

Effect of the Third Acrylated Vinyl Comonomer on Absorption and Desorption Properties of Styrene–Divinylbenzene–Alkyl Acrylate Terpolymers, Imbibing Solvent on a Water Surface

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ABSTRACT: A series of imbibitor terpolymer beads was prepared by radical suspension copolymerization of styrene–divinylbenzene with varied contents of acrylated vinyl monomers, *n*-butyl acrylate and 2-ethyl hexyl acrylate, as the third comonomer. A DVB content of 6 wt % and a mixture of 60/40 wt % toluene/*n*-heptane as the diluent were used throughout this study. The influence of acrylated vinyl comonomers on bead properties and swelling properties was investigated. The imbibitor beads are capable of absorption and desorption of organic solvents having solubility parameters in the range of 14.9–20.9 (MPa)^{1/2}. Styrenic imbibitor beads were swelled in a toluene/*n*-heptane mixture of 50% by volume and the kinetics of absorption was studied. The imbibitor beads could absorb the toluene/*n*-heptane mixture completely within 20 min and yielded a maximum swelling ratio of 6.8. The diffusion coefficient values of these beads were in the range of 6.40×10^{-6} to 1.52×10^{-5} cm² s⁻¹. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 504–516, 2001

Key words: styrene–divinylbenzene; styrene–divinylbenzene–*n*-butyl acrylate; styrene–divinylbenzene–2-ethyl hexyl acrylate; absorption–desorption; solubility parameters; spilled organic solvents

INTRODUCTION

The growing interest in styrene–divinylbenzene (Sty/DVB) copolymer beads in recent years is due

to their great number of applications.^{1,2} These copolymer beads prepared by suspension copolymerization in the presence of an inert diluent have been utilized in a wide variety of industrial purposes, mainly in chromatography, as ion exchangers, as absorbents in chemical, medical, and agricultural applications, and as resins for the removal of organic solvents.^{3,4} Their efficiency in these applications depends mainly on their structure and swelling properties. It has been established that the properties of these copolymers ob-

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tained by suspension polymerization are greatly influenced by the polymerization conditions: monomers, diluent nature, crosslinking degree, reaction temperature, and polymerization time.

The heterogeneous porous structure, developed as a result of phase separation, can be controlled using a diluent mixture as the pore-forming agent as well as by the degree of crosslinking. When Sty and DVB are copolymerized by a suspension process in the presence of a good solvent (good diluent) for the polymer chains, two kinds of bead structures can be obtained: gel or macroporous beads. At low DVB content, the final structure is an expanded gel. When the DVB content and dilution degree are high, a macroporous copolymer is obtained. On the other hand, when the diluent is a poor solvent for the polymer chains (bad diluent), phase separation during the polymerization process takes place and it is responsible for the formation of a macroporous structure. When mixtures of good and bad diluents are used, the copolymers present a porous structure with intermediary characteristics in relation to the copolymers prepared with the pure diluent.^{5,6}

The macroporous terpolymers made with the methyl methacrylate comonomer as the third monomer were prepared using a mixture of *n*-heptane/2-ethyl-1-hexanol as the diluent.⁷ The relationship between the pore structure and swelling properties of the obtained terpolymers and the contents of the crosslinking agent, diluent, and the third monomer were studied by Iayadene and coworkers.⁸ The objectives of this present work were to study the effects of acrylated vinyl monomers of *n*-butyl acrylate or 2-ethyl hexyl acrylate as the third comonomer on bead properties and to study the absorption and desorption properties of these beads.

EXPERIMENTAL

Materials

Sty (commercial grade, Shell Chemicals, Yokkai-chi City, Mie, Japan), *n*-butyl acrylate (*n*-BA; commercial grade, Union Carbide, Shibuya City, Tokyo, Japan), 2-ethyl hexyl acrylate (2-EHA; commercial grade, Union Carbide, Shibuya City, Tokyo, Japan), and DVB (67% DVB isomers and 33% ethyl vinylbenzene measured by GC, technical grade, Merck, Hohenbrunn, Germany) were each extracted with a 10% aqueous sodium hydroxide solution and water, dried over anhydrous

