

Porous Properties of Poly(glycidyl methacrylate-*co*-trimethylolpropane trimethacrylate) Resins Synthesized by Suspension Polymerization

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Received 2 October 2000; accepted 9 June 2001

ABSTRACT: Porous copolymer beads of 2,3-epoxypropyl methacrylate (glycidyl methacrylate, GMA) crosslinked with 2-ethyl-2-(hydroxymethyl)-propan-1,3-diol trimethacrylate (trimethylolpropane trimethacrylate, TRIM) were prepared with toluene and octan-2-one as porogens by suspension polymerization. With an increase in the ratio of porogen to monomer, the total pore volume of poly(GMA-*co*-TRIM) increases significantly, whereas the surface area hardly changes. The total pore volume also depends on the nature of the porogen, exhibiting a maximum at the larger GMA contents in the monomer mixture of 50% v/v with octan-2-one and of 60% v/v with toluene, compared to that at the GMA content of 25% v/v with a 9/1 v/v mixture of cyclohexanol and dodecan-1-ol [Verweij, P. D.; Sherrington, D. C. *J Mater Chem* 1991, 1 (3), 371]. The surface area decreases significantly with an increase in the ratio of GMA to TRIM, almost regardless of the nature of the porogen. The porous properties of poly(GMA-*co*-TRIM) was well explained on the basis of phase separation, particularly taking into account not only the solubility parameters of the resulting polymer network and porogen but also the rigidity of TRIM. The porous poly(GMA-*co*-TRIM) may be a promising polymer matrix of novel materials for separation of boron isotopes. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2374–2381, 2002

Key words: glycidyl methacrylate; trimethylolpropane trimethacrylate; porous property; suspension polymerization; characterization

INTRODUCTION

Polymer beads of 2,3-epoxypropyl methacrylate (glycidyl methacrylate, GMA), poly(GMA), are very attractive for the development of new materials for separation of boron isotopes (^{10}B and ^{11}B),^{1,2} because epoxy groups are very effective at introducing various chelating ligands into the beads through a ring-opening reaction.^{3,4} We reported that a poly(glycidyl methacrylate-*co*-divi-

nybenzene) resin functionalized with bis(2-hydroxyethyl)amine exhibits much higher selectivity toward ^{10}B than ^{11}B ,² because ^{10}B is more fractionated to tris(2-hydroxyethyl)amine borate and bis(2-hydroxyethyl)amine borate with a tetrahedral coordination geometry, estimated boron complexes bound on the resin, than to boric acid with a planar triangular coordination geometry in aqueous solution.^{1,5} The chelating resin also possesses a higher capacity for boron uptake than the corresponding poly(styrene-*co*-divinylbenzene) resins, because of its higher hydrophilic property.²

To enable crosslinked poly(GMA) to possess the largest possible content of GMA while retaining good porous and mechanical properties, 2-ethyl-

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Journal of Applied Polymer Science, Vol. 83, 2374–2381 (2002)
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DOI 10.1002/app.10218

2-(hydroxymethyl)-propan-1,3-diol trimethacrylate (trimethylolpropane trimethacrylate, TRIM) is considered advantageous as a crosslinker to yield poly(GMA-*co*-TRIM) resins, because of the increased number of double bonds and almost equal reactivity of TRIM compared to ethylene dimethacrylate and divinylbenzene and others.⁶ Verweij and Sherrington⁷ confirmed that in suspension polymerization of GMA with TRIM, by using a cyclohexanol-dodecan-1-ol mixture as a porogen, both the pore volume and the surface area decrease with increasing GMA/TRIM ratio and that the pore volume abates with an increase in the monomer/porogen ratio. Walenius et al.⁸ demonstrated that the pore-size distribution shifts toward larger pores in the dry state as the GMA/TRIM ratio increases and that the pore size distributions in the dry and swollen states shift toward smaller pores when the monomer/porogen ratio becomes larger. Recently, Kotha et al.⁹ reported that both the pore volume and the surface area decrease with reducing molar fraction of crosslinking comonomer for poly(GMA) crosslinked with TRIM, 2,2-bis(hydroxymethyl)-propan-1,3-diol triacrylate, or 2-ethyl-2-hydroxymethyl-propan-1,3-diol triacrylate by using cyclohexanol as a porogen. The dependences of the pore structure of poly(GMA-*co*-TRIM) on the GMA/TRIM, monomer/porogen ratios in suspension polymerization strongly imply that the compatibility of the resulting polymer network with porogen primarily dominates the porous properties of poly(GMA-*co*-TRIM). Accordingly, the selection of a less polar porogen may realize porous poly(GMA-*co*-TRIM) with a larger GMA content, because GMA is more polar than TRIM. Such poly(GMA-*co*-TRIM) would be a favorable precursor of novel materials for separation of boron isotopes.

