Pore Size in One-Step Swelling and Polymerization of Monodisperse Polymer Beads

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ABSTRACT: Crosslinked polystyrene beads were prepared at low swelling ratios by one-step swelling and polymerization method. Pore size of the beads was observed based on the GPC calibration curves. It is found that: (1) the pore size increases as the swelling ratio decreases; (2) when a good solvent is used as the porogen the pore size increases with the crosslinking monomer content; and (3) at high crosslinking monomer content the pore size does not depend on the porogen solubility. The effects are discussed in terms of polymer miscibility, including phase separation between the seed and bead polymers. © 2000 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 38: 3270–3277, 2000

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INTRODUCTION

In 1995 Ogino et al. improved the swelling and polymerization method of monodisperse polymer beads.[1] His new method uses one-step swelling: polymer seed particles are swelled directly by a monomer and porogen mixture. The old method, invented by Ugelstad, is a two-step swelling method.[2] The seed particles are first swelled by an activating solvent and then swelled by the monomer and porogen mixture. The porogen does not react during the polymerization process but remains within the newly formed beads, pores are obtained after the porogen is finally removed. The activating solvent is a low molecular weight material, which leads to a large increase in the monomer swelling capacity of the seed particles. The new method makes preparation of monodisperse polymer beads easier. Although the swell-ing ratio is lower than that of the multistep swelling, with large seed particles the size of the obtained beads is still in the right range of LC packing materials. Ogino et al. obtained a series of pore size just by controlling the oil (monomer and porogen)/seed swelling ratio with one recipe. This is a convenient way of pore size controlling.

Svec and Frechet summarized the control variables of pore size in suspension polymerization as: (1) the percentage of the crosslinking monomer in the polymerization mixture, (2) the percentage of the porogen in the polymerization mixture, (3) the composition of the porogen, and (4) the reaction temeprature.[3] The porogen solubility and composition are the most useful variables when the first two are fixed, as Moore showed 36 years ago in the first article of the scope.[4]

As to the swelling and polymerization the above control variables are still useful. Articles are found discussing the crosslinking monomer effect,[5,6] the porogen effect,[5,7] and the temperature effect.[8] Special attention has been paid to the polymer porogen effect.[5–7,9–11] The polymer poro-

gens are: (1) the seed polymer, which dissolves in the polymerization mixture, (2) the additional polymer, which is polymerized from the monomer absorbed by the seed particles and later dissolves in the polymerization mixture with the seed polymer. Most of polymerization using the polymer porogen can be looked as the one-step swelling and polymerization if just the last step is looked at.

Pore formation is a process of polymer phase separation. In suspension polymerization only the phase separation of polymer solution is considered, because the polymerization mixture only contains the newly formed bead polymer and the porogen. In swelling and polymerization the polymerization mixture contains one more component—seed polymer, the phase separation between the bead polymer and the seed polymer should also be considered. Polymer miscibility study shows that the phase separation between polymer–polymer takes place much easier than that of polymer solution.[12,13] A small difference in composition or chain structure can cause the phase separation of polymers. For instance a linear polymer may be immiscible with the branched polymer of the same monomer.[14,15] If the swelling ratio is low, the seed polymer makes a considerable part of the polymerization mixture. If the porogen is a solvent of both the seed and bead polymers, it is impossible to have the phase separation of polymer solution during polymerization. The phase separation of polymer–polymer becomes dominant in the pore formation.

There are two methods for determination of pore size distribution of the beads. Mercury intrusion is good for measuring large pores, while gas adsorption is good for small pores. The two methods should be combined in order to give a complete picture of pore size distribution in the beads. The third method is based on the GPC calibration curves, which gives not a real but information of pore size distribution.[1,7,9,11,16,17] In order to do this, the GPC calibration curves should be plotted as lg M-K, where M is molecular weight and K the distribution coefficient. If the pore volumes of the beads are close, lg M-V_e plot can also be used. Crosslinked polystyrene beads swell in solvent, which changes the pore size distribution. However, for the high density of crosslinking beads the GPC calibration curves still make sense. Also, the GPC experiment should be run with a poor solvent as the eluent.