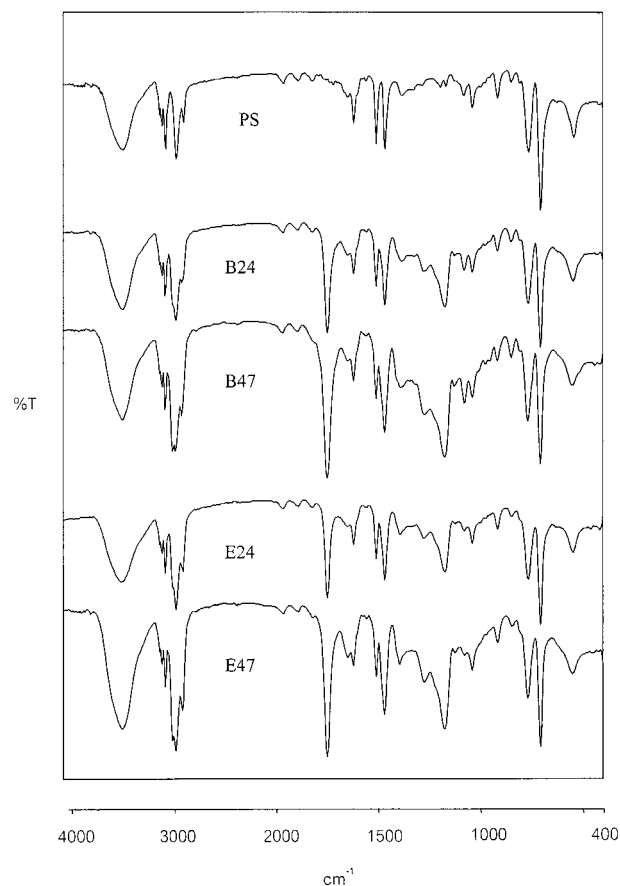


Figure 1 FTIR spectra of synthetic imbibor beads of runs PS, B24, B47, E24, and E47 in a KBr pellet.

sodium sulfate, and passed through an activated aluminum oxide column to remove the inhibitors. They were stored in a refrigerator prior to use. The diluents, toluene, and *n*-heptane (analytical grade, J.T. Baker, Phillipsburg, NJ), and other solvents were used as received.

Polymerization

Sty-DVB copolymers were prepared in aqueous suspension polymerization. The initiator, benzoyl peroxide (BPO, 97% purity moistened with 25% of water, Merck, Hohenbrunn, Germany) of 0.5 wt % in relation to the monomers, was dissolved in the selected monomers and diluent mixture. Poly(vinyl alcohol) (PVA) from Fluka (Buchs, Switzerland) of 0.1 wt % was used as a suspending agent. The monomer phase weight fraction for all reactions was 0.1.

The suspension copolymerization process was then run in a 1-L four-necked reaction flask fitted with a variable mechanical stirrer, thermometer,

Table I Effect of the Third Comonomer on Bead Properties

Parameter	Type of Copolymer				
	PS	B24	B47	E24	E47
Sty/DVB/3 rd comonomer (wt %)	94/6/0	70/6/24	47/6/47	70/6/24	47/6/47
% Yield	49	50	49	48	51
Bead-size distribution (wt %)					
< 0.42 mm	3.33	1.97	5.64	1.06	5.17
0.49–0.59 mm	10.91	10.33	11.60	8.90	11.43
0.59–0.84 mm	11.87	16.72	13.33	17.94	12.56
0.84–2.0 mm	68.23	64.87	60.78	67.75	62.81
> 2.0 mm	5.66	6.11	8.65	4.35	8.03
Density (g cm ⁻³)	1.0266	1.0245	1.0232	1.0199	1.0179

PS, polystyrene; B, *n*-butyl acrylate; E, 2-ethyl hexyl acrylate.

nitrogen gas inlet, and reflux condenser. The solution containing the monomers, the diluents [toluene (Tol) and heptane (Hep)] and the initiator was poured into the reactor, which contained the aqueous solution of the suspending agent. The copolymerization process was performed at 70°C for 10 h while stirring in a thermostatically con-

trolled oil bath. After the reaction was completed, the resulting copolymer beads were washed with hot water and extracted with acetone in a Soxhlet apparatus for 10 h to remove the diluents and the residual monomers. Finally, they were dried under a vacuum at 60°C for 24 h. Opaque spherical beads of 0.84–2.0 mm in diameter were obtained.

