *J. Am. Chem. Soc.* **1959**, *81*, 2748. Baun, C. E. H.; Ledwith, A. *Q. Rev. Chem. Soc.* **1962**, *16*, 361. Furakawa, J. *Polymer* **1962**, *3*, 87. Fowells, D. W.; Schuerch, C.; Bovey, F. A.; Hood, F. P. *J. Am. Chem. Soc.* **1967**, *89*, 1396. Huang, S. S.; Mathis, C.; Hogen-Esch, T. E. *Macromolecules* **1981**, *14*, 1802.

(3) Toshiyosu, Y.; Taniguchi, Y.; Kimura, K.; Fujishiro, R.; Yoshiharo, M.; Tagaki, W.; Oae, S. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1878.

(4) Durst, T.; Viau, R.; McClory, M. R. *J. Am. Chem. Soc.* **1971**, *93*, 3077. Durst, T.; Viau, R.; Vanden Elgen, R.; Nguyen C. H. *Chem. Commun.* **1971**, 1334. Durst, T. *J. Am. Chem. Soc.* **1969**, *91*, 1034. Bielmann, J. F.; Vincens, J. J. *Tetrahedron Lett.* **1978**, *34*, 1399. Rauk, A.; Buncel, E.; Moir, R. Y.; Wolfe, S. *J. Am. Chem. Soc.* **1965**, *87*, 5498. Fraser, R. R.; Schuber, F. J.; Wigfield, Y. Y. *Ibid.* **1972**, *94*, 8795.

(5) Previous attempts to prepare poly(vinyl *p*-tolyl sulfoxide) converted little monomer into polymer. See: Mulvaney, J. E.; Orraviani, R. A. *J. Polym. Sci., Part A-1* **1970**, *8*, 2293. Kunieda, N.; Kinoshita, M.; Imoto, M. *J. Polym. Sci., Polym. Lett. Ed.* **1971**, *9*, 241.

(6) Rayner, D. R.; Miller, E. G.; Bickart, P. B.; Gordon, A. J.; Mislow, K. *J. Am. Chem. Soc.* **1966**, *88*, 3138. Rayner, D. R.; Gordin, A. J.; Mislow, K. *Ibid.* **1968**, *90*, 4854. Cram, D. J.; Pine, S. H. *Ibid.* **1963**, *85*, 1096.

(7) Stereochemical nomenclature conforms with that used in organic chemistry. Therefore the stereoselective reaction of **3** with **2** refers to the preferential formation of a chiral methine carbon. It does not indicate whether stereoselectivity results from the reaction of one-face of an achiral carbanion preferentially or if one of two interconverting diastereomeric ion pairs react only syn or anti to the counterion. The latter is a stereospecific reaction. The stereoelective addition of **3** to **2** indicates that one enantiomer of **2** reacts with one enantiomer of **3** preferentially. Thus a reaction may occur with stereoselection and stereoelection.

(8) Buese, M. A.; Hogen-Esch, T. E. *Macromolecules* **1984**, *17*, 118.

(9) The Cahn–Ingold–Prelog convention is used, with subscript S denoting sulfur chirality. The configuration of any oligomer or chain end is listed starting with the initiator fragment. Polymeric triads are listed as if the next sequential pair of chiral centers were that which contain the chiral ion pair. When optically active reagents are used the notation is for the major enantiomer formed. When racemic reagents are used it should be understood that the notation stands for relative configurations with both enantiomers present in equal quantities. In all other cases the notation refers to relative configurations.

(10) Buese, M. A.; Hogen-Esch, T. E. *J. Am. Chem. Soc.* **1985**, *107*, 4509.

(11) The ion pair α to the sulfinyl group is chiral. These two diastereomeric ion pairs can epimerize to an equilibrium mixture of the two forms. The ion pair chain ends that may interconvert are referred to as a pair of epimers throughout this paper.

(12) The relative integration of ^{1}H NMR signals for the methyl and aromatic protons was used to determine the degree of polymerization of the various oligomers.

(13) For example, the symmetric methylated dimers R_SSR_SS-**7b** and R_SSS_SR-**7b** cleanly separated from the asymetric dimers R_SSR_SR-**7b** and R_SSS_SS-**7b**.

