

Syntheses of Acrylate Core/Shell Imbiber Beads by Seeded Suspension Copolymerization and One-Stage Copolymerization for Solvent Absorption–Desorption

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ABSTRACT: Seeded suspension copolymerization or a one-stage copolymerization was used to synthesize acrylate core/shell imbiber beads. A two-stage polymerization technique was used for seeded suspension polymerization. The seed particles for poly(methyl acrylate) or poly(2-ethylhexyl acrylate) were synthesized first in a mixed solvent of toluene/isooctane containing the ethylene glycol dimethacrylate (EGDMA) crosslinking agent. These beads were swollen in styrene-EGDMA-BPO (benzoyl peroxide) and then polymerized in the aqueous phase to produce the polystyrene (PS) shell. The one-stage copolymerization was carried out in toluene/isooctane containing methyl methacrylate (MMA), styrene (St), EGDMA, and BPO at 75°C for 10 h to give a core/shell copolymer of St-MMA morphology. The appearance of core/shell imbiber beads prepared from these two techniques varied from monomer to monomer. This article describes the preparation, characterization, and application of the core/shell beads for organic solvent absorption/desorption. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 670–682, 2002

Key words: core-shell polymers; copolymerization; glass transition; polystyrene

INTRODUCTION

The core/shell particles are usually prepared by a series of consecutive polymerization sequences with different monomer types, where the second monomer is polymerized in the presence of seed particles of the first monomer. Seed particles can

be prepared either in a separate step, or formed in situ during one-stage polymerization. The resulting particles are commonly referred to as “core/shell” particles, implying a particle structure with the initially polymerized polymer located in the center of the particle and the later-formed polymer becoming incorporated into the outer shell layer. Grancio and William¹ proposed the nonuniform core/shell theory of particle growth in seeded emulsion polymerization of styrene onto polystyrene seed particles. They found no concentration gradient from the center of the particle to its

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surface, because styrene is miscible with polystyrene in all proportions and a polymer particle is swollen homogeneously with its monomer. Okubo et al.² synthesized micron-sized monodisperse PMMA/PS particles at a PMMA/PS ratio of 2 : 1 (by weight) by seeded dispersion polymerization, in which the core polymer is PMMA and the shell is polystyrene. Seeded dispersion polymerization accumulates polymer layers in their order of production, regardless of the hydrophobicity of the core or the shell-forming polymer. Cho and Lee³ studied the morphology of composite latex particles prepared by PMMA-seeded emulsion polymerization of styrene that could be controlled by various reaction parameters. In their study, the PS is the shell material and PMMA is in the core. In the present work, we set out to investigate the syntheses of core/shell imbiber polymer beads by seeded suspension polymerization compared with a one-stage copolymerization of several monomers. The imbiber beads so obtained were tested for organic solvent absorption/desorption.

Materials

Styrene (St) and methyl methacrylate (MMA) were from Eternal Resin Co., Ltd. (Rayong, Thailand). Methyl acrylate (MA) from Lenso Asia Public Co., Ltd., Thailand; 2-ethylhexyl acrylate (2-EHA) from Union Carbide Co., Ltd., Thailand; and ethyleneglycol dimethacrylate (EGDMA) from BDH Laboratory Supplies, England, were purified to be free from inhibitors. Each monomer was extracted with 10% aqueous sodium hydrox-

Table I Basic Conditions for the Preparation of Poly(methyl acrylate) and Poly(2-ethylhexyl acrylate) Seeds

Composition ^a	Poly(methyl acrylate)	Poly(2-ethylhexyl acrylate)
Organic phase		
MA : EGDMA	85/15	—
2-EHA : EGDMA	—	93/7
BPO, wt %	0.4	0.4
Toluene/isooctane	80/20	60/40
Aqueous phase		
PVP K-90, wt %	0.2	0.2
Inhibitor, ^b wt %	0.4	0.4

^a The composition was polymerized at the polymerization time of 10 h at 75°C with an agitation rate of 250 rpm.

^b Hydroquinone sulfonic acid potassium salt.

Table II Seeded Suspension Polymerization of Poly(methyl acrylate) and Poly(2-hexylethyl acrylate) with Styrene Monomer

Composition ^a	Poly(methyl acrylate)/polystyrene	Poly(2-EHA)/polystyrene
Organic phase		
Seed particles, g	3	3
St/EGDMA, 85/15, g	10	—
St/EGDMA, 93/7, g	—	10
BPO, wt %	0.4	0.4
Aqueous phase		
PVP K-90, wt %	0.2	0.2
Inhibitor, ^b wt %	0.16	0.16

^a The composition was polymerized at the polymerization time of 10 h at 75°C with an agitation rate of 250 rpm.

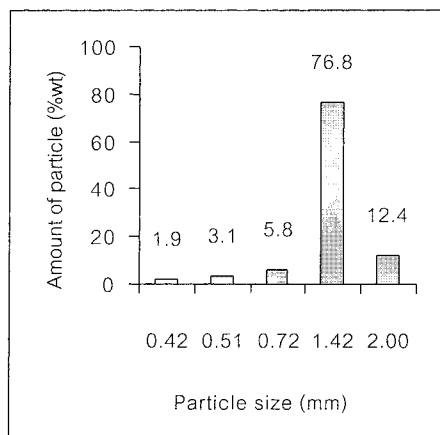
^b Hydroquinone sulfonic acid potassium salt.

ide; the monomer was then washed with distilled deionized water until pH 7 was obtained. Finally, the monomer was passed through an activated aluminum oxide column, neutral, and basic type (Fluka, Steinheim, Switzerland). Benzoyl peroxide (BPO) with 25% water was obtained from Merck Co., Ltd. (Honenbrunn, Germany). Poly(N-vinyl pyrrolidone) or PVP K-90 was obtained from Chameleon Reagents, Osaka, Japan. The viscosity-averaged molecular weight of the polymer is 360,000. Other reagents and solvents (diluent) were of commercial grade and used as received.