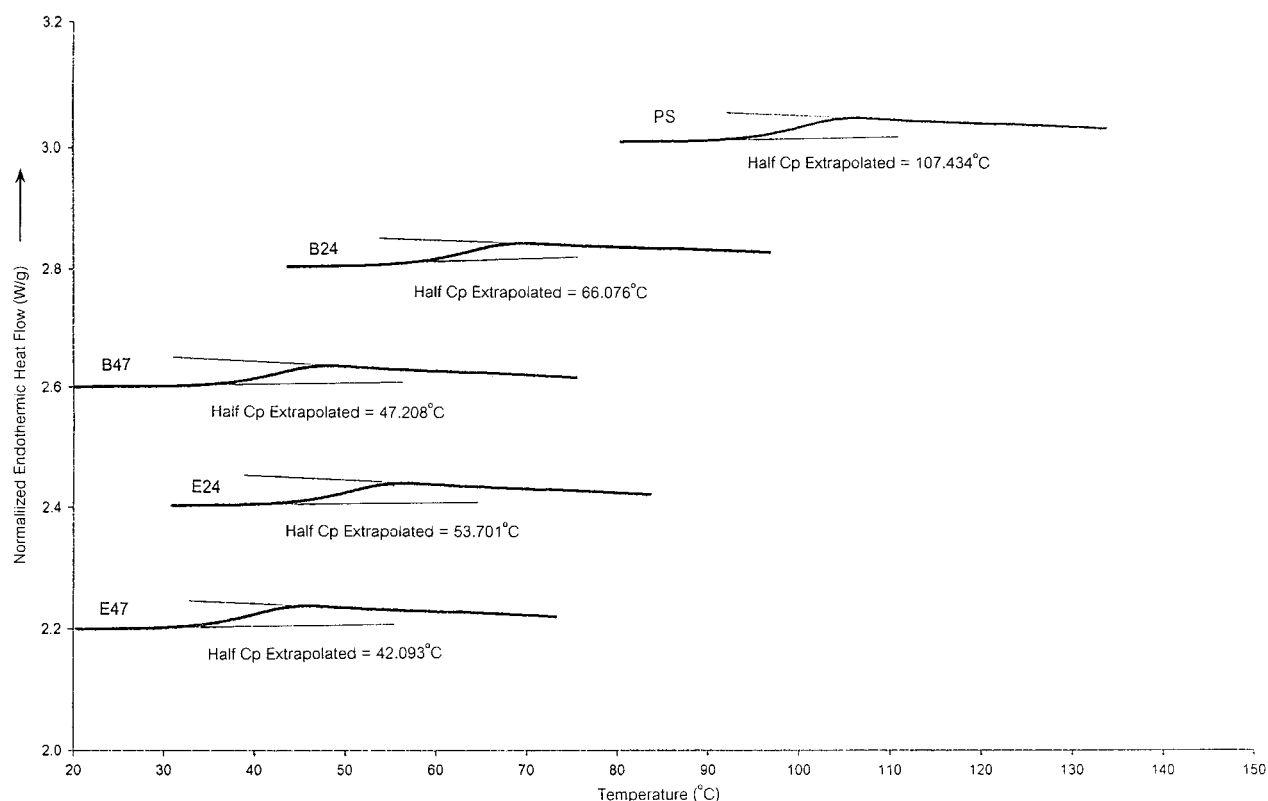


Figure 2 DSC traces of Sty-DVB copolymers prepared from various acrylated vinyl comonomers.

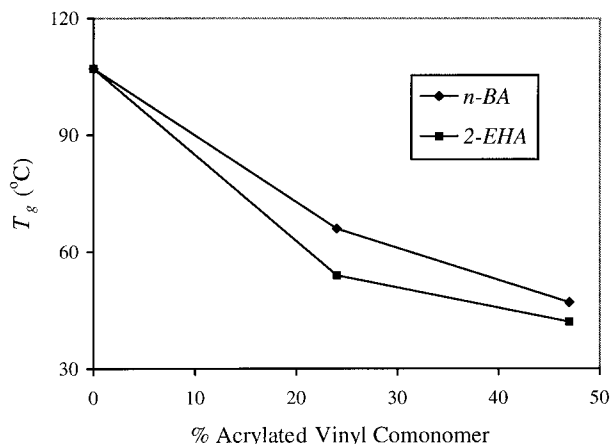


Figure 3 Effect of the acrylated vinyl comonomer concentration on the glass transition temperature of the terpolymer beads.

Characterization

The dry copolymer beads were coated with a thin layer of gold under a vacuum and examined using a scanning electron microscope (JEOL JSM-6400, Sundbyberg, Sweden) to characterize the surface morphology of the copolymer beads. The copolymer bead density was determined using the liquid-displacement technique following the ASTM D-792 test method.

The swelling measurements of imbiber copolymer beads were carried out in various solvents at room temperature. The swelling ratio, S , was determined gravimetrically by subsequent immersing the dry copolymer beads in Tol for 24 h. The swelling ratio of the beads was calculated by

$$S = 1 + \left(\frac{W_s}{W_p} - 1 \right) \frac{\rho_p}{\rho_s} \quad (1)$$

where W_p is the weight of the copolymer before swelling or the dry polymer weight; W_s , the weight of the copolymer at equilibrium; and ρ_s and ρ_p , the densities of solvent and polymer, respectively.

Differential scanning calorimetric (DSC) experiments were carried out using a Perkin-Elmer DSC-7 (Gaithersburg, MD) controlled by a 7500 PC. The copolymer beads were heated from 10 to 150°C at a heating rate of 20°C/min under a nitrogen atmosphere, annealed for 5 min at 150°C, and quenched to room temperature. The second scan was recorded at the same heating rate as the previous scan up to 150°C and the glass transition (T_g) was determined as the midpoint of the endo-

thermic displacement between two linear baselines.

The absorption and desorption properties of the imbiber beads were investigated. For the absorption of a 50/50 vol % Tol/*n*-Hep mixture, the bead was placed in a mini-Petri dish ($1.5 \times 1 \text{ cm}^2$) containing an excess amount of the Tol-Hep solution where its swollen bead diameter was measured as a function of time until the volume of the bead was constant. For desorption, the fully swollen bead was placed on a filter paper in a Petri dish with a cover to reduce solvent evaporation. The bead diameter was measured as a function of time by a stereomicroscope (Olympus SZH 10, Shinjuku-Ku, Tokyo, Japan) with a Luzex-F software program of Nireo QJ 8500.

RESULTS AND DISCUSSION

Methyl methacrylate (MMA), as a third acrylated vinyl comonomer, was previously prepared by the similar procedure as for the copolymerization of *n*-BA or 2-EHA. Although the Hep absorption of the Sty/DVB/MMA beads is increased and its absorption in Tol is decreased relative to the Sty/DVB beads, the former absorption is still low (at a maximum of two- to threefold). Therefore, it is practically not attractive to incorporate MMA as the third acrylated vinyl comonomer in this study. Only *n*-BA and 2-EHA are of current interest as third monomers in solvent imbiber beads.