In this study, we describe the suspension polymerization of GMA with TRIM by using toluene and octan-2-one as porogens, they being less polar than cyclohexanol, to yield porous poly(GMA-*co*-TRIM) with a larger content of GMA. We discuss especially the dependence of the porous properties of the resulting poly(GMA-*co*-TRIM) on the GMA/TRIM ratio, the monomer/porogen ratio, and the property of the porogen, on the basis of phase separation.

EXPERIMENTAL

Materials

All reagents and solvents were purchased from Wako (Wako Pure Chemical Co. Ltd., Osaka, Ja-

pan) and were used as received unless otherwise stated. The initiator 2,2'-azo-bis(isobutyronitrile) (AIBN) was recrystallized from methanol prior to use.

Polymerization Procedure

The system of suspension polymerization was composed of an organic phase with GMA and TRIM as monomers and either toluene or octan-2-one as a porogen, and an aqueous phase with poly(vinyl pyrrolidone) (PVP, average $M_w \approx 40,000$) as a stabilizer. The ratio of the organic phase to the aqueous phase is 18% v/v. The AIBN content was 1% w/v of the monomer phase and the PVP content was 3% w/w of the organic phase. The polymerization was carried out at 73°C for 8 h. The products were washed thoroughly with distilled water and ethanol and then dried under vacuum at 60°C for 48 h. The dried polymer beads were purified with acetone in a Soxhlet extractor and then dried under vacuum at 60°C for more than 48 h.

Characterization

The specific surface area of the polymer beads was determined from the adsorption/desorption isotherms of nitrogen by using the BET equation¹⁰ (Autosorb-I, Quanta Chrome, USA). The pore volume and the pore-size distribution were measured by mercury porosimetry (Autopore III 9420, Micromeritics, USA). FTIR spectra were obtained from KBr pellets on a Perkin-Elmer model 2000 spectrophotometer. The microstructure of the polymer coated with gold was observed with a JSM-5310 scanning electron microscope (JEOL, Tokyo, Japan). The particle size distribution of poly(GMA-*co*-TRIM) beads was measured by a LMS-24 laser micron sizer (Seishin, Tokyo, Japan).

RESULTS

The Composition and the Particle Size Distribution of Poly(GMA-*co*-TRIM)

The elemental weight fractions of each resulting polymer are very close to those of the initial monomer mixture of GMA and TRIM, respectively, as shown in Table I. With an increase in the molar ratio of epoxy groups to ester groups in the monomer mixture, the intensity ratio $S(910)/S(1733)$ increases linearly in Figure 1, where $S(910)$ and $S(1733)$ denote the absorbances at 910

Table I The Composition of Poly(GMA-co-TRIM) Determined by Elemental Analysis

GMA in Monomer (% v/v)	Porogen	Monomer in Organic Phase (% v/v)	Element Weight Fractions in the Resultant Polymer ^{a,b} (wt %)		
			C	H	O
25	Toluene	33	61.3 (62.7)	7.99 (7.58)	30.71 (29.72)
50	Toluene	33	60.3 (61.5)	7.66 (7.41)	32.04 (31.09)
67	Toluene	33	59.8 (60.7)	7.74 (7.31)	32.46 (31.99)
40	Octan-2-one	33	59.9 (62.0)	7.87 (7.48)	32.23 (30.52)
50	Octan-2-one	33	59.4 (61.5)	7.80 (7.41)	32.8 (31.09)
67	Octan-2-one	33	59.1 (60.7)	7.75 (7.31)	33.15 (31.99)

^a The oxygen fraction of each polymer was calculated by subtracting the carbon and hydrogen fractions.