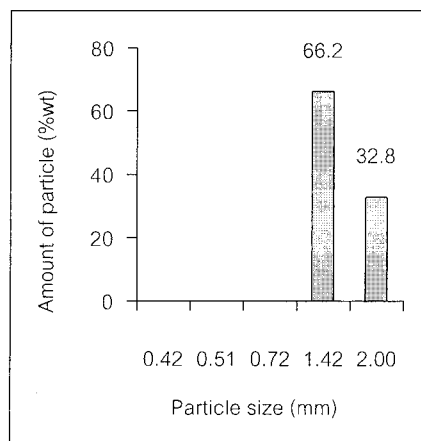
Methodology

Suspension Polymerizations of Methyl Acrylate and 2-Ethylhexyl Acrylate

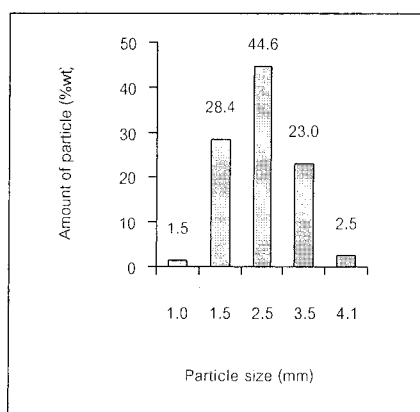
The core particles were prepared by suspension polymerization of MA or 2-EHA with EGDMA as a crosslinker and BPO as an initiator in the presence of organic diluents. The water phase was composed of PVP K-90 stabilizer and the aqueous inhibitor, hydroquinone sulfonic acid potassium salt. The polymerization was carried out in a 500-cm³ flask fitted with a mechanical stirrer, nitrogen gas inlet, and condenser at 75°C for 10 h. The beads were washed with water and then extracted with acetone (commercial grade, Merck, Germany) in a Soxhlet extractor to remove the diluent and residual materials. The beads were finally sieved and vacuum dried at 60°C for 24 h. The basic conditions for suspension polymerization of PMA



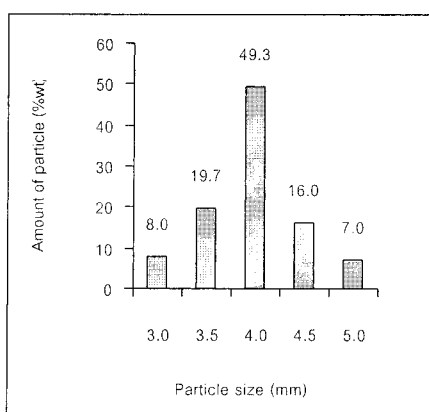
(a) poly(methyl acrylate) seed



(b) poly(methyl acrylate)/polystyrene



(c) poly(2-ethylhexyl acrylate) seed



(d) poly(2-ethylhexyl acrylate)/polystyrene

Figure 1 Bead size distribution: (a) poly(methyl acrylate) seeds (top left); (b) poly(methyl acrylate)/polystyrene (top right); (c) poly(2-ethylhexyl acrylate) seeds (bottom left); (d) poly(2-ethylhexyl acrylate)/polystyrene (bottom right).

seeds and P(2-EHA) seeds are presented in Table I. The seeded suspension polymerizations of PMA/PS and P(2-EHA)/PS core/shell beads are described in Table II.

Seeded Suspension Polymerizations of Poly(methyl acrylate)/Polystyrene and Poly(2-ethylhexyl acrylate)/Polystyrene Core/Shell Imbiber Beads

After the seed beads of PMA or P(2-EHA) had been cleaned, they were sieved into fractions to classify the size range as shown in Figure 1. The large beads sieved weighing 3 g each were swollen in the St/EGDMA solution with a weight ratio of 85/15, BPO initiator, and the mixed diluent. The seed polymer beads were swollen

at room temperature in a closed container for 14 h. The swollen beads were then drained on a sieve to separate the excess St/EGDMA monomer, and were dispersed in the aqueous phase containing PVP K-90 suspending agent and hydroquinone inhibitor with a constant rate of agitation (250 rpm). Polymerization was then carried out for 10 h at 75°C, as for the seed polymers. After the polymerization was complete, the polymer beads were washed with distilled water and extracted by acetone in a Soxhlet extractor to remove the residual materials. Finally, the beads were dried overnight in a vacuum oven at 60°C. The poly(2-EHA) seeds of 3 g were swollen in St/EGDMA solution of a

Table III Basic Recipe and Conditions for One-Stage Polymerization of Methyl methacrylate and Styrene

Material	Concentration
Organic phase	
St/MMA/EGDMA: 46.5/46.5/7, wt %	100
BPO, wt %	0.4
Toluene/isooctane	70/30
Aqueous phase	
PVP K-90, wt %	0.7
Hydroquinone sulfonic acid potassium salt inhibitor, wt %	0.11

The mixture was homogenized at 2000 rpm for 10 min. The mixture was polymerized at 75°C for 10 h with 160-rpm agitation.

weight ratio of 97/3. They were polymerized similarly to PMA as described in Table II.

One-stage Suspension Copolymerization of Styrene and Methyl Methacrylate Core/Shell Imbiber Beads

An aqueous phase containing the PVP K-90 suspending agent and hydroquinone sulfonic acid potassium salt (inhibitor) was poured into a beaker containing an organic phase. The organic phase containing BPO was dissolved in MMA, St, EGDMA, and toluene/iso-octane diluent. The mixture was agitated with a high-speed homogenizer (2000 rpm). Then polymerization of the mixture was carried out in a flask fitted with a mechanical stirrer, nitrogen gas inlet, and a condenser at 75°C for 10 h. The basic recipe and conditions for the one-stage copolymerization of MMA and St are shown in Table III. The core/shell beads were washed with distilled water and extracted with acetone in a Soxhlet extractor to remove the diluents. The beads were finally sieved and vacuum dried at 60°C for 24 h.

Characterization

The polymer beads were analyzed for the particle size distribution by wire gauze of different mesh sizes. The selected polymer beads were stained with RuO₄ vapor for 30 min, coated with gold, and photographed using an electron microscope (JEOL JSM-6400). Glass transition temperatures (T_g) of the polymer beads were measured calorimetrically with a differential scanning calorimeter (Netzsch 200 Selb/Bavarian, Germany). The swelling ratios of the beads⁴ were determined by

the image analysis technique with a stereo microscope equipped with a CCD camera coupling with a Luzex-F software program (Nireo QJ-8500, Olympus SZH 10, Tokyo, Japan). Solvent absorption and desorption of the polymer beads was carried out according to our previous work.⁴

RESULTS AND DISCUSSION

Seeded Suspension Polymerization of Core/Shell Imbiber Beads

Poly(methyl acrylate)/Polystyrene Beads and Poly(2-ethylhexyl acrylate)/Polystyrene Beads

The properties of PMA seeds and PMA/PS core/shell polymer beads are shown in Table IV and the particle size distribution is shown in Figure 1. The percentage conversion of PMA seeds is relatively low (60%), with an average for the particle size of 1.40 mm, while the PMA/PS polymer also has a low conversion (50%) with the average particle size of 1.61 mm. Considering Figure 1(a) and (b), PMA seeds and PMA/PS beads in the range of 0.84 to 2.0 mm occupied 76.8 and 66.2% of the distribution, respectively. This range of particle sizes is good for absorption and desorption of solvent spilled on a water surface, because the beads are large enough to observe by the naked eye.