(14) The area under the LC trace for trimers was very small relative to that for tetramer, pentamer, and higher oligomers under all conditions.

(15) The poorest signal-to-noise ratio observed was a factor of 20.

(16) In contrast to the intense yellow color of the THF solution of **2**, which diminished in intensity upon addition of an equivalent of **3**, the THF solution of **10** at the same concentration is almost colorless and becomes intensely yellow upon mixing with **3**.

(17) For longer chain lengths the chain should be able to catalyze the interconversion of the epimers also. This is indicated in lithium binding studies with the four diastereomers of **7b** and with **3**: Buese, M. A.; Hogen-Esch, T. E.; Xu, W. Y.; J. Smid, J. *Makromol. Chem.*, in press.

(18) Recent GPC studies of the anionic polymerization of **3** indicate that a high molecular weight polymer with a narrow molecular weight distribution can be formed: Kanga, R.; Hogen-Esch, T. E., unpublished results.

(19) The polymerization of vinyl phenyl sulfone has been investigated previously: Boor, J., Jr. *J. Polym. Sci., Part A-1* **1971**, *9*, 249.

Macroporous Gels. 2. Polymerization of Trimethylolpropane Trimethacrylate in Various Solvents

J.-E. Rosenberg and P. Flodin*

Department of Polymer Technology, Chalmers University of Technology, S-412 96 Gothenburg, Sweden. *Received June 3, 1986*

ABSTRACT: Free-radical polymerization of trimethylolpropane trimethacrylate (TRIM) was performed in various solvents. Several of the resulting polymers were found to be macroporous. The BET surface area as well as the amount of unreacted carbon–carbon double bonds of the resulting polymers varied with the solubility parameter of the solvent used as the pore-forming agent. The pore size distribution of poly(TRIM) made in ethyl acetate was found to vary with the polymerization conditions. It differed appreciably from that of poly(TRIM) made in toluene. The small pores showed three maxima, one pronounced at 20 Å and two less pronounced at about 26 and 36 Å, instead of the single one observed from poly(TRIM) made in toluene.

Introduction

Polymeric macroporous systems have different structural properties dependent upon the polymerization conditions.[1]

In a previous paper,[2] the preparation and structure of trimethylolpropane trimethacrylate (TRIM) polymers made with toluene as the pore-forming agent were described. In this paper we shall describe the influence of the solvent's solubility parameter on the pore size distribution and the morphology of poly(TRIM). The solvents used had solubility parameters in the range of 15.1×10^3 $(J/m^3)^{1/2}$ (heptane) to 24.8×10^3 $(J/m^3)^{1/2}$ (benzyl alcohol).

A detailed study was performed of the pore size distributions of poly(TRIM) made in ethyl acetate. The polymers were studied with covered nitrogen adsorption–desorption isotherms (BET and BJH), mercury porosimetry, shrinkage experiments, solid–state ^{13}C NMR spectroscopy, and scanning electron microscopy.

Experimental Section

Polymerization. Trimethylolpropane trimethacrylate (TRIM, technical quality containing more than 98% TRIM from Merck

Table I
BET Surface Area and the Amount of Unreacted Carbon-Carbon Double Bonds Present in Some TRIM Polymer Xerogels Made with Different Solvents (30% Initial Monomer Concentration in Polymerization)

solvent	10^{-3} δ, $(J/m^3)^{1/2}$	BET surface area, m^2/g	unreacted C=C bonds, %
heptane	15.1	0	16.2
cyclohexane	16.8	306	17.4
xylene	18.0	516	15.7
toluene[a]	18.2	370	9.0
ethyl acetate	18.6	480	16.7
chlorobenzene	19.4	293	15.5
benzyl alcohol	24.8	0	11.5

[a] Values from ref 2.