Table I. Molecular Weights of Polystyrene Standard Samples

No	M_w	M_{GPC}	M_n	M_w/M_n
1	25,000,000			
2		3,310,000		
3	1,740,000		1,630,000	1.07
4	1,050,000		974,000	1.08
5		483,000		
6	341,000		318,000	1.07
7		114,000		
8	20,900		20,300	1.03
9		10,100		
10		4000		
11	2900		2700	1.07
12	860		750	1.15

This article is dedicated to the pore size controlling in one-step swelling and polymerization. The crosslinked polystyrene beads are prepared at low swelling ratios by Oginos' method. The pore size is observed based on the GPC calibration curves. The effects of control variables are discussed in terms of polymer miscibility. Attention is paid to the role of seed polymer.

EXPERIMENTAL

Materials

Polyvinyl pyrrolidone (PVP) is a product of Sigma Chemical Company. The molecular weight is 40,000. Other chemicals are made in China in analytical or chemical pure, in which divinylbenzene (DVB) is of 45% content, the degree of polymerization of polyvinyl alcohol (PVA) is 1750, sodium dodecylsulfate (SDS) is of >90% content. Polystyrene standard samples of GPC are prepared at Institute of Chemistry, Academia Sinica, except that the highest molecular weight sample was obtained from Acros, U.S. Molecular weights of the polystyrene samples are listed in Table I.

Synthesis of Polymer Seeds

Polymer seeds were prepared based on a dispersion polymerization method.[18] The only modification was the initiator used in this experiment was benzyl peroxide (BPO), rather than azobisizobutyronitrile (AIBN). AIBN decomposes at 40–60 °C, while BPO decomposes at 80–100 °C. AIBN

Table II. Properties of Seed Particles

| | d (μ) | | | |
No	1	2	ϵ	M_{GPC}
1	2.5			
2	3	3.22	0.026	5000
3	2			5000
4	3			
5	2.5	2.65	0.025	5800

d-1: estimated from the calibration scale in microscope. d-2 and ϵ: measured from the SEM micrographs.

would result in a too fast initiation at the polymerization temperature 70 °C. In a 100 mL conical flask placed was a homogenous solution of 80 mL ethanol, 20 mL styrene(S), 1g PVP and 1g BPO. The flask, connected with a condenser, was thermostated at 70 °C in a water bath and magnetically stirred. Through the condenser a Teflon pipe was inserted in the solution, the other end of the pipe was connected with a nitrogen cylinder. Nitrogen was bubbled in the reaction mixture for the first 8 h of the reaction. The reaction was conducted for 24 h. With reaction going the solution turned turbid and finally the seed particles were obtained. The particles were washed with water three times. Each time the turbid water was separated by centrifuge. Table II gives properties of the seeds, where ϵ is defined as $\epsilon = \sigma/d$, σ is the standard deviation of seed size and d is the average seed size.

Synthesis of Monodisperse Polymer Beads

In a 2000 mL three-necked bottle charged was a homogeneous solution of 10 g PVA, 2 g SDS and 1000 mL distilled water. The solution was stirred at 120 rpm in a water bath of 25 °C. 50 mL of seed suspension (5–20 mL seed particles) was added in the bottle. Then an emulsion of monomer was added dropwise in 2 h in the bottle. The emulsion was made of a solution of 5 g PVA, 1 g SDS and 500 mL distilled water and a solution of 100 mL monomer mixture and 1 g AIBN by using an ultrasonic disrupter. The monomer mixture was made of S, DVB, and porogen toluene, ethyl benzene or n-amyl alcohol. After the monomer mixture was completely absorbed by the seed particles, kept temperature of the water bath at 70 °C for 16 h and then at 95 °C for 2 h. The polymer beads were washed with water, methanol, and toluene. Table III shows preparation conditions and properties of the beads. In the Table, the pore volume V_p is difference in the elution volumes of benzene and the polymer at permeation limit, V_t is the total volume of the column. For the beads of low crosslinking density the V_p/V_t ratio can be larger than 0.5. Figures 1 and 2 are the SEM micrographs of the beads.