Table IV shows the properties of the polymer seed beads, P(2-EHA), and the core/shell polymer of P(2-EHA)/PS. The average percentage conversion of the seed polymer is relatively low at around 50%, because of its stickiness and rubbery-like nature, while that of the core/shell P(2-EHA)/PS is as high as 91%. The average polymer particle size was found in the same range as that of the PMA and PMA/PS particles. The PMA seeds and PMA/PS beads have a

Table IV Properties of Polymer Seeds and Core/shell Imbiber Polymer Beads

Type of Polymer	Conversion, %	Average Particle Size, mm	Swelling Ratio in Toluene
PMA seed	60	1.40	4.0
PMA/PS	50	1.61	2.5
P(2-EHA) seed	52	2.5	5.9
P(2-EHA)/PS	91	4	2.9
PS/PMMA ^a	63	0.73	5.6

^a From the one-stage copolymerization.

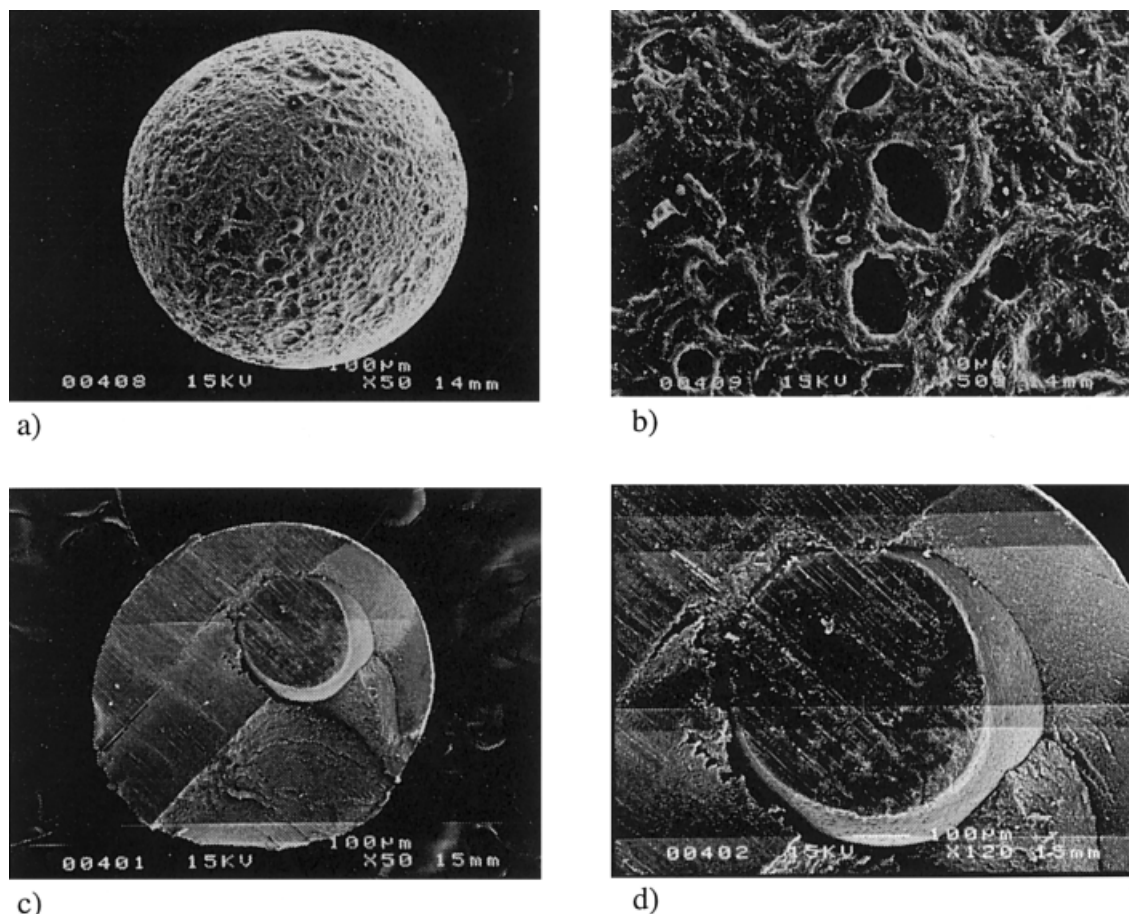


Figure 2 SEM micrographs of core/shell polymer beads: (a) top left: surface of poly(methyl acrylate)/polystyrene (50 \times); (b) top right: surface of poly(methyl acrylate)/polystyrene (500 \times); (c) bottom left: cross-sectional surface of poly(methyl acrylate)/polystyrene (50 \times); (d) bottom right: poly(methyl acrylate)/polystyrene (120 \times).

smaller size, whereas those of P(2-EHA) and P(2-EHA)/PS are much larger. Figure 2(a)–(b) shows SEM micrographs of the surface and cross-sectional morphology of PMA/PS seed particles. The polymer beads have a porous structure with randomly distributed, interconnecting pores on their surfaces.

The polymerization process of the macroporous copolymer beads can be explained in detail as follows: in a seed suspension polymerization, a dispersed phase consisting of a monomer mixture, diluent mixture, and initiator is dispersed in a continuous phase by a dispersing agent. When the crosslinking agent (ethylene glycol dimethacrylate, EGDMA) with a very large monomer reactive ratio is added, the EGDMA-rich copolymer composed of straight chains is then formed at the beginning of the polymerization. When the polymerization proceeds, the monomers are converted

to the crosslinked copolymers and the nuclei formed become insoluble in both monomers and diluents. Consequently, the phase separation occurs gradually between the copolymer and the diluent. Thus, a copolymer-rich phase yields the spherical primary particles having a lower surface free energy. At a certain conversion of monomers, as the content of EGDMA monomer is relatively higher, the copolymers formed cannot become nuclei, and are merely adsorbed on the primary particles. Thus, the primary particles grow and agglomerate. In addition, entanglement of the copolymer molecules takes place among the primary particles leading to combination and fixation of the particles. After the residual diluent in the polymer agglomerates is extracted, macroporous copolymer bead surfaces are then obtained.⁵ In Figure 2(a) and (b), one can see that the surface of PMA/PS is porous, spreading