^b The values in parentheses denote the calculated weight fractions of the initial mixture of GMA and TRIM.

and 1733 cm^{-1} , because of the epoxy and ester groups, respectively.¹¹ Accordingly, we can consider that GMA and TRIM are quantitatively copolymerized to yield poly(GMA-co-TRIM) with the same content of GMA as that in the initial monomer mixture.

The particle size distribution of poly(GMA-co-TRIM) beads ranges largely from 100 to 700 μm under a constant content of PVP of 3% w/v in the

organic phase, the volume of which is 18% v/v of that of the aqueous phase. Thus, the particle size distribution hardly depends on the monomer content in the organic phase (Fig. 2) as well as on the GMA content in the monomer mixture.

Effect of the Monomer Content on the Pore Structure

We examined the dependence of the porous properties of poly(GMA-co-TRIM) on the monomer

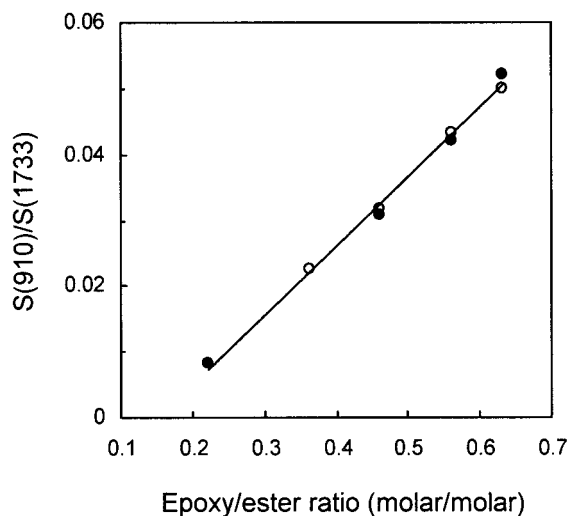


Figure 1 Plot of the IR intensity ratio of S(910)/S(1733) in the polymer against the molar ratio of epoxy groups to ester groups in the initial monomer mixture. Porogens: toluene (●) and octan-2-one (○); monomer content, 33% v/v.

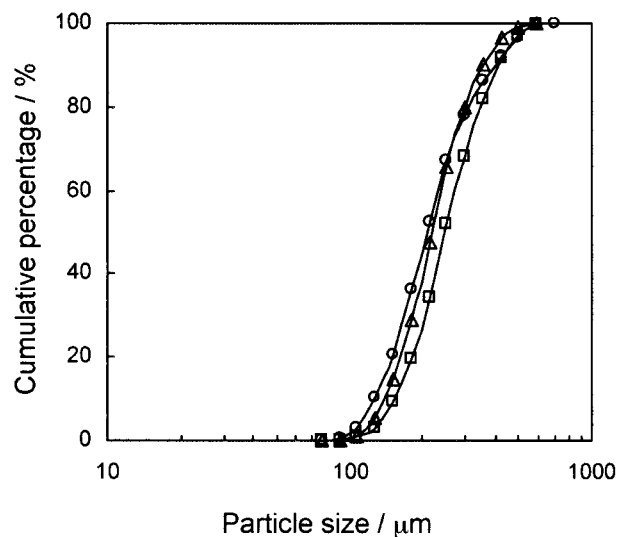


Figure 2 Particle size distribution of poly(GMA-co-TRIM) beads. Conditions: monomer contents, 25 (○), 33 (□), and 50% v/v (△); GMA content in monomer, 50% v/v; Porogen: octan-2-one.

content in the organic phase under the equal volume ratio of GMA/TRIM = 1. Increasing the monomer content in the organic phase from 25 to 50% v/v with either toluene or octan-2-one as a porogen, the pore volume of poly(GMA-*co*-TRIM) decreases greatly, with nearly the same surface area, as shown in Figure 3. The pore-size distributions shift toward the smaller pore sizes with an increase in the monomer content in toluene and octan-2-one in Figures 4(a) and 4(b), respectively. The most frequent pore size decreases from 147 to 38 nm with toluene and from 117 to 60 nm with octan-2-one. Thus, the total pore volume of poly(GMA-*co*-TRIM) is controlled mainly by the amount of toluene and octan-2-one in the organic phase, indicating they can act as a porogen in creating the permanent porous structure of the polymer resin. Figure 3 shows that the effect of the monomer content on the pore volume is much stronger with toluene as a porogen than with octan-2-one.