AG or Alfa Products) was polymerized in solution at 73 °C in a solvent (analytical grade) as diluent and azobis(isobutyronitrile) (AIBN, analytical grade) as initiator. The solvents used were benzyl alcohol, cyclohexane, ethyl acetate, *n*-heptane, chlorobenzene, and *p*-xylene. A polymerization experiment was performed as follows. Twenty milligrams of AIBN was weighed into a 50-mL Hypo-vial. The vial was sealed, evacuated, and filled with nitrogen. Then 20 mL of a solution containing monomer (30%) and solvent (70%) was added. The vial was placed in a shaking bath at 73 °C. After about 15 min gelation started, and after 5 min more the entire reaction volume was occupied by a stiff gel. The vial was kept in the shaking bath for 8 h before cooling.

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

Texture Determination. The surface areas were determined by adsorption of nitrogen according to the BET method.[3] The pore size distributions for small pores were obtained from nitrogen adsorption–desorption measurements according to the BJH method.[4] 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 at a radius larger than 50 Å was determined by mercury porosimetry (Micromeritics 9300). Scanning electron microscopy studies were carried out at two magnifications, 20 000 and 100 000 times (Jeol JSM 35).

Solubility Parameter Determination. The solubility parameter of poly(TRIM) was determined by bed swelling measurements in solvents with different solubility parameters according to ref 5. The solubility parameter used throughout the Results and Discussion section is the total solubility parameter.[6] The bed volume was measured both before (V_0) and after (V) swelling the polymeric gel in various solvents, and the bed swelling was calculated as $(V - V_0)/V_0$. The polymer used was made with 40% initial monomer concentration in toluene. The swelling experiments were found to be highly reproducible.

Determination of Unreacted Carbon–Carbon Double Bonds. The determination of the absolute amount of unreacted methacrylate groups was carried out with 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, 176 ppm vs. Me_4Si) ones. The difference is large enough to almost completely resolve the two peaks. This together with nearly similar contact times[2] makes quantitative measurements possible.

Results and Discussion

Trimethylolpropane trimethacrylate (TRIM) was solution polymerized in different solvents. The polymer gels were made as blocks by a conventional solution polymerization technique. The solubility parameter dependence on the macroporosity and the residual amount of unreacted carbon–carbon double bonds in poly(TRIM) have been studied for the different solvents listed in Table I. Studies of the macroporous structures as a function of the monomer concentration (5–50%) and the initiator concentration (0.005–1%) with ethyl acetate as pore-forming agent have also been carried out. The initiator concentration did not influence the gel structure at all within the interval studied.

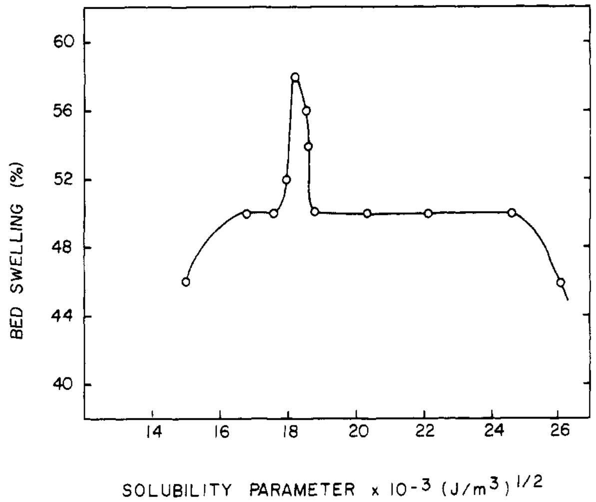

Figure 1. Dependence of bed swelling of poly(TRIM) on the solubility parameter of different solvents used as swelling agents (the line is drawn only as a visual aid).

Solubility Parameter. It is well-known that a change in the properties of the pore-forming agent to more "nonsolvent"-like conditions for the polymer has a profound influence on the gel structure and allows a wider set of porous textures to be obtained.[7-12] In order to find a dependence of the porous structure on the solvent used, we have investigated the influence that the difference in solubility parameters between the polymer and the solvent have on the BET surface area and the amount of unreacted carbon–carbon double bonds present in the polymer.