To confirm the copolymerization between Sty, DVB, and *n*-BA or 2-EHA as the third comonomer, the functional groups of the synthetic terpolymer beads were investigated by FTIR. The IR spectra of Sty networks in KBr pellets were recorded on a Perkin-Elmer FTIR spectrometer 1760X (Gaithersburg, NJ). The existence of Sty/DVB/*n*-BA terpolymers (runs B24, B47) and Sty/DVB/2-EHA terpolymers (runs E24, E47) is demonstrated by comparing their spectra with the Sty-DVB copolymer (run PS) spectrum, as presented in Figure 1. From the spectra, we found that all the synthetic beads show the important peaks of *para*-, *meta*-disubstituted aromatic rings at 860–800 and 810–750 cm^{-1} , respectively, whereas these spectra of terpolymers obviously show the additional peaks of C=O stretching at 1730 cm^{-1} and C—O stretching at 1160 cm^{-1} . Furthermore, the spectral features of C=O and C—O intensified when increasing the concentration of the acrylated vinyl comonomer.

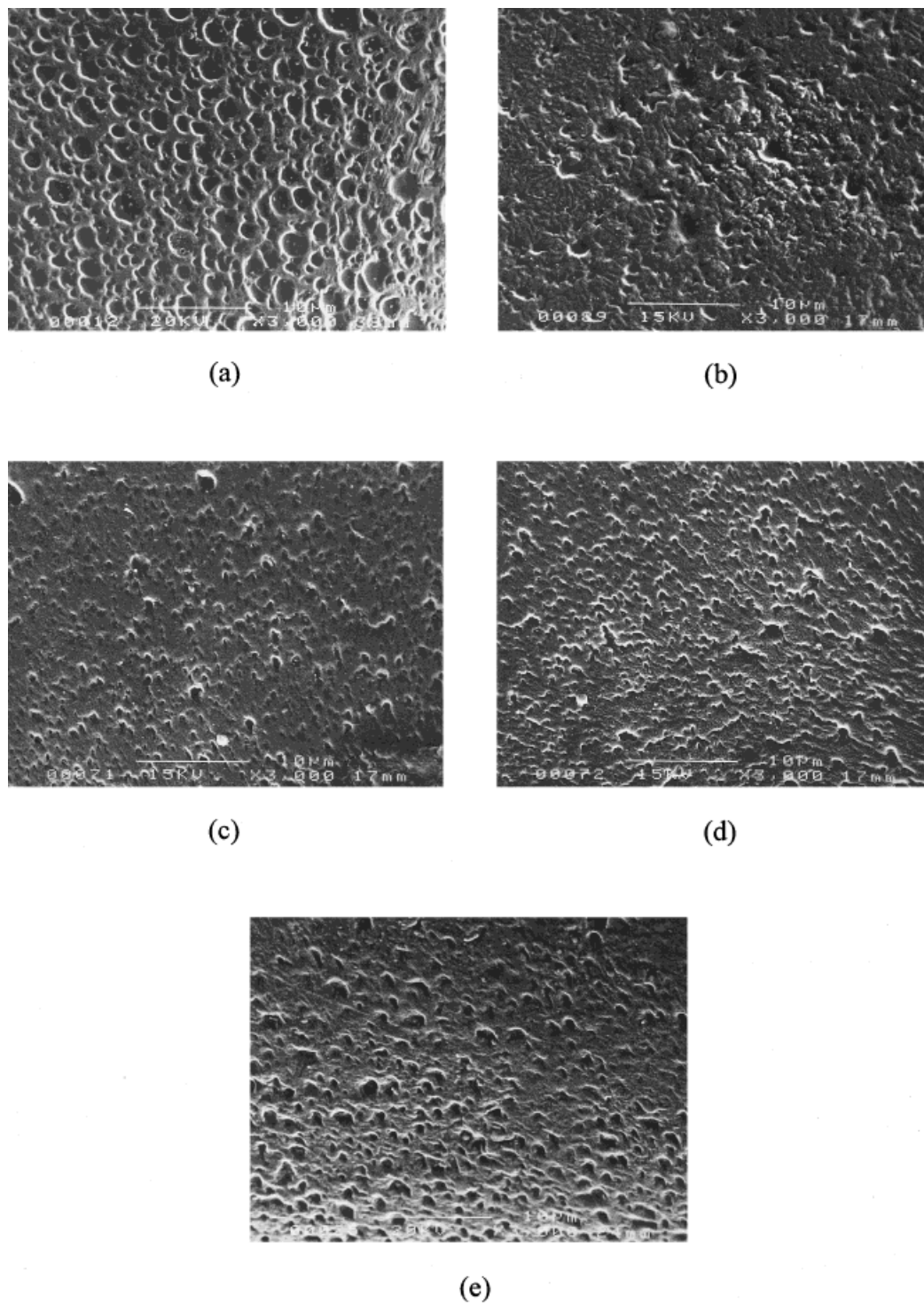


Figure 4 SEM photographs of imbibed beads: (a) PS; (b) B24; (c) B47; (d) E24; (e) E47 ($\times 3000$).