Effect of the GMA Content on the Pore Structure

Figure 5 shows the dependence of the pore structure of poly(GMA-*co*-TRIM) on the GMA content with toluene or octan-2-one as a porogen under the equal volume ratio of monomer/porogen = 1/2. With an increase in the GMA content, the specific surface area decreases strikingly, similar to the result with the cyclohexanol-dodecan-1-ol (9/1

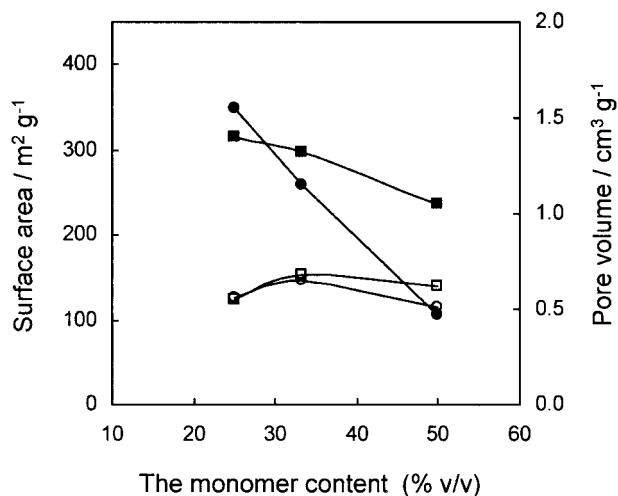


Figure 3 Effects of the monomer content in the organic phase on the pore structure. Pore volumes with toluene (●) and octan-2-one (■) as porogens; surface areas with toluene (○) and octan-2-one (□) as porogens. The GMA content in the monomer mixture is 50% v/v.

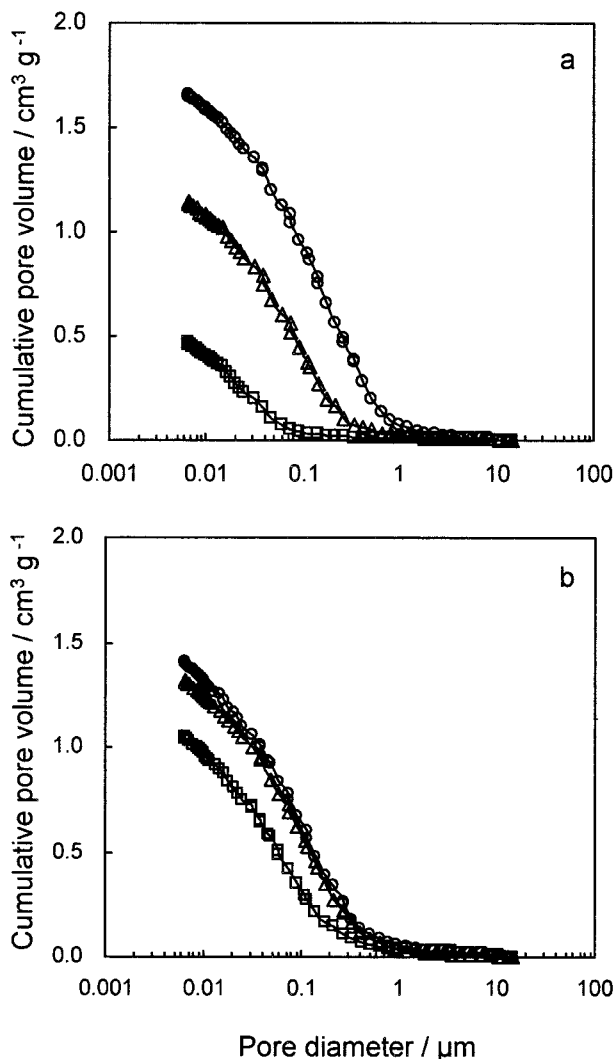


Figure 4 Effects of the monomer content in the organic phase on the pore-size distribution with toluene (a) and octan-2-one (b) as porogens. Conditions: monomer contents, 25 (○), 33 (△), and 50% v/v (□); GMA content in monomer, 50% v/v.