The solubility parameter of poly(TRIM) was detected by bed swelling tests in different solvents. The maximum swelling observed was in toluene which has a solubility parameter of 18.2×10^3 $(J/m^3)^{1/2}$ (Figure 1). This values was taken to be the solubility parameter of poly(TRIM). This seems reasonable in comparison with the solubility parameters of poly(methyl methacrylate) [$\delta = 18.6 \times 10^3$ $(J/m^3)^{1/2}$] and poly(propyl methacrylate) [$\delta = 18.0 \times 10^3$ $(J/m^3)^{1/2}$].

It was observed that TRIM polymerized in solvents with δ values of 19.4×10^3 $(J/m^3)^{1/2}$ or higher was transparent before drying. All other solvents tested gave polymers which were white or turbid. The BET surface area was found to vary considerably when the solubility parameter of the solvent was changed (Table I). The results in Table I also indicate that it is more difficult to create macroporosity in poly(TRIM) when $|\delta_{pol} - \delta_{solv}|$ is greater than about 2×10^3 $(J/m^3)^{1/2}$. This observation is supported by estimations made from data concerning the styrene–divinylbenzene system reported by Guyot.[1]

Experiments with ethyl acetate [$\delta = 18.6 \times 10^3$ $(J/m^3)^{1/2}$] as solvent gave a TRIM polymer with a structure different from that of poly(TRIM) made in toluene [$\delta = 18.2 \times 10^3$ $(J/m^3)^{1/2}$] as judged by BET surface area measurements and scanning electron microscopy. The results of TRIM polymerized in toluene have been discussed in a previous paper.[2] The greater difference in solubility parameters between the polymer and ethyl acetate leads to less interaction between the polymer network and the solvent during polymerization. In the following we shall mainly discuss ethyl acetate as the pore-forming agent.

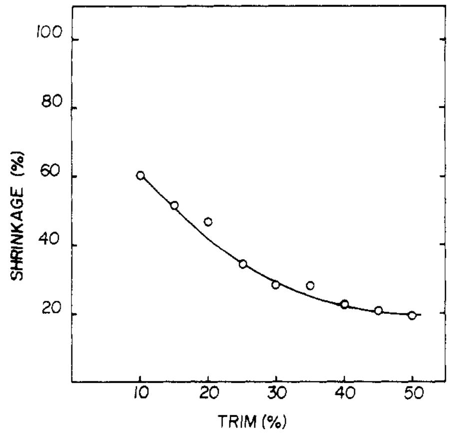

Figure 2. Dependence of shrinkage, caused by removal of ethyl acetate, on the initial monomer concentration in the polymerization.

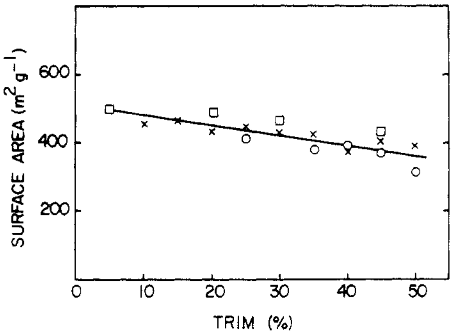

Figure 3. Dependence of BET surface area on the initial monomer concentration (solvent = ethyl acetate).

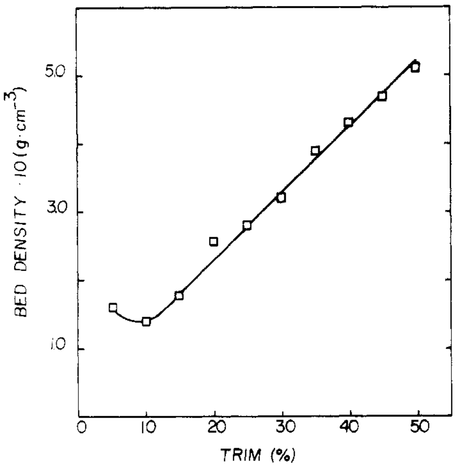

Figure 4. Dependence of bed density on the initial monomer concentration (solvent = ethyl acetate).

Ethyl Acetate as Solvent. Removal of ethyl acetate from the polymer caused shrinkage which varied with the initial monomer concentration. As one could expect, the shrinkage decreased with increasing initial monomer concentration (Figure 2). Although there was considerable shrinkage, the gels maintained their microstructure as can be seen from the large surface area as determined by BET measurements (Figure 3).