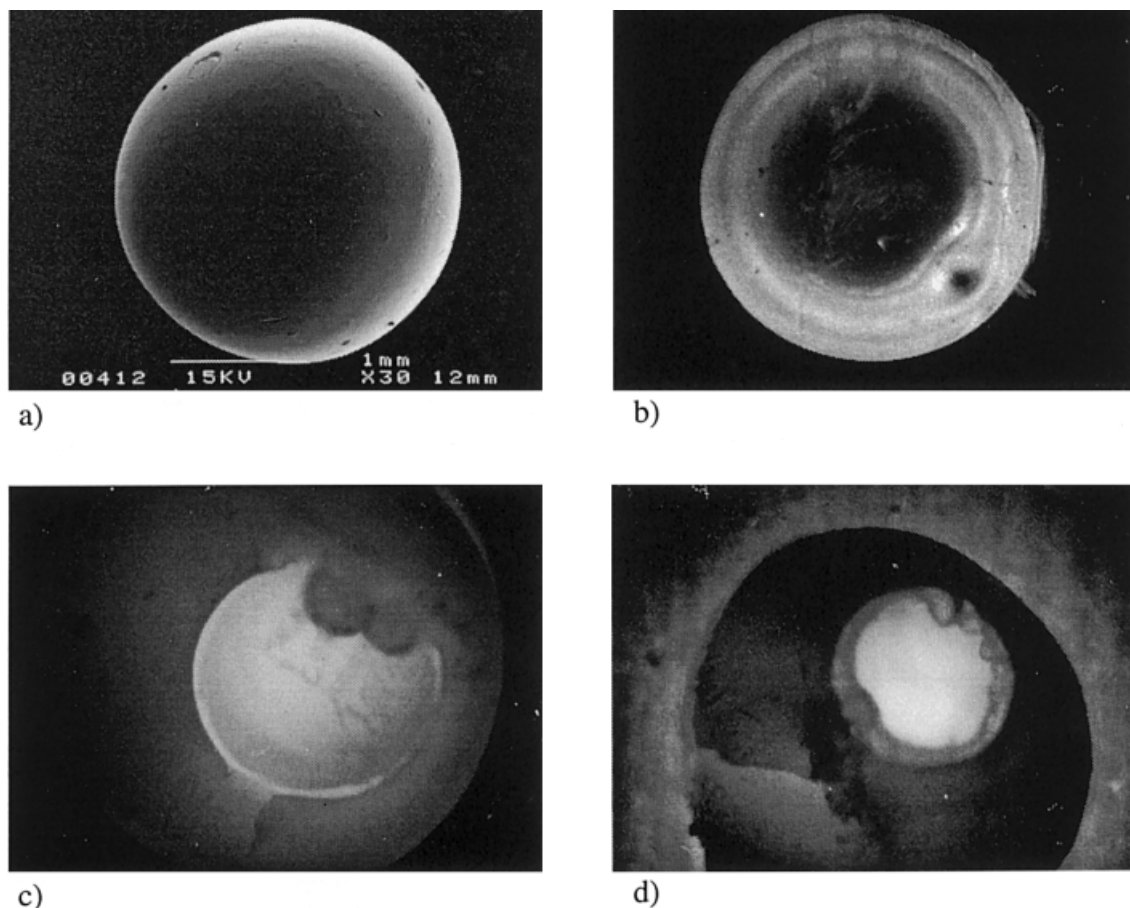


Figure 3 Core/shell polymer beads: (a) SEM photomicrograph of the core P(2-EHA), (top left); (b) cross-sectional view of optical micrographs of P(2-EHA)/PS, (top right); (c) optical micrographs of P(2-EHA)/PS without staining (bottom left); and (d) with RuO_4 vapor staining (bottom right).

throughout the sphere surface, which is attributed to the phase separation and solvent extraction.

The core/shell morphology viewed from the cross-sectional photomicrograph indicates a hard polymer shell and soft polymer core. In the shell, there was more than one layer. The middle layer adhered to its core polymer, whereas the outermost layer was thick and hard. Therefore, a crack developed when it was cut by a razor blade. When the cross-sectional morphology of the bead is viewed [Fig. 2(c) and (d)], more than three outer layers are observed. The inner core is PMA, and the other three shells contain PS. The thin internal layer next to the core polymer could be a copolymer layer of P(MA-co-St). The subsurface and thick surface of polystyrene are deposited sequentially. Shen et al.⁶ prepared monodisperse microscopic PMMA/PS composite particles by

seeded emulsion polymerization of styrene in PMMA seed particles, which were initially prepared by dispersion polymerization. They found three types of polystyrene domains embedded in a continuous PMMA matrix as internal, subsurface, and surface domains. They pointed out that the subsurface PS domains maintained the kinetic-controlled type of morphology, and the surface PS domains did not change at all. This indicates that the subsurface domains were formed under high viscosity conditions and the surface domains were generated during the period close to the end of polymerization. We also found a bead morphology similar to that of Shen et al. In our case, we explained that the thin internal layer could possibly be the copolymer layer due to the swelling step, and the other two layers are brittle PS resulting from the crosslinking reaction.

The P(2-EHA) bead surfaces (top left in Fig. 3)

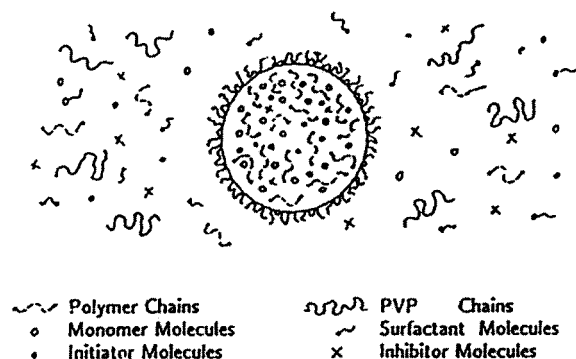


Figure 4 Schematic representation of suspension polymerization system.

are smooth, transparent, and soft. Likewise, the P(2-EHA)/PS beads have a heterogeneous structure and are opaque. The photomicrographs of a P(2-EHA)/PS bead, its surface, and a cross-sectional view of P(2-EHA)/PS are presented in Figure 3(b). Besides its surface features as stated above, the beads have two parts. The dark central part is P(2-EHA), and there is an onion-like morphology with alternating white and gray layers (multilayers). Because the seed particles were swollen in the monomer solution before polymerization, penetration of the solution with more monomers (St/EGDMA) in the seed-swelling step induced the solvent absorption and releasing effect. A similar composite morphology of SARM (solvent absorption/releasing method) proposed by Okubo et al.⁷ could also be used to explain our results. The SARM is a unique method for reconstruction of particle morphology. They found that toluene is the key factor in the formation of the multilayered (onion-like) structure of PMMA/PS composite particles. As mentioned above, we also observed an onion-like morphology with alternate white and gray layers (multilayer) in the outer shell. As shown in the cross-sectional view, Figure 3(b) (upper right), the dark, central core is possibly the P(2-EHA) and the alternating white layers in the shell are PS. In the bottom left photomicrograph [Fig. 3(c)], the unstained core/shell bead and the stained bead of P(2-EHA)/PS in the photomicrograph, Figure 3(d) (bottom right), indicate that the outer layer is PS because only the PS layer could be stained by RuO_4 vapor.