Table III. Preparation Conditions and Properties of S-DVB Copolymer Beads

| | | | | | | d (μ) | | | V_p/V_t | |
No	Seed	Oil/Seed	M/P	DVB% in Monomer	Porogen	1	2	ϵ	1	2
1	1	20	50/50	45	A	8	7.88	0.053		0.37
2	2	20	50/50	45	A	10				0.39
3	2	12	66/33	12	E	7				0.57
4	3	12	66/33	12	E	5				0.52
5	4	5	60/40	45	T	5			–	–
6	1	20	60/40	45	T	7	6.93	0.086	0.35	
7	5	5	60/40	15	T	5				0.47
8	1	17.5	60/40	45	T	6	5.81	0.026		–
9	2	17.5	60/40	15	T	7				0.50
10	3	5	50/50	45	A	5				–
11	5	20	50/50	45	T	8				0.43
12	5	20	80/20	45	T	7			0.32	
13	4	20	100/0	45	–	10			0.24	

M: monomer, P: porogen, A: n-amyl alcohol, E: ethyl benzene, T: toluene. d-1: estimated from the calibration scale in microscope. d-2 and ϵ: measured from the SEM micrograph. V_p/V_t: measured from the GPC experiment with 1 (THF) or 2 (MEK) as the eluent.
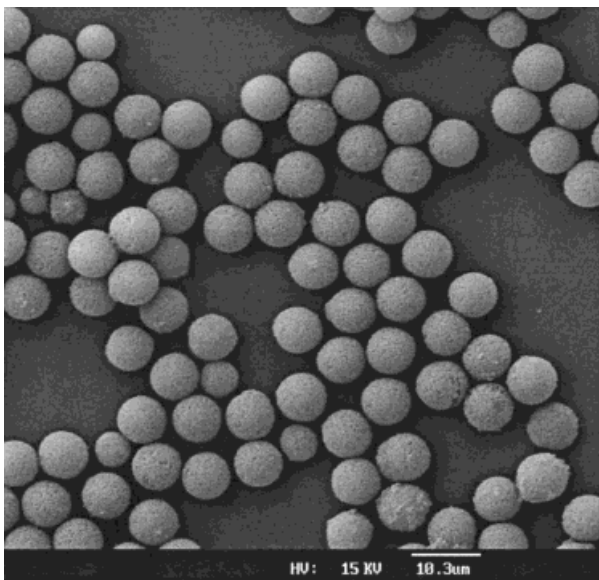
Figure 1. SEM micrograph of polymer beads 6 in Table III.

GPC Experiment

The beads in tetrahydrofuran (THF) or methyl ethyl ketone (MEK) were slurry packed into a column of $\phi 4$ i.d. $\times$ 250 mm at 25 MPa. GPC experiments were run on a Shimadru LC3A apparatus at room temperature, with the packing solvent as the eluent.
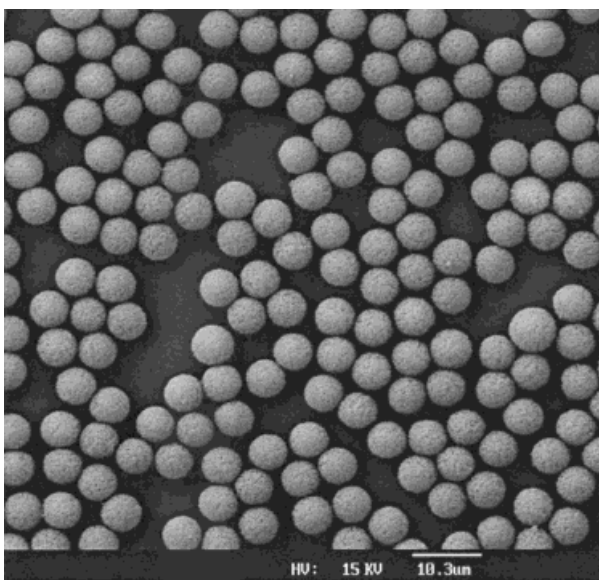

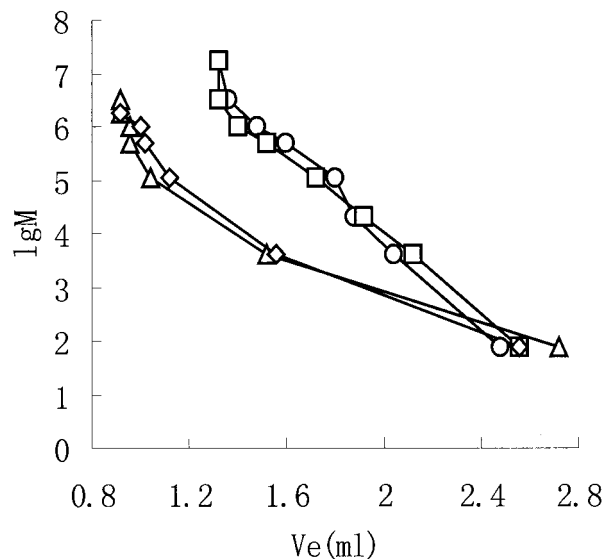**Figure 2.** SEM micrograph of polymer beads 8 in Table III.