The imbibed terpolymer beads were prepared by suspension copolymerization using a 60/40 wt % Tol/*n*-Hep mixture as the diluent at various acrylated vinyl monomer concentrations. The

bead-size distribution was reported as the percentage of the weight of the beads by classification after passing various sieve sizes. Most of the bead sizes were in the range of 0.84–2.0 mm. The

Table II Swelling Ratio of the Synthetic Copolymer Beads in Various Solvents

Solvent	Solubility Parameter (MPa) ^{1/2}				Swelling Ratio of the Copolymer				
	δ_D	δ_P	δ_H	δ_T	PS	B24	B47	E24	E47
Hexane	14.9	0	0	14.9	2.0	2.2	2.4	2.7	3.2
Heptane	15.3	0	0	15.3	2.0	2.2	2.4	2.7	3.2
Cyclohexane	16.8	0	0.2	16.8	2.6	3.9	4.1	5.1	5.9
Trichloroethane	17.0	4.3	2.0	17.6	8.2	7.5	6.7	7.1	6.2
Carbon tetrachloride	17.8	0	0.6	17.8	8.3	7.7	7.4	7.2	6.8
Xylene	17.8	1.0	3.1	18.0	8.7	8.0	7.4	7.7	7.1
Toluene	18.0	1.4	2.0	18.2	9.3	8.1	7.9	8.2	7.3
Benzene	18.4	0	2.0	18.6	9.6	8.6	8.3	8.1	7.2
Chloroform	17.8	3.1	5.7	19.0	9.7	8.5	7.9	7.9	7.1
Chlorobenzene	19.0	4.3	2.0	19.6	9.6	8.3	7.8	7.7	6.7
Methylene chloride	18.2	6.3	6.1	20.3	8.6	8.0	7.6	7.3	6.4
Ethylene chloride	19.0	7.4	4.1	20.9	7.9	7.3	6.9	6.7	6.0

bead-size distribution and density are presented in Table I.

In this study, the glass transition temperatures and incremental changes in heat capacity at T_g were measured by a calorimetric method. The DSC thermograms of the terpolymers synthesized with different Sty/*n*-BA and Sty/2-EHA feed ratios are shown in Figure 2. The T_g values were found to be in the range of 42–107°C. It can be seen that varying the feed ratio of the terpolymer has a direct impact on the glass transition of the resulting terpolymers. Figure 3 presents the relation between T_g and the *n*-BA or 2-EHA content. The T_g of the terpolymer decreased as the amount of *n*-BA or 2-EHA increased. This effect is due to the low glass transition temperature of poly(*n*-butyl acrylate) (P-*n*-BA; -54°C) and poly(2-ethyl hexyl acrylate) or (P-2-EHA; -50°C).⁹ The terpolymer rich in *n*-BA or 2-EHA possesses the lowest T_g at 47.21 or 42.09°C, respectively, whereas the Sty-DVB copolymer with 6% wt DVB (PS) has the highest T_g at 107°C.

Figure 4 shows electron micrographs for terpolymers prepared with (a) 94/6 Sty/DVB, (b) 70/6/24 Sty/DVB/*n*-BA, (c) 47/6/47 Sty/DVB/*n*-BA, (d) 70/6/24 Sty/DVB/2-EHA, and (e) 47/6/47 Sty/DVB/2-EHA in the presence of a 60/40 wt % Tol/*n*-Hep mixture as the diluent. A more porous structure [Fig. 4(b–e)] is observed on the beads having a higher acrylated vinyl monomer content, but with a less uniform pore-size distribution compared with Sty-DVB [Fig. 4(a)]. The increasing amount of the acrylated vinyl comonomer enhanced the porous structure. This can be explained by the following fact: The presence of acrylated vinyl

comonomers increased the hydrogen and dipole interactions and decreased the thermodynamic affinity between the copolymers and the diluent. As expected, a decrease in the thermodynamic affinity of the polymer and solvent promotes the formation of beads with porous surfaces. The copolymers produced by 47/6/47 Sty/DVB/*n*-BA and 47/6/47 Sty/DVB/2-EHA showed a regular distribution of the small pores.

Solubility of Copolymer Beads

The solubility parameter of a new polymer may be determined by any of several means. In this case, the polymer is crosslinked, so the solubility parameter may be determined by swelling experiments. The best solvent is defined (for the purposes of the experiment) as the one with the closest solubility parameter to that of the copolymer beads. This solvent also swells the polymer the most. Several solvents of varying solubility parameters are selected, and the crosslinked polymer is swelled to equilibrium in each solvent. The swelling ratio, S , is plotted against the solvent solubility parameter; that of the solvent that gives the maximum swelling ratio is defined as the solubility parameter of the polymer. The determination of the solubility parameter of the synthetic copolymers using the swelling experiment in various solvents is shown in Table II and Figure 5. Figure 5 indicates that the solubility parameters of the synthetic copolymers from runs PS, B24, B47, E24, and E47 are about 19.0, 18.8, 18.6, 18.3, and 18.2 (MPa)^{1/2}, respectively. According to the extent of the hydrogen bonding, the