For the seeded suspension polymerization, the polymerization system is depicted in Figure 4, where a large circle represents the swollen seed particle surrounded by the aqueous phase. There are three possible polymerization sites, namely in

the aqueous phase, in the interior, and at the surface. Overall, the extent of polymerization in an aqueous phase is considered to be small for three reasons: (1) most of the monomer and initiator are concentrated inside the large particles because of their low water solubility. (2) A large amount of water-soluble inhibitor is used, and this inhibitor is expected to reside mainly in the aqueous phase. (3) No significant amounts of secondary particles were found in the aqueous phase after polymerization. Therefore, the polymerization of styrene is expected to proceed predominantly inside the seed particles, in the interior, and at the surface of particles.

Because the seed particles are large, the polymerization in the interior of the particles (referred to as an internal polymerization) resembles a bulk polymerization. The polymerization near the surface (referred to as a surface polymerization) is expected to follow a bulk-like polymerization mechanism with the additional effects of surface phenomena such as radical absorption and desorption.⁵ A mechanism of the morphology development of the seeded suspension polymerization is proposed here, and is schematically represented in Figure 5. Before polymerization, the swollen poly(meth)acrylate seed particles have a uniform composition, as shown in Figure 5(A). As soon as the polymerization is initiated, phase separation occurs and polystyrene domains are found throughout the particles [i.e., in the interior and at the surface, as shown in Fig. 5(B)]. The existing polystyrene domains grow, and new domains form until a critical concentration of styrene is reached, as shown in Figure 5(C). After this point,

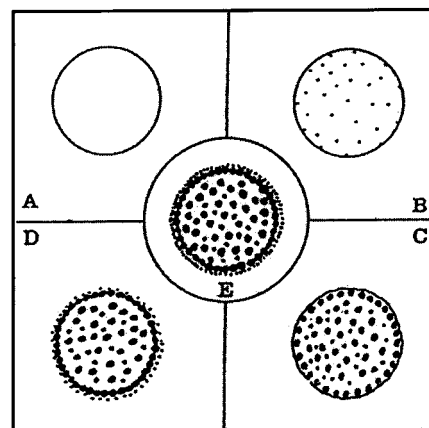


Figure 5 Schematic representation of seeded polymerization of PS/PMMA core/shell bead formation (the dark areas are PS and the white areas for PMMA).

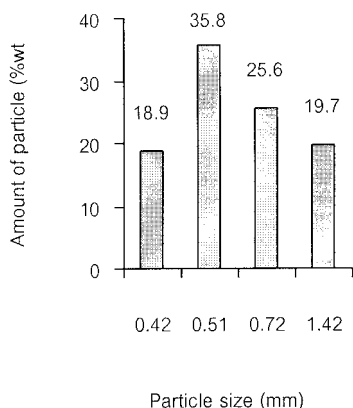


Figure 6 Particle size distribution of the polystyrene/poly(methyl copolymerization methacrylate) core/shell beads from a one-stage polymerization.

the internal polymerization slows dramatically, while the surface polymerization does not. The polystyrene domains in the interior of the particle (the internal domain) essentially stop growing, while those at the surface continue to grow and become interconnected with one another, forming a spherical subsurface crust of polystyrene.

With the further consumption of styrene monomer, the viscosity continuously increases, the diffusion rate of radicals is reduced, and the depth of absorbed radical diffusion and radical desorption decreases. Finally, newly produced polymer chains cannot diffuse into the surface domain, as shown in Figure 5(D). After that, the growth of the subsurface domains essentially stops and only the surface domains continue to grow until the end of polymerization, as shown in Figure 5(E). We can conclude that the core/shell morphology of PMA/PS and P(2-EHA)/PS is thus obtained.

One-Stage Suspension Copolymerization

In this study, the core/shell imbibers of styrene/methyl methacrylate were synthesized by a one-stage suspension polymerization. The appropriate conditions for such a synthesis are presented in Table III. Figure 6 shows the polymer particle size distribution of PS/PMMA from a one-stage copolymerization. The highest particle size distribution frequency (35.8%) is for the particle size of 0.51 mm, while the larger sizes of 0.72 and 1.42 mm have rather low frequencies of 25.8 and 19.7%, respectively.

Figure 7 shows the beads of polystyrene/poly(methyl methacrylate) extracted in cyclohexane for 24 h. The hollow structure of bead particles so

obtained gives poly(methyl methacrylate) shells. The missing polymer of the core material caused by the cyclohexane extraction is PS because PS is soluble in cyclohexane while PMMA is not. In this study, polystyrene was dissolved in hot cyclohexane, yielding a hollow bead structure.⁸ In addition, the hydrophilicity/hydrophobicity of the two monomers plays an important role in the core/shell morphology of the resulting beads. It can thus be explained that polystyrene makes up the core, and poly(methyl methacrylate) is in the shell, because the latter is more hydrophilic and cannot dissolve in cyclohexane. In the one-stage suspension polymerization, it is notable that, in most cases, the morphology of polymer beads obeys kinetic control in the phase separation of the polymer. The more hydrophilic polymer tends to be distributed preferentially in the shell while the more hydrophobic polymer stays in the core.⁵ The mechanism of morphological formation of core/shell beads is as follows. A portion of the polymeric stabilizer, PVP or poly(vinyl pyrrolidone) becomes chemically grafted on the surface of poly(methyl methacrylate) particles due to their similar polarity. Then, the poly(methyl methacrylate) is pulled outwards by the PVP to the outer layer (interface) of the particle or its interface close to the continuous aqueous phase, whereas the more hydrophobic polystyrene moiety remains in the center of the bead as a core material. Consequently, the resulting morphology of the particle is of polystyrene/poly(methyl methacrylate) core/shell type.⁹

Glass Transition Temperature of Core/Shell Beads

In this study, the glass transition temperatures of core/shell beads were measured by differential scanning calorimetry. Table V shows glass transition temperatures of crosslinked polystyrene/poly(methyl methacrylate) beads prepared by one-stage polymerization, the core/shell beads of crosslinked poly(methyl acrylate)/polystyrene, and crosslinked poly(2-ethylhexyl acrylate)/polystyrene. The latter two were prepared by seeded suspension polymerization. The glass transition temperature of polystyrene/poly(methyl methacrylate) was 119.4°C, even though this single glass transition temperature normally indicates that the copolymer resulting from the single-stage polymerization was compatible in every portion and polymerized together to become a one-phase polymer. The glass transition temperatures of the crosslinked poly(methyl methacrylate) are 85 to