v/v) mixture as a porogen,⁷ as shown in Figure 5(a). On the other hand, the pore volume reaches its maximum at the GMA content of 60% v/v with toluene and of about 50% v/v with octan-2-one, as shown in Figure 5(b). It is worth noting that poly(GMA-*co*-TRIM) prepared with toluene and octan-2-one exhibits higher porosity at the larger GMA content than that with the cyclohexanol-dodecan-1-ol (9/1 v/v) mixture,⁷ as clearly shown in Figure 5(b). From Figure 6(a), the pore-size distributions of poly(GMA-*co*-TRIM) prepared with toluene as a porogen shift toward larger pore sizes and broaden with an increase in the GMA content up to 60% v/v, beyond which it is replaced

by smaller pore sizes accompanied by a narrowing to a diameter of about 80 nm. Compared with this polymer, poly(GMA-*co*-TRIM) prepared with octan-2-one exhibits a slight dependence of the pore-size distribution on the GMA content, with a narrowing to a diameter of around 100 nm under a GMA content of 67% v/v, as shown in Figure 6(b).

Figure 7 shows images by scanning electron microscopy (SEM) of the fractures of poly(GMA-*co*-TRIM) with different GMA contents prepared with toluene as a porogen. The SEM observation demonstrates clearly that increasing the GMA

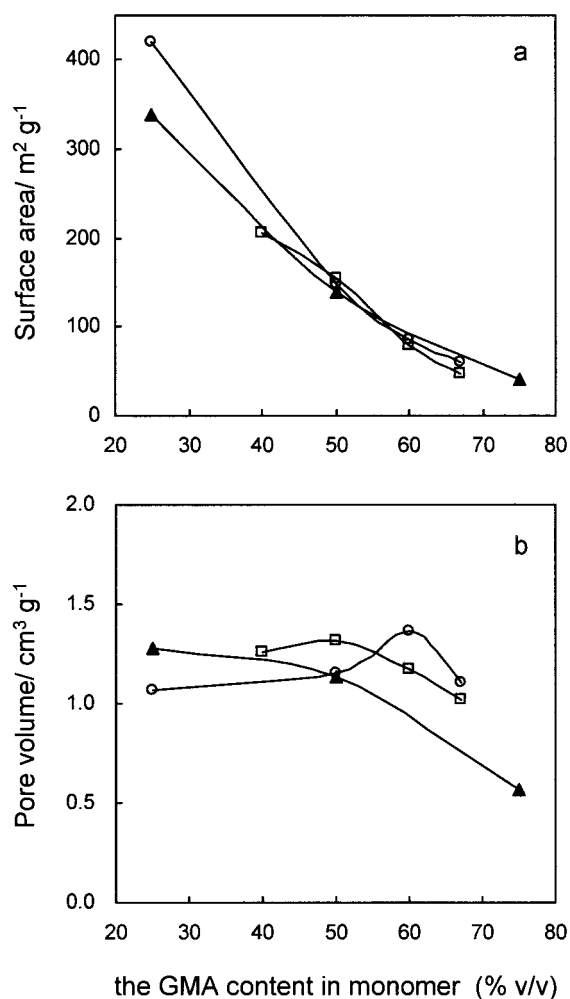


Figure 5 Effects of the GMA content in the initial monomer mixture on the pore structure: surface area (a) and pore volume (b). Porogens: toluene (○) and octan-2-one (□); monomer content, 33% v/v. The surface area and the pore volume with the cyclohexanol-dodecan-1-ol (9/1, v/v) mixture as a porogen (▲) are cited from a report by Verweij and Sherrington⁷ for comparison.