The bed density dependence on the monomer concentration was found to pass through a minimum at an initial monomer concentration in polymerization of 10%. For monomer concentrations above 10%, the dependence was almost linear as is shown in Figure 4. The influence of the monomer concentration on the pore volume is shown in Figure 5. It had a maximum for polymers made with an initial monomer concentration of about 20%.

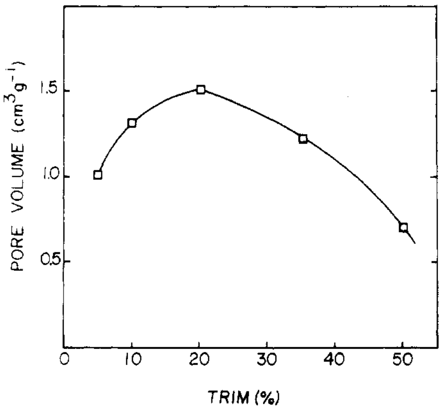

Figure 5. Dependence of pore volume on the initial monomer concentration (solvent = ethyl acetate).

Table II

Radius Corresponding to the Maximum Amount of Large Pores (r > 50 Å), Measured with Mercury Porosimetry, for Different Initial Monomer Concentrations, Contact Angle = 140° and Mercury Surface Tension = 485 dyn/cm (Solvent = Ethyl Acetate)

initial monomer concn, %	max pore radius, μm	initial monomer concn, %	max pore radius, μm
10	0.320	40	0.033
20	0.120	50	0.010
30	0.075		

SEM investigations of the TRIM polymer xerogels made in ethyl acetate showed one basic structure made of spheres (nodules) which had agglomerated in large unshaped entities enclosing large holes (Figure 6). The size of the nodules was independent of the initial monomer concentration. The agglomerated entities had diameters of 0.05–0.1 μm. The size of the holes in the structure diminished with increasing monomer concentrations and the structural details became more difficult to observe.

Large Pores. Mercury porosimetry was used to measure the distribution of pores having a radius larger than 50 Å. These pores will in the following be designated large pores. The maxima in pore size distributions were found to be displaced toward larger pore sizes when the initial monomer concentration decreased. In Figure 7 the pore size distributions for large pores are plotted for four different monomer concentrations, and in Table II the maximum pore radius is given together with the initial monomer concentrations for some TRIM polymers.

At monomer concentrations above 20%, the pore volume in the xerogels decreased with increasing initial monomer concentration as shown in Figure 5. This decrease is due to the more dense framework formed when the amount of monomer was increased. This is also supported by the mercury porosimetry measurements, where the maximum pore radii were displaced toward smaller pore sizes (Figure 7). The shrinkage and bed density curves also indicate that the framework in the xerogels was more resistant to shrinkage and thus mechanically stronger.

When the initial monomer concentration was decreased to 20%, an enlargement of the large pores occurred (Figure 7) due to the dilution. A further decrease in the initial monomer concentration below 20% resulted in a decrease of the amount of large pores because some of them collapsed (the pore volume decreased and the shrinkage increased). However, the remaining large pores had increased in size (Figure 5). When the monomer concentration was decreased below 10%, the collapse started to