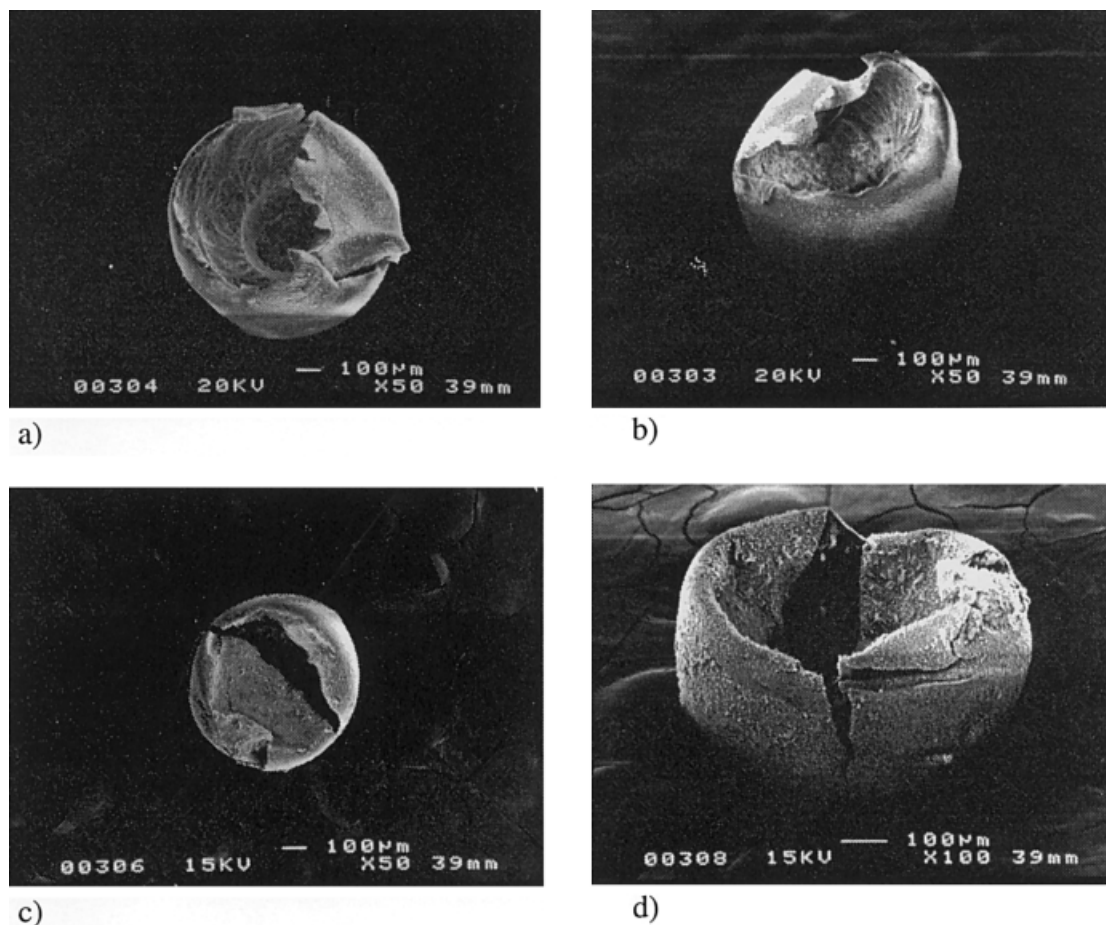


Figure 7 SEM micrographs of PS/PMMA beads after 24-h extraction in cyclohexane.

105°C,¹⁰ and those of the crosslinked polystyrene are 90 to 110°C.¹¹ It may be because the glass transition temperatures of crosslinked PMMA and PS are very close and overlap with each other. This heterogeneous morphology was confirmed by the cyclohexane extraction result of the

PS/PMMA core/shell bead, a two-phase morphology.

For the PMA/PS core/shell imbibed beads, there are two transitions in glass transition temperatures. The higher glass transition temperature was for polystyrene at 143.4°C, and the lower

Table V Glass Transition Temperatures of the Core/shell Polymer Beads

Type of Core/Shell	Glass Transition Temperature				
	Experimental Value, °C			Literature Value, °C	
	$T_{g\text{core}}$	$T_{g\text{shell}}$	Single T_g	$T_{g\text{core}}$	$T_{g\text{shell}}$
PS/PMMA	—	—	119.4	90–110 (nc-PS) 10 (nc-PMA)	85–105 (nc-PMMA)
PMA/PS	27 (c-PMA)	143.4 (c-PS)	—	22.6 (c-PMA) –85 (nc-P(2-EHA))	113.1 (c-PS)
P(2-EHA)/PS	–21.6 (c-P(2-EHA))	113.1 (c-PS)	—	–50 (c-P(2-EHA))	—

nc = noncrosslinked polymer; c = crosslinked polymer.

glass transition temperature was for crosslinked poly(methyl acrylate) at 27.0°C, because the glass transition temperature of the noncrosslinked poly(methyl acrylate) is only 10.0°C.¹² Another two transitions were found in the temperature profile for P(2-EHA)/PS. The higher glass transition temperature was for the crosslinked polystyrene at 113.1°C, and the lower glass transition temperature was for the crosslinked poly(2-ethylhexyl acrylate) at -21.6°C. The glass transition temperature of the noncrosslinked poly(2-ethylhexyl acrylate) is -85.0°C.⁸ The glass transition temperatures of crosslinked poly(methyl acrylate) and poly(2-ethylhexyl acrylate) are 22.6°C and -50.0°C,¹¹ respectively. From the above results, it can be concluded that the presence of ethylene glycol dimethacrylate, as the crosslinker in core/shell beads, had a marked effect, increasing the glass transition temperature of core/shell beads. The crosslinker directly affected the glass transition temperature and the limited macromolecular relaxation that reduced chain flexibility.⁷ When a PMA or P(2-EHA) core was used in toluene swelling (Table IV), the polymer chains were more flexible, and could then be freely disentangled in the organic solvent leading to the higher solvent absorption. When the rubbery core seeds were polymerized with the glassy polymer of PS, the more rigid shell polymer caused by the higher glass transition temperature could then be less accessible to the solvent molecules. Therefore, its solvent absorption was smaller. When the PS/PMMA core/shell polymer is used to absorb the same solvent, it seems that this core/shell polymer is more effective for solvent absorption. Its swelling ratio in toluene is 5.6, because it has the lower glass transition temperature of 119°C. In addition, it can be described that the limited macromolecular relaxation by crosslinking sites in these networks reduced the chain flexibility, resulting in a lower swelling ratio in the seeded suspension polymerization. The extent of crosslinking polymerization is thus the major contributor to the flexibility and relaxation of these beads.