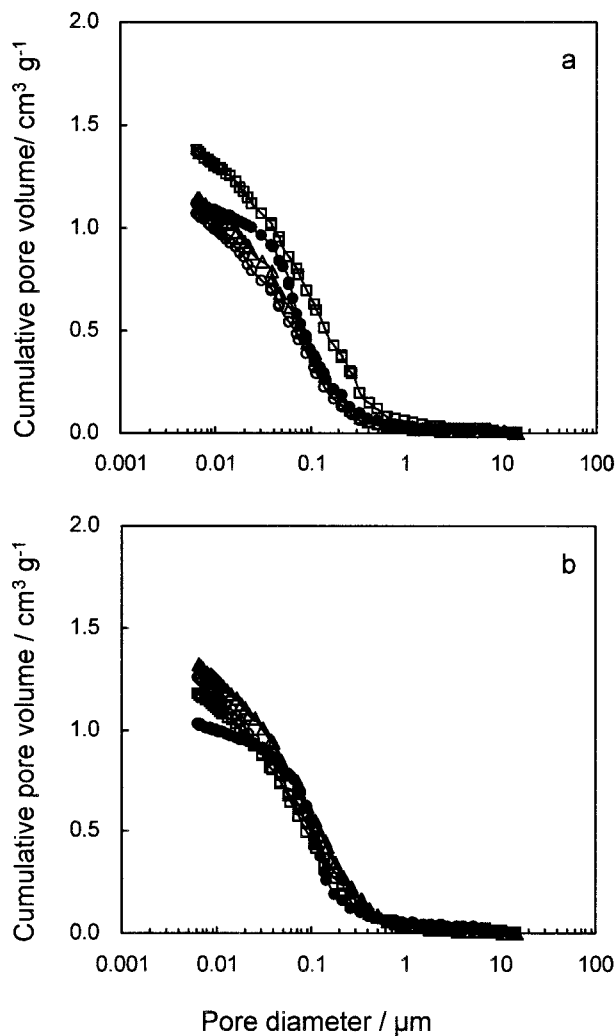


Figure 6 Effects of the GMA content in the initial monomer mixture on the pore size distribution with toluene (a) and octan-2-one (b) as porogens. GMA contents in monomer, 25 (○), 50 (△), 60 (□), and 67% v/v (●); monomer content, 33% v/v.

content causes larger aggregations of the microgel particles to yield a larger pore size, consistent with the result in Figure 6(a).

DISCUSSION

We have demonstrated that the porous properties of poly(GMA-*co*-TRIM) prepared by suspension polymerization are controlled not only by the ratio of porogen to monomer under the same GMA/TRIM ratio, particularly with respect to the total pore volume (Fig. 3), but also by the GMA/TRIM ratio under the same porogen/monomer ratio, in