Figure 3. GPC calibration curves of the beads prepared with different batches of seeds. The eluent is MEK. Circle, square, triangle, and diamond are beads 1–4 in Table III, respectively.

RESULTS AND DISCUSSION

Reproducibility of Beads Synthesis

In this work five batches of seeds are used for beads synthesis. Although the seeds are prepared with one recipe, size and molecular weight of the seeds vary in a certain range. This is because reaction temperature and stirring speed of the experiment have variations. Reproducibility of beads synthesis is examined with different batches of seeds. Polymer beads 1–4 in Table III are prepared for this purpose. Figure 3 is the GPC calibration curves of the beads with MEK as the eluent. In most cases of this article , MEK is used as the eluent. α values of the Mark–Houwink equation of polystyrene in MEK and THF are 0.58–0.64 and 0.70–0.73, respectively.[19] Compared with THF, MEK is a poorer solvent and a better choice for characterizing pore size of the beads. It can be seen that although more than one batch of seeds is used, the beads prepared with one recipe still give very close GPC calibration curves. We also repeated beads synthesis with one batch of seeds, a good reproducibility is again obtained. This shows that the batch variation of seeds is not large enough to influence the pore formation. We therefore do not consider the batch problem in the following discussion.
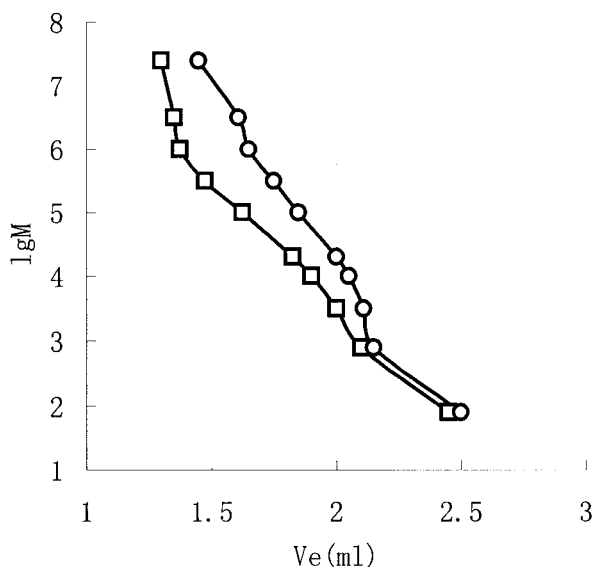
Figure 4. GPC calibration curves showing the effect of swelling ratio to pore size. The eluent is THF. Circle and square are beads 5 and 6 in Table III , respectively.

Swelling Ratio

Ogino et al. prepared the polymer beads with one recipe in a broad range of the oil/seed swelling ratio (v/v, through the text) 10–200. In their preparation toluene was the porogen. With decreasing the swelling ratio the pore size of the beads increased from 3 to 55 nm. However they obtained broken beads at swelling ratio 5.[1] This is because the DVB content in the monomer is too high in their preparation (70%), which makes the beads brittle. In our experiment the DVB content is 45%, good beads are obtained at swelling ratio 5. Compared with swelling ratio 20 the permeation limit of GPC increases from 1×10^6 to 1×10^7, as shown in Figure 4. Our experiment confirms their results.

That the swelling ratio has an effect to the pore size is unique to the swelling and polymerization. This is because the seed polymer takes part in the pore formation through phase separation. Although the seed polymer is made of the same monomer styrene as the bead polymer, the composition and chain structure can be different from the bead polymer. For example, the seed polymer may have PVP chemically bond,[20] and the molecular chain of the bead polymer undergoes a tremendous change during polymerization: from branched at the beginning to fully crosslinked at the end of polymerization. These are the motive

forces for the phase separation between the seed and bead polymers, which even is the only phase separation in the reaction mixture with porogen toluene. The phase separation finally results in an inhomogeneous structure on a large scale in the beads. The more the seed polymer, the larger scale the inhomogeneous structure, the larger the pores. Hosoya and Frechet found that even <1% of seed polymer in the enlarged swelled droplets played an important role in the pore structure.[7] This role becomes dominant at low swelling ratios. In origin, the effect of swelling ratio is the seed polymer effect. With the swelling ratio increasing, the pore size should be more and more close to that of suspension polymerization, if the same recipe is used.