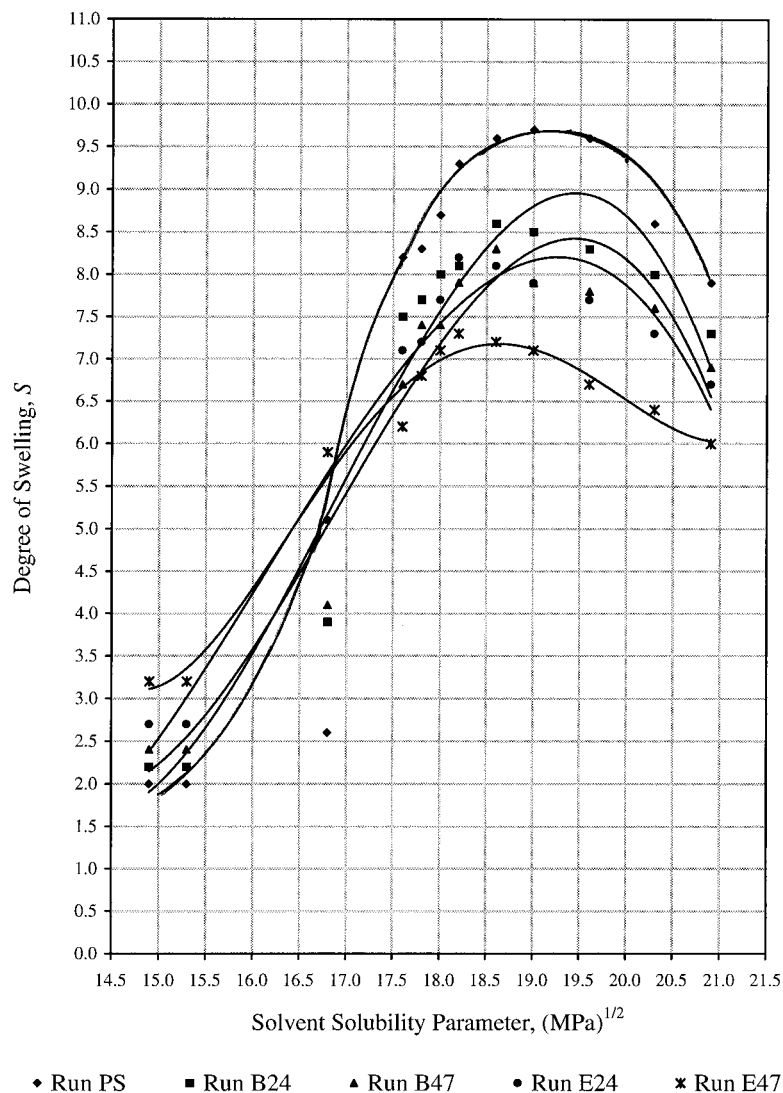


Figure 5 Comparison of solubility parameters of synthetic copolymer beads by swelling experiments.

series of solvents used in this experiment comprises poorly hydrogen-bonding solvents. The results show that the highest swelling ratio of copolymer beads (run PS) for the poorly hydrogen-bonding solvent, chloroform, is 9.7 and the lowest ratio, for hexane, is 2.0. On the other hand, when the copolymers were prepared in the presence of *n*-BA or 2-EHA in the monomer composition, the highest swelling ratios of the copolymer beads in runs B24, B47, E24, and E47 in the same of solvents are 8.6, 8.3, 8.2, and 7.3, respectively, and the lowest ratios are 2.2, 2.4, 2.7, and 3.2, respectively. These can be explained in that only the nonpolar moiety of Sty causes the highest maximum swelling of the copolymer beads (run PS) in

the poorly hydrogen-bonding solvents. By increasing the polar moiety by copolymerizing *n*-BA or 2-EHA monomers in the resulting copolymer chains (runs B24, B47, E24, and E47), the maximum swelling ratio of these copolymers in the poorly hydrogen-bonding solvents decreases.

Furthermore, the monomer structure of the copolymer was also considered. It is inevitably noted that adding the comonomer *n*-BA or 2-EHA to the Sty-DVB system increases the aliphatic portion of the copolymer chains; the swelling ratio of the terpolymers in the aromatic solvents, such as benzene, Tol, and xylene, consequently decreased. On the other hand, the swelling ratio of these terpolymers increased in the aliphatic sol-