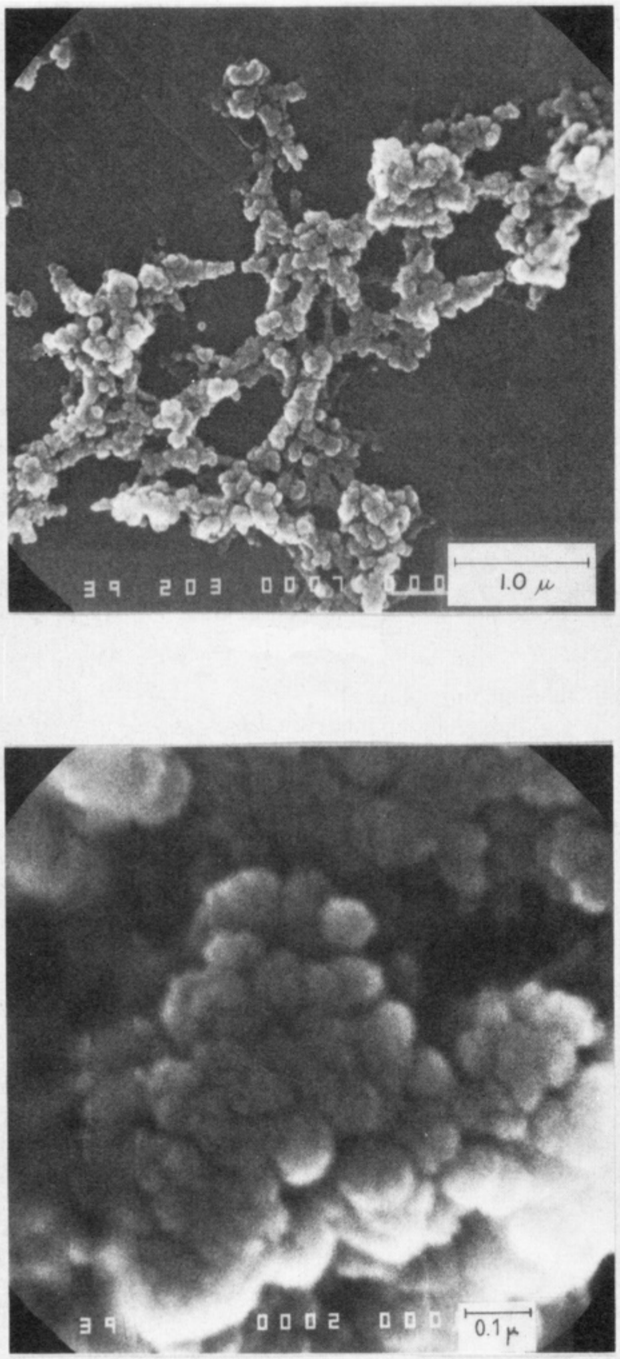

Figure 6. Scanning electron micrograph of a ground poly(TRIM) bead: (a, top) initial monomer concentration, 20%, ×16 000; (b, bottom) initial monomer concentration, 45%, ×80 000.

dominate over the enlargement of the large pores. A probable cause is a weakening of the framework building up these pores. This is supported by the minimum in the bed density curve in Figure 4. At very low monomer concentrations, no porosity was obtained.

Small Pores. The dependence of the BET surface area on the initial monomer concentration is shown in Figure 3. The surface area decreased almost linearly with increasing initial monomer concentration. The surface area, which is dominated by small pores (<50 Å), was large in all polymers made in ethyl acetate. This occurred even for polymers which shrunk considerably upon removal of solvent.

The pore size distributions with respect to small pores (BJH method) gave for high monomer concentrations three maxima: one (a sharp peak) at a radius of 20 Å and two less pronounced at radii of 26–27 and 35–37 Å (Figure 8).

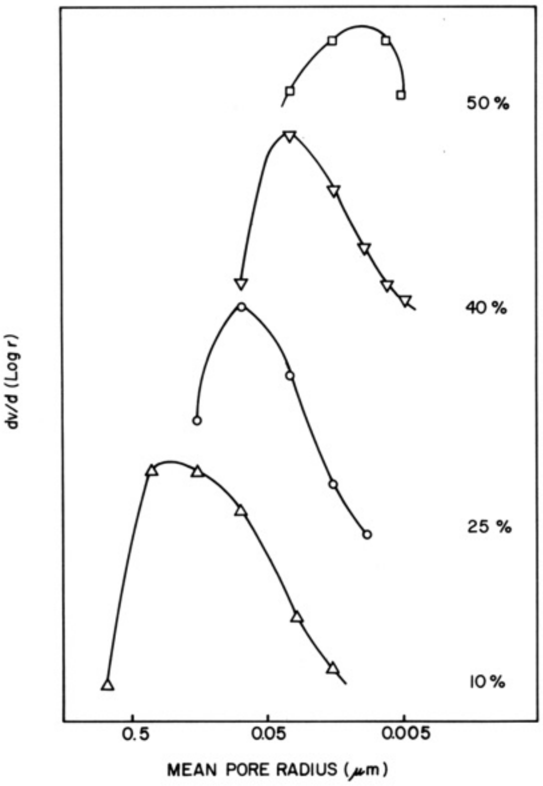

Figure 7. Pore size distributions for large pores, measured with mercury porosimetry, for four different polymers made with different initial monomer concentrations, 10%, 25%, 40%, and 50% (interfacial contact angle = 140°; mercury surface tension = 485 dyn/cm).