Crosslinking Monomer

Using a polystyrene/*n*-heptane mixture as the porogen Cheng et al. observed a decreasing trend of the pore size from 100 to 40 nm with increasing the DVB content from 5–25%. In their experiment the mercury intrusion was used for the pore size measurement.[5] Galia et al. concluded that when a polystyrene/dibutyl phthalate solution was used as the porogen the DVB content in oil drops did not change the pore size distribution within a broad range of DVB concentration (30–80%).[6] In our experiment the effect of crosslinking mono-
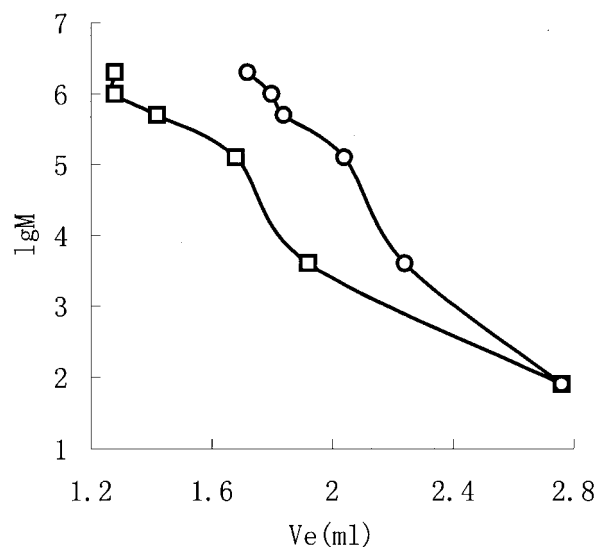

Figure 5. GPC calibration curves showing the effect of DVB content to pore size. The eluent is MEK. Circle and square are beads 5 and 7 in Table III, respectively.
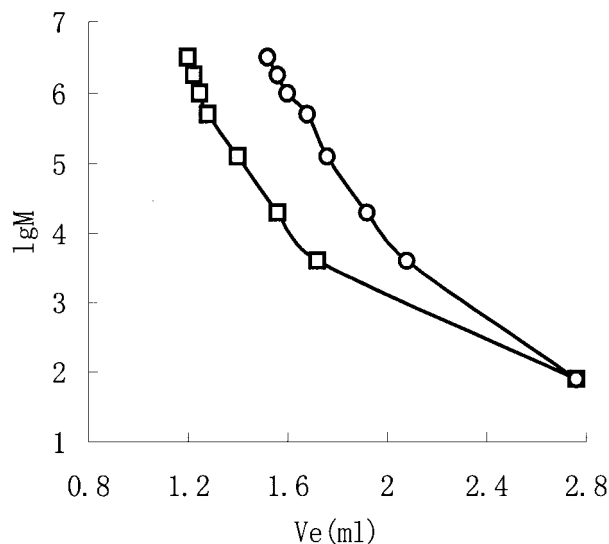
Figure 6. GPC calibration curves showing the effect of DVB content to pore size. The eluent is MEK. Circle and square are beads 8 and 9 in Table III, respectively.

mer is observed at low (15%) and high (45%) content, and at two swelling ratios. A good solvent toluene is chosen as the porogen. Figures 5 and 6 show the effect of crosslinking monomer at swelling ratios 5 and 17.5. We can see that more macropores are obtained at the high DVB content.

Therefore, increasing the content of crosslinking monomer can decrease, have no effect to, or increase the pore size of the beads depending on the polymerization conditions. In Chengs' experiment a nonsolvent n-heptane was used as the porogen, molecular weight of polystyrene was high (m.w. 1.49×10^6). Polymerization started in a very inhomogeneous mixture. The bead polymer precipitated as interior particles immediately after it was polymerized. Agglomeration of the interior particles formed pores. The pore size increased at the presence of high molecular weight polystyrene and decreased at high density of crosslinking. In our experiment a good solvent toluene was used as the porogen, molecular weight of the seed polymer was low (~5000). Polymerization started in a homogeneous solution. The interior particles formed at the later stage of polymerization due to the phase separation of the seed and bead polymers. The interior particles swelled in toluene and then the soft particles coalesced through further crosslinking into larger particles. A high DVB content favors for forming larger interior particles. In Galias' experiment a very poor solvent dibutyl phthalate was used as the porogen. Molecular weight of polystyrene was low too (no data in the text, judged by the recipe: 0.13 g benzoyl peroxide to 2.6 mL styrene).The solubility of dibutyl phthalate was in between of n-heptane and toluene. It was expected to see a less dependence of pore size on the DVB content. This is the first reason of the observed less dependency. Although the DVB contents were in a broad range of 30–80%, most of which were in the range of high crosslinking density. Any dependence of pore size on the DVB content would be leveled off. This probably is the second reason of the observed less dependency. In summary, it is possible that the dependence of pore size on crosslinking monomer content is determined by solubility of the porogen solvent to the bead polymer.