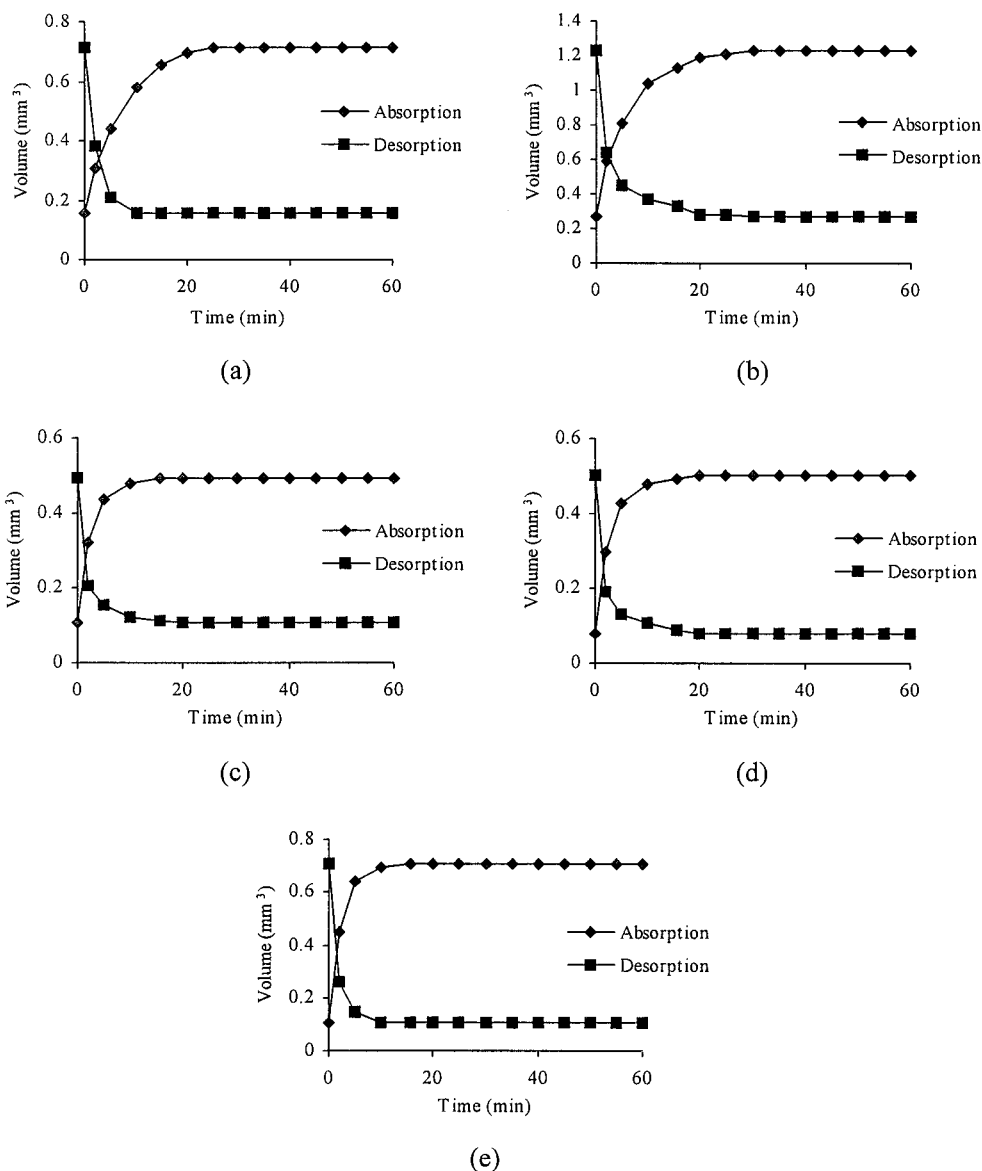


Figure 6 Variation of imbibed bead volume with time for (a) PS, (b) B24, (c) B47, (d) E24, and (e) E47.

vents, such as hexane, Hep, and cyclohexane, as shown in Figure 5. Increasing the number of carbon atoms of the acrylated vinyl monomer incorporated in the Sty-DVB copolymer beads from 4 (*n*-BA) to 6 (2-EHA) enhances the absorption of the aliphatic hydrocarbon solvents of hexane, Hep, and cyclohexane. This result could be explained by the solubility parameter.

Solvent Absorption and Desorption of the Copolymer Beads

One traditional application of imbibed beads is the removal of solvents or oil spills with similar

solubility parameters. The absorption and desorption phenomena are thus quite important. The absorption of the imbibed beads in a 50/50 vol % Tol/*n*-Hep mixture was investigated by an optical microscope, based on the increase in the bead size upon swelling in the solvent mixture. Tol and *n*-Hep are of interest as representatives of aromatic and aliphatic solvents, respectively. Figure 6 shows an increase in bead volume with swelling time. Ingression of the solvent mixture into a dry bead was readily visible, but the polymer continued to swell well after a uniformly transparent appearance had been reached.¹⁰ The curves comprise three stages: (i) a short initial