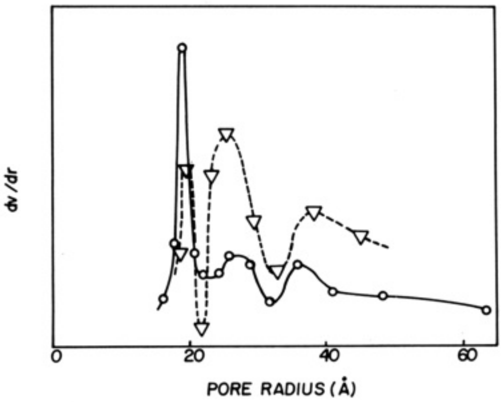

Figure 8. BJH pore size distributions for small pores in two different polymers made with different initial monomer concentrations: (- - -) 20% and (—) 50% (solvent = ethyl acetate).

Decreasing the initial monomer concentration in the polymerization resulted in a decrease of the amount of pores with a radius of 20 Å and an increase of those with radii of 26–27 and 35–37 Å as shown in Figure 8. This should be compared to the 20-Å single peak observed when TRIM was polymerized in toluene.[2]

The solubility parameter seems to have a great influence of the small pores of poly(TRIM). A strong interaction yields a narrow pore size of 20 Å. It is reasonable to assume that the solubility parameter of TRIM is very similar to that of MMA [$\delta = 18.0 \times 10^3$ $(\mathrm{J/m^3})^{1/2}$]. The ethyl group can cause slightly different values, but its contribution can be estimated by the group contribution method[5] to be less than 0.2×10^3 $(\mathrm{J/m^3})^{1/2}$.

The solvent in the beginning of a polymerization is a mixture of the inert solvent and the monomer. During polymerization the monomer is consumed, which shifts the

Macromolecules 1987, *20*, 1522–1526

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 $|\delta_{\mathrm{pol}} - \delta_{\mathrm{solv}}|$ 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]

Acknowledgment. We thank the National Swedish Board for Technical Development for financial support of this work.

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

References and Notes

(1) Guyot, A.; Bartholin, M. *Prog. Polym. Sci.* **1982**, *8*, 277.
(2) Rosenberg, J.-E.; Flodin, P. *Macromolecules* **1986**, *19*, 1543.
(3) Brunauer, S.; Emmett, Ph.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309.
(4) Barret, E. P.; Joyner, L. G.; Halenda, P. P. *J. Am. Chem. Soc.* **1951**, *73*, 373.
(5) Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 2nd ed.; Wiley: New York, 1975.
(6) Hansen, C. M. *J. Paint Technol.* **1967**, *39*, 104, 505, 511.
(7) Seidl, J.; Malinsky, J.; Dusek, K.; Heitz, W. *Adv. Polym. Sci.* **1967**, *5*, 113.
(8) Kun, K. A.; Kunin, R. *J. Polym. Sci.* **1968**, *A1*(6), 2689.
(9) Sederel, W. L.; de Jong, G. J. *J. Appl. Pol. Sci.* **1973**, *17*, 2835.
(10) Haupke, K.; Pientka, J. *J. Chromatogr.* **1974**, *102*, 117.
(11) Millar, J. R.; Smith, D. G.; Kressman, T. R. E. *J. Chem. Soc.* **1965**, 304.
(12) Wieczorek, P. P.; Kolarz, B. N.; Galina, H. *Angew. Macromol. Chem.* **1984**, *126*, 39.

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

J.-E. Rosenberg and P. Flodin*

Department of Polymer Technology, Chalmers University of Technology, S-412 96 Gothenburg, Sweden. *Received June 3, 1986*

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

0024-9297/87/2220-1522$01.50/0