Porogen

In suspension polymerization the role of porogen is critical. Pore size is dependent on solubility, composition, and content of porogen. In swelling and polymerization the role of porogen depends on the swelling ratio first. When the swelling ratio is large, the seed polymer is negligible, the porogen effect to pore size is similar to that in suspension polymerization. Otherwise the porogen effect depends on the other conditions of polymerization. Hosoya et al. found that a good solvent gave a concave GPC calibration curve, indicating a large content of small pores, while a nonsolvent gave a convex GPC calibration curve, indicating a large content of large pores.[7] The swelling ratio in their experiment was over 165, so they saw a similar effect as in suspension polymerization. Cheng et al. also studied the porogen effect.[5] They found that the pore size obtained from the polystyrene (m.w. 1.49×10^6)/toluene solution was larger than that obtained from the polystyrene(m.w. 1.49×10^6)/n-hexane mixture. The swelling ratio (3) and DVB content (15%) were both low in their experiment. In our experiment, the polymer beads are obtained at swelling ratios 5 and 20 and with a high DVB content 45%. Figure 7 shows that the solubility of porogen makes no difference in the pore size. The porogens toluene and n-amyl alcohol are the solvent and nonsolvent of polystyrene, respectively. The permeation limits and calibration curves of the beads made with the two porogens are almost identical. The two experiments show that pore size of the beads obtained at the low swelling ratios in swelling and polymeriza-

tion has a different dependence on the porogen solubility from that of the beads obtained at the large swelling ratios (as Hosoya et al.) or in suspension polymerization. In Chengs' case larger interior particles were obtained in toluene because precipitation of the bead polymer took place later. So they found that the pore size with a good solvent porogen was larger than that with a nonsolvent. In our case the two porogens represent two different mechanisms of pore formation. The nonsolvent porogen causes the phase separation of polymer solution as the bead polymer is immiscible with the porogen. With the solvent porogen the phase separation of seed and bead polymers leads to the pore formation. Both make larger pores at high DVB contents.

Figure 8 shows the effect of porogen content. With increasing the content of porogen in the polymerization mixture, the permeation limits of GPC are almost same but the pore volume increases. This is reasonable because the pore size is determined by polymer miscibility, while the pore volume is determined by content of porogen.

CONCLUSIONS

In one-step swelling and polymerization of monodisperse S-DVB beads the pore size can be controlled by the swelling ratio, crosslinking mono-
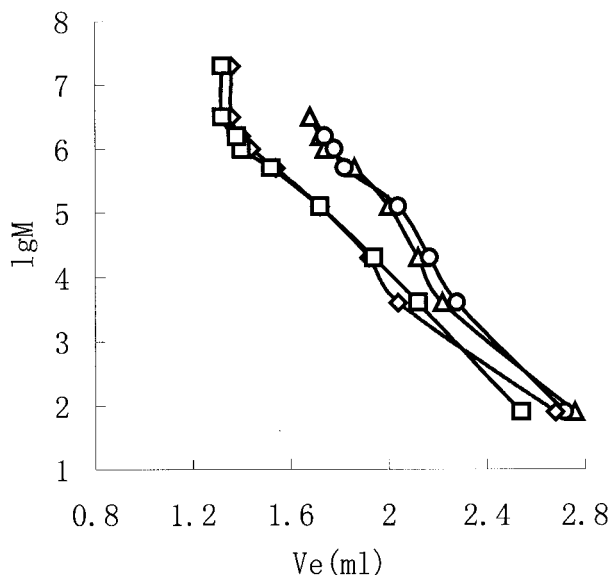