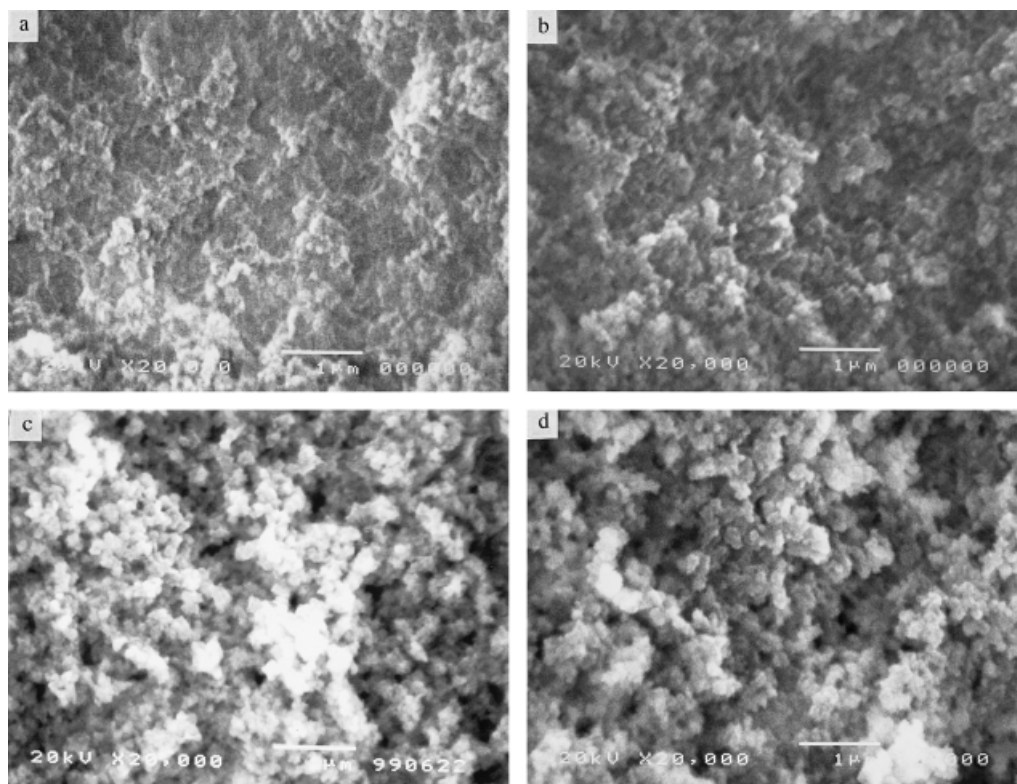


Figure 7 SEM images of fractures of the polymers prepared with GMA contents of 25 (a), 50 (b), 60 (c), and 67% v/v (d) with toluene as a porogen. Monomer content, 33% v/v.

particular, with respect to the surface area (Fig. 5). The dependence of the total pore volume on the porogen content is commonly observed in a polymer network of styrene and divinylbenzene.¹² On the other hand, it is very interesting that the surface area depends largely on the monomer composition almost regardless of the nature of the porogen and that the dependence of the total pore volume on the monomer composition differs according to the porogen. Thus, poly(GMA-*co*-TRIM) with maximum pore volume is obtained at a higher GMA content (60% v/v) with toluene as a porogen, at a low GMA content (25% v/v) with a 9/1 v/v mixture of cyclohexanol and dodecan-1-ol,⁷ and at an intermediate GMA content (50% v/v) with octan-2-one.

It is well known that the morphology of polymer matrices is principally determined by phase separation during polymerization,¹² which is largely dependent on the compatibility of the polymer network with the porogen. In the case of good compatibility, the phase separation at the greater conversion of monomer to polymer creates a network of interconnecting individual microgel

particles to yield a polymer matrix with a high surface area and a pore-size distribution with a maximum in the region of micro- to mesopore. On the other hand, in the case of poor compatibility, the phase separation at the lower conversion induces not only aggregation of microgel particles but also in-filling of small pores to form a polymer matrix with a low surface area and a pore-size distribution shifted to the macropore region. This concept leads qualitatively to further aggregation of microgel particles of poly(GMA-*co*-TRIM) with an increase in the ratio of porogen to monomer, which is responsible for the shift of the pore size distribution from mesopores to macropores in Figure 4.

Accordingly, the compatibility of a polymer network with a porogen can be evaluated in terms of the difference in solubility parameter between them, $|\delta_p - \delta_s|$, where δ_p and δ_s are the solubility parameters of the polymer network and the porogen, respectively.¹² We estimated the δ_p values of poly(GMA-*co*-TRIM) with different molar GMA/TRIM ratios from the group contribution method¹³:

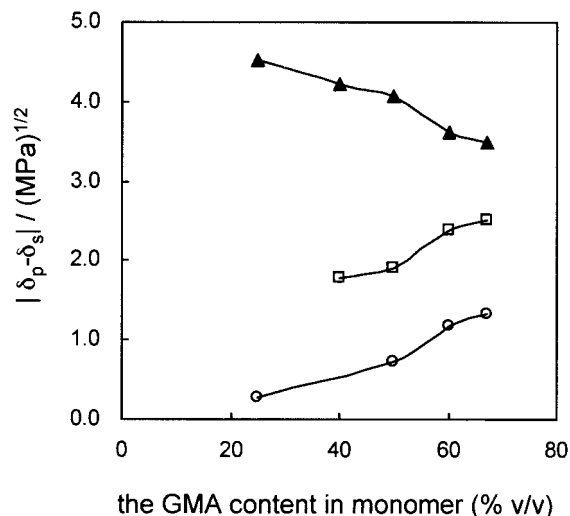


Figure 8 Dependences of the difference in the solubility parameter $|\delta_p - \delta_s|$ on the GMA content and the porogen. Porogens: toluene (○), octan-2-one (□), and a mixture of cyclohexanol-dodecan-1-ol (9/1, v/v) (▲).