Absorption and Desorption of Core/Shell Polymer Imbiber Beads

The absorption of the core/shell imbiber beads in toluene : isooctane solvent was carried out based on increases in bead volume upon swelling in solvents. Figure 8 shows the absorption/desorption of the core/shell PS/PMMA beads prepared

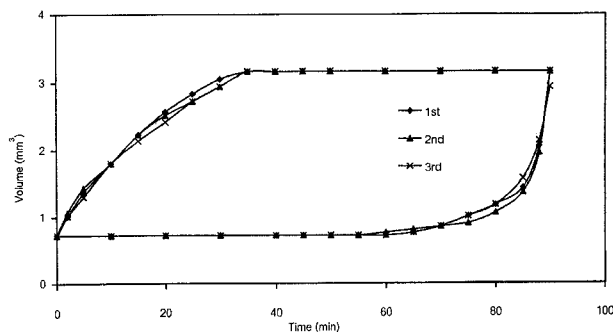


Figure 8 Absorption and desorption of the PS/PMMA beads by one-stage suspension polymerization with time.

by one-stage copolymerization. We found three stages for both absorption and desorption as follows: An initial stage of high absorption rate was due to solvation of the network chains. The main driving force in this region is the changes in free energies of the solvent and elastic deformation during the expansion of the network. The second stage of the slow absorption rate is caused by the pore structure and dimension. The third stage of the plateau value is because of the absorption saturation resulting from no difference in pressure or equilibrium pressure between the bead and the bulk solvent. Table VI gives the absorption times of the core/shell beads at the first and the second stages. The PS/PMMA beads obtained by a one-stage copolymerization can absorb faster than those obtained by seeded suspension polymerization. For the seeded suspension copolymerization, the absorption rates of the two types of core/shell polymers are similar due to the similar functional groups although the T_g values are different.

The desorption of the core/shell beads was measured based on the interaction between the absorbed solvent and the absorbing substrate (e.g., cellulose filter paper) being higher than the solvent interaction with the polymer network. Figure 8 also shows the desorption of the core/shell beads. We found three stages of desorption for those as well. The first stage of a high desorption rate is caused by the different free energies of the solvent, the substrate, and the relaxation of the network. The second stage of a slow desorption rate is related to the pore dimensions of the core/shell beads (by a one-stage polymerization of PS/PMMA). For the one-stage polymerization, the absorption rate increases slowly, and there is no sharp difference in the first and second stages of

Table VI Absorption–Desorption Time of Core/shell Beads in Toluene : Isooctane

Type of Beads	Sorption Time, min			
	First Stage		Second Stage	
	Absorption	Desorption	Absorption	Desorption
PS/PMMA	10	15	10–35	10–25
PMA/PS	5	5	10–55	10–40
P(2-EHA)/PS	5	5	5–60	10–35

desorption. The hard and brittle core material of the beads could cause the slow absorption rates. The third stage of desorption releases a very small amount of retained solvent. Table VI also shows that the PS/PMMA beads can desorb faster at the first and second stages than PMA/PS and P(2-EHA)/PS beads.

Diffusion Coefficient

The diffusion coefficient of the bead in the solvent could be calculated from eqs. (1) and (2), as follows:⁴

$$\tau = a^2/D, \quad (1)$$

where τ is a characteristic swelling time, a is the final radius of the fully swollen gel, and D is the diffusion coefficient of the gel in the liquid. For eq. (2), one can get the following expression:

$$\ln(\Delta a_t/\Delta a_0) = \text{const.} - t/\tau \quad (\text{for } t/\tau > 0.25), \quad (2)$$

where Δa_t is the difference between the size (radius) at time t and that at the saturation swelling, and Δa_0 is the total change in radius throughout the entire swelling process. The characteristic

swelling time τ could be obtained from the slope of the $\ln(\Delta a_t/\Delta a_0) - \text{time}$ plot. Table VII shows the diffusion coefficients of the copolymer beads in toluene : isooctane solvents. The poly(2-ethylhexyl acrylate)/polystyrene has the highest diffusion coefficient, because of the long chain length of the aliphatic portion. It is noted that the chemical nature of the long chain aliphatic portion resembles that of isooctane in mixed solvents. The diffusion coefficient of polystyrene/poly(methyl methacrylate) beads is higher than that of poly(methyl acrylate)/polystyrene beads. The solvent absorption of the acrylate and methacrylate polymers depends on the substituent group at the alpha-carbon atom, in which a small substituent group provides higher flexibility to the chains to ease the polymer chains to absorb solvents. From Table IV, we see that when the PMA seeds, PMA/PS core/shell beads, P(2-EHA) seeds, P(2-EHA)/PS beads (all from seeded suspension copolymerization), and PS/PMMA core/shell beads were each swollen in toluene, one could observe the following swelling ratios of 4.0, 2.5, 5.9, 2.9, and 5.6, respectively. The diffusion coefficient of the solvent in the beads also indicated that PS/PMMA had higher values for the first, second, and third absorption cycles than the PMA/PS

Table VII Diffusion Coefficient of the Core/shell Beads in Toluene : Isooctane Solvents

Beads	Diffusion Coefficient		
	First Absorption $\text{mm}^2 \text{min}^{-1}$	Second Absorption $\text{mm}^2 \text{min}^{-1}$	Third Absorption $\text{mm}^2 \text{min}^{-1}$
PS/PMMA	0.1737	0.1434	0.1242
PMA/PS	0.0777	0.0755	0.0711
P(2-EHA)/PS	0.7614	Bead distortion	Bead distortion

Table VIII Swelling Ratio of the Polymer Beads in Various Solvents

Solvent	Solubility Parameter (MPa) ^{1/2}				Type of Polymer Beads		
	δ_d	δ_p	δ_h	δ_T	PS/PMMA	Seeded PMA	Seeded P(2-EHA)
<i>i</i> -octane	14.3	0	0	14.3	1.5	1.4	1.5
Hexane	14.9	0	0	14.9	1.5	1.4	1.5
Heptane	15.3	0	0	15.3	1.7	1.4	1.6
Cyclohexane	16.8	0	0.2	16.8	1.7	1.4	2.1
Xylenes	17.8	1.0	3.1	18.0	5.3	2.0	2.7
Toluene	18.0	1.4	2.0	18.2	5.9	2.5	2.9
Benzene	18.4	0	2.0	18.6	6.6	2.5	3.0
Chloroform	17.8	3.1	5.7	19.0	6.5	7.6	5.2
Methylene dichloride	18.2	6.3	6.1	20.3	5.7	6.2	4.0
1,2-Dichloroethylene	19.0	7.4	4.1	20.9	5.5	6.1	3.6

beads. Unfortunately, the P(2-EHA)/PS beads could be used only for one-time absorption, because the core/shell structure collapsed with separation between the core and the shell.