Figure 7. GPC calibration curves showing the effect of porogen solubility and swelling ratio to pore size. The eluent is MEK. Circle, triangle, square, and diamond are beads 5, 10, 11, and 2 in Table III, respectively.
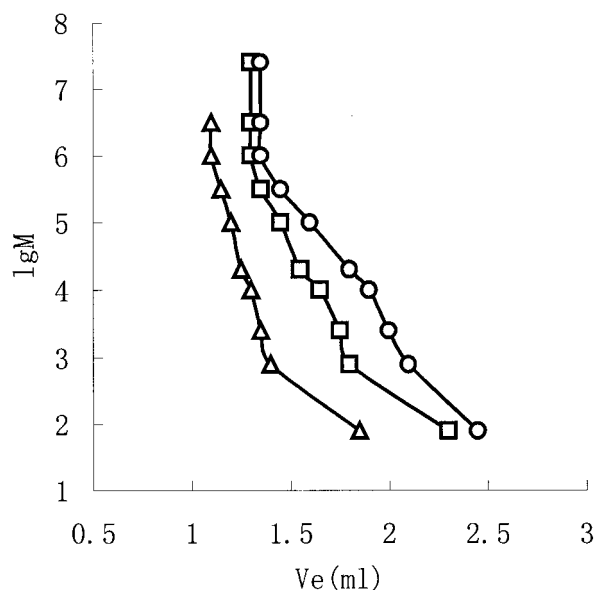

Figure 8. GPC calibration curves showing the effect of porogen content to pore size. The eluent is THF. Circle, square, and triangle are beads 6, 12, and 13 in Table III, respectively.

mer, and porogen. The lower the swelling ratio the larger the pore size. If a good solvent toluene is used as the porogen, more macropores are obtained at high content of crosslinking monomer DVB. When the swelling ratio is low and the DVB content is high, the porogen solubility makes no difference in the pore formation, both the solvent and nonsolvent porogens give almost identical GPC calibration curves. The effects of pore controlling variables are discussed in terms of polymer miscibility, including the phase separation of seed and bead polymers.

REFERENCES AND NOTES

1. Ogino, K.; Sato, H.; Tsuchiya, K.; Sazuki, H.; Moriguchi, S. J Chromatogr 1995, 699, 59.
2. Ugelstad, J.; Kaggerud, K. H.; Hansen, F. K.; Berge, A. Makromol Chem 1979, 180, 737.
3. Svec, F.; Frechet, J. M. J. Science 1996, 273, 205.
4. Moore, J. C. J Polym Sci 1964, A2, 835.
5. Cheng, C. M.; Micale, F. J.; Vanderhoff, J. W.; El-Aasser, M. S. J Polym Sci 1992, A30, 235.
6. Galia, M.; Svec, F.; Frechet, J. M. J. J Polym Sci 1994, A32, 2169.
7. Hosoya, K.; Frechet, J. M. J. J Polym Sci 1993, A31, 2129.

8. Svec, F.; Frechet, J. M. J. Macromolecules 1995, 28, 7580.

9. Wang, Q. C.; Hosoya, K.; Svec, F.; Frechet, J. M. J. Anal Chem 1992, 64, 1232.

10. Frechet, J. M. J. Makromol Chem Macromol Symp 1993, 70/71, 289.

11. Wang, Q. C.; Svec, F.; Frechet, J. M. J. J Polym Sci 1994, A32, 2577.

12. Flory, P. J.; Eichinger, B. E.; Orwoll, R. A. Macromolecules 1968, 1, 287.

13. Olabisi, O.; Robeson, L. M.; Shaw, M. T. Polymer–Polymer Miscibility; Academic Press: New York, 1979; Chapter 2.

14. Hill, M. J. Polymer 1994, 35, 1991.

15. Chai, Z.; Sun, R.; Li, S.; Karasz, F. E. Macromolecules 1995, 28, 2297.

16. Berek, D.; Novak, I.; Grubisic-Gallot, Z.; Benoit, H. J Chromatogr 1970, 53, 55.

17. Nikolov, R.; Werner, W.; Halasz, I. J Chromatogr Sci 1980, 18, 207.

18. Lee, W.-C.; Lin, C.-H.; Ruaan, R.-C.; Hsu, K.-Y. J Chromatogr 1995, 704, 307.

19. Polymer Handbook, 3rd ed.; Brandrup, J.; Immergut, E. H., Ed.; Wiley: New York, 1989; Chapter VII.

20. Lok, K. P.; Ober, C. K. Can J Chem 1985, 63, 209.