$$\delta_i = \frac{\rho_i \sum_j F_j}{M_i},$$

where F_j is the group molar attraction constant of Van Krevelen,¹⁴ M_i is the average molecular weight of polymer i and was calculated from the molar contents of GMA and TRIM in the initial monomer mixture, and ρ_i is the density of polymer i and was measured in heptanes at 25°C. The calculated solubility parameters of TRIM and GMA are 18.50 and 19.50 (MPa)^{1/2}, respectively. The calculated value of TRIM is in good agreement with the experimental value of 18.20 (MPa)^{1/2}.⁶ The difference in δ for the system with toluene as a porogen is shown in Figure 8, where the δ_s value of toluene is 18.20 (MPa)^{1/2}.¹³ With an increase in the GMA content, the difference $|\delta_p - \delta_s|$ increases and, accordingly, the compatibility of the polymer network with toluene decreases. Based on the abovementioned concept, this indicates earlier phase separation with more GMA content, which seems consistent with the further aggregation of the microgel particles illustrated in Figure 7.

In Figure 8, the difference $|\delta_p - \delta_s|$ is also shown for the polymerization system with a 9/1 v/v mixture of cyclohexanol and dodecan-1-ol as a porogen, as reported by Verweij and Sherrington.⁷ Because cyclohexanol and dodecan-1-ol possess much greater solubility parameters [23.3 and 20–21 (MPa)^{1/2}] than toluene,¹³ the differ-

ence $|\delta_p - \delta_s|$ with the mixture is much larger than that with toluene in all the GMA contents (Fig. 8). Accordingly, we expect that the polymer network of GMA and TRIM exhibits earlier phase separation from the alcohol mixture than from toluene to yield a polymer matrix with less surface area in the former solvent than in the latter. However, the surface area of poly(GMA-co-TRIM) prepared with the alcohol mixture⁷ is close to that with toluene, as already described in Figure 5(a).

The network formation for radical crosslinking polymerization proceeds generally through intramolecular crosslinking between pendant vinyl groups in a macromolecule to form a primary particle, and then intermolecular crosslinking between resultant particles inducing multiple crosslinking to yield microgel particles.¹⁵ Thus, the formation of the microgel particles depends strongly on the features of monomers,⁶ as well as the property of solvent used in polymerization because of a thermodynamically excluded volume effect on the intermolecular crosslinking.¹⁶ According to Rosenberg and Flodin,⁶ the rigid structure of TRIM prevents intramolecular cyclization and multiple crosslinking during the radical polymerization of TRIM monomers, which are elemental processes essential for the formation of microgel particles.¹⁵ This will cause phase separation at the greater conversion of monomer, in spite of the large difference $|\delta_p - \delta_s|$ with the 9/1 v/v mixture of cyclohexanol and dodecan-1-ol. With an increase in the GMA content, the resultant GMA-TRIM copolymer chains probably exhibit higher flexibility, which is advantageous to intramolecular crosslinking and multiple crosslinking. Thus, we can expect that the increase in GMA content induces phase separation at the lower conversion of monomers, to give a polymer matrix with a lower surface area, consistent with the result with the alcohol mixture⁷ (Fig. 5a). The difference of the total pore volume of poly(GMA-co-TRIM) in changing the porogen (Fig. 5b) is probably due to the excluded volume effect, because the porogens have different solubility parameters, as shown in Figure 8.

CONCLUSIONS

We have successfully synthesized macroporous poly(GMA-co-TRIM) with toluene and octan-2-one as porogens by suspension polymerization. The total pore volume of poly(GMA-co-TRIM) is controlled primarily by the ratio of porogen to

monomer and secondarily by the nature of the porogen, whereas the surface area is largely determined by the ratio of GMA to TRIM. Thus, we have prepared beads of porous poly(GMA-co-TRIM) with a maximal pore volume at the greater GMA contents of 60 and 50% v/v using toluene and octan-2-one, respectively, in comparison to those with a larger pore volume at the GMA content of 25% v/v using a 9/1 mixture of cyclohexanol and dodecan-1-ol.⁷ The porous poly(GMA-co-TRIM) is expected to be a promising polymer matrix for novel materials for separation of boron isotopes.

T.H. expresses sincere gratitude to Professor David C. Sherrington (University of Strathclyde, U.K.) for kind instruction in the suspension polymerization of GMA and TRIM and useful discussions.

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