Swelling Ratio of Polymer Imbiber Beads

Several organic solvents of varied solubility parameters were selected to determine the approximated solubility parameter of the polymer beads and their application as solvent absorption beads.

The polystyrene/poly(methyl methacrylate) prepared by the one-stage suspension polymerization and both the poly(methyl acrylate)/polystyrene and the poly(2-ethylhexyl acrylate)/polystyrene prepared by seeded suspension polymerization show some capacity of solvent absorption as shown in Table VIII. Three kinds of solvents were used in this study. The first kind comprises aliphatic hydrocarbons, namely isooctane, hexane, heptane, and cyclohexane; the second is aromatic hydrocarbons, namely xylenes, toluene, and benzene; the third is halogenated hydrocarbons, namely chloroform, methylene chloride, and ethylene chloride.

The results in Table VIII show that the highest swelling ratio for the core/shell beads of polystyrene/poly(methyl methacrylate) prepared by the one-stage suspension polymerization is 6.6 times in benzene and 6.5 times in chloroform. Additionally, the highest swelling ratios of the seeded core/shell beads of poly(methyl acrylate)/polystyrene, and poly(2-ethylhexyl acrylate)/polystyrene prepared by seeded suspension polymerization, are 7.6 and 5.2 times in chloroform, respectively. It can be stated that all core/shell beads gave an

increasing swelling ratio with increasing solubility parameters of the solvents. All the beads absorbed more aromatic solvents than aliphatic solvents. The core/shell beads of polystyrene/poly(methyl methacrylate) polymer prepared by one-stage suspension polymerization had a higher swelling ratio than those of poly(methyl acrylate)/polystyrene and poly(2-ethylhexyl acrylate)/polystyrene, both prepared by seeded suspension polymerization. Based on the highest swelling ratio, it can, hence, be concluded that the solubility parameter of the polymer beads is very close to the solubility of the aromatic hydrocarbon solvents ($\delta_T = 19.0 \text{ MPa}^{1/2}$). It is possible to estimate the solubility parameter of these three beads as of about $19.0 \text{ MPa}^{1/2}$ as shown in Figure 9, which is the highest swelling ratio of all core/shell beads.

As mentioned earlier, Okubo et al. discussed the SARM effect on the unique morphology of PMMA/PS composite particles by toluene, and we also found a similar morphology in the P(2-EHA)/PS imbiber beads. The imbiber beads of PS/PMMA and PS/PMMA could withstand toluene absorption and desorption for more than three cycles without a loss of their spherical shape (indicating relatively constant diffusion coefficients). At this stage, we can only postulate that our imbiber beads might have the same SARM morphology. More work is underway.

CONCLUSIONS

Synthesis of solvent absorption–desorption core/shell beads by suspension polymerization was

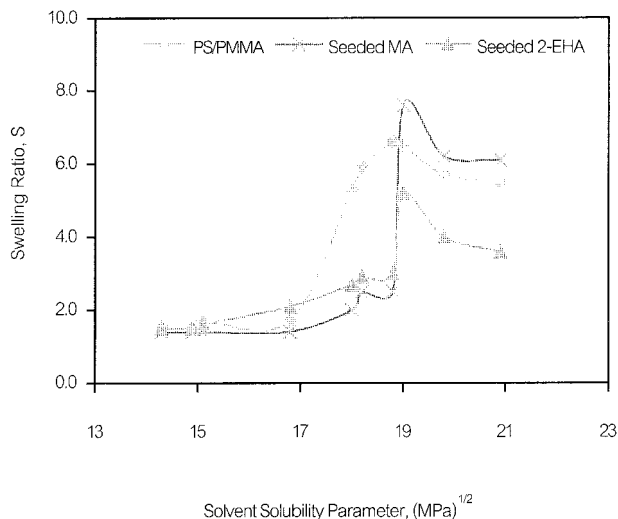


Figure 9 Swelling ratios of the polymer beads in organic solvents.

carried out. In the one-stage suspension copolymerization, the polymer beads had a heterogeneous structure without a specific morphology, whereas the polymer beads from the seeded suspension polymerization had a heterogeneous structure with a distinct shell separated from the core of the corresponding polymers. In the one-stage suspension copolymerization, hydrophilicity/hydrophobicity of the comonomers controls the core/shell morphology of the bead. The more hydrophilic polymer threads (PMMA) are distributed preferentially in the shell, while the more hydrophobic ones (PS) reside in the core. For the seeded suspension polymerization, a swelling step of the seed beads was carried out, and the subsequent polymerization produced several unique core/shell morphologies. For a hard polymer core (high T_g) such as PMA in the PMA/PS bead, an internal layer, subsurface and outer shell morphology was observed because of monomer diffusion into the seed polymer. For a soft polymer core (lower T_g), the outer shell comprising a multilayer or onion-like structure of the harder polymer is imbedded in the matrix of the soft polymer material, like in the case of P(2-EHA)/PS. Penetration of the monomer solution in the seed-swelling step induced the solvent absorption and releasing effect according to Okubo's

observation. Polystyrene/poly(methyl methacrylate), poly(methyl acrylate)/polystyrene, and poly(2-ethylhexyl acrylate)/polystyrene were able to absorb aromatic hydrocarbon solvents better than aliphatic hydrocarbon solvents, because the solubility parameters of aromatic solvents and the polymer beads are very similar. The estimated solubility parameter values of polystyrene/poly(methyl methacrylate), poly(methyl acrylate)/polystyrene, and poly(2-ethylhexyl acrylate)/polystyrene are 18.8, 19.0, and 19.0 $\text{MPa}^{1/2}$, respectively. The diffusion coefficients of polystyrene/poly(methyl methacrylate), poly(methyl acrylate)/polystyrene, and poly(2-ethylhexyl acrylate)/polystyrene were in the ranges of 0.1242–0.1743 $\text{mm}^2 \text{min}^{-1}$, 0.0711–0.0777 $\text{mm}^2 \text{min}^{-1}$, and 0.7614 $\text{mm}^2 \text{min}^{-1}$, respectively.

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