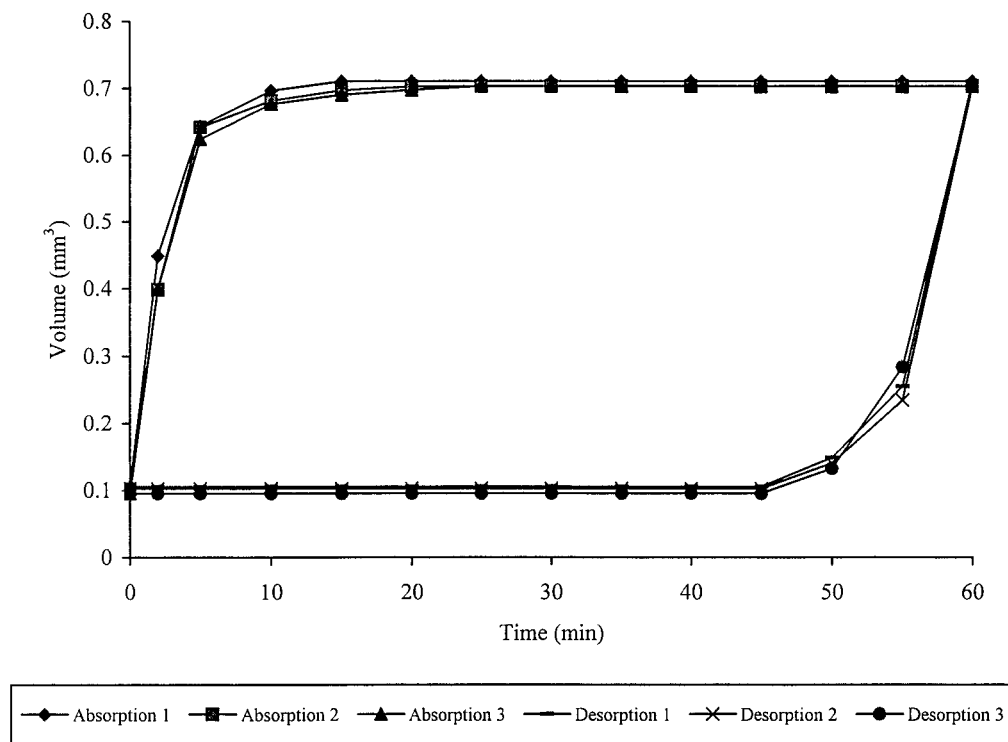


Figure 7 Cyclic absorption and desorption of a 50 vol % Tol/*n*-Hep mixture by E47 imbibed beads.

stage of a high absorption rate due to the solvation of network chains; the main driving force of this process is the change in the free energies of mixing and elastic deformation during the expansion of the network, (ii) a longer stage of a constant, slow absorption rate due to the resistance of diffusion into the pore on account of the pore structure and dimensions, and (iii) a third stage of a plateau value because of absorption saturation. From the curves, the initial stage of absorption lasted about 10 min, and the bead volume increased rapidly since the network began to expand by absorbing the surrounding solvent and equilibrium was reached within 60 min.

Figure 6 also shows the variation of the swollen bead volume with the desorption time. The curve can be similarly divided into three stages: (i) a short initial stage of a high desorption rate, (ii) a longer stage of a slow desorption rate, and (iii) a third stage of no solvent loss (plateau) or a very low, undetectable desorption rate. The solvent-swollen bead volume lost its solvent rapidly and reached its original volume in 40 min. All these beads retained their initial size stability during and after the desorption process.

The imbibed copolymer beads could be used to absorb and desorb the solvents repeatedly for

many cycles. The repeated absorption and desorption behaviors of the second and third cycles were also of the same magnitude as in the first cycle, as shown in Figure 7. The very slight difference in volume between the first-cycle absorption and the second-cycle absorption may be attributed to (1) the network of the beads slightly changing and (2) some homopolymer molecules dissolving. During absorption and desorption, the imbibed copolymer beads still retained their spherical shape throughout several cycles; they did not collapse after repeated uses. The copolymer beads could be applied to absorb and desorb waste organic solvents and petroleum for many cycles. This is similar to the hysteresis-like behavior of swelling and deswelling of the Sty-DVB copolymer in Tol as reported by Kiatkamjornwong and coworkers.¹¹ It was also found that the sorption capacity of the crosslinked polymer with respect to the solvent depends on its swelling history. From Figure 7, the sorption capacity (or swelling ratio) of second and third cycles was slightly lower than that of the first cycle. Therefore, the absorption capacity was due to the memory of the polymeric macrostructure or the change in the looseness of the polymeric macrostructure.

Absorption Kinetics

The swelling of the imbibed beads is determined by the solvent properties of the polymer and the degree of crosslinking. A good solvent and lightly crosslinked polymer will give a high degree of swelling; a poor solvent and highly crosslinked polymer will cause a small degree of swelling. The kinetics of liquid absorption was determined by a direct measurement of the diameter of a single bead as a function of time while it was immersed in the solvent. The absorption kinetics of the bead can be written in analogy with first-order kinetics. For $t/\tau > 0.25$, the following equation was obtained¹²:

$$\ln\left(\frac{\Delta a_t}{\Delta a_0}\right) = K - \frac{t}{\tau} \quad (2)$$

where Δa_t is the difference between the radius at time t and that at a saturated swelling, and Δa_0 , the total change in radius throughout the swelling process. The characteristic swelling time τ was defined by

$$\tau = \frac{a^2}{D} \quad (3)$$

where D is the diffusion coefficient of the bead in the liquid and a is the final radius of the fully swollen gel. The characteristic swelling time provides a useful tool for measuring the absorption of imbibed beads.

For comparison of the swelling or absorption behavior of imbibed beads of different compositions, it is difficult to select polymer beads of identical size for the swelling measurements. The characteristic swelling time was determined from the reciprocal of the slope in $\ln(\Delta a_t/\Delta a_0)$ versus t plots that are shown in Figure 8. Table III gives the values of the characteristic swelling time and diffusion coefficient determined in these experiments. The characteristic swelling time and diffusion coefficient of the beads in a 50/50 vol% Tol/*n*-Hep mixture were in the ranges of 3.3–8.0 min and 6.40×10^{-6} to 1.52×10^{-5} cm² s⁻¹, respectively.

Table III shows that the diffusion coefficient of the copolymer beads in a 50/50 vol % Tol/*n*-Hep mixture increased when the third comonomer was changed. The chemical structures of the copolymers with an acrylated vinyl comonomer, either *n*-BA or 2-EHA, contain both aliphatic and

aromatic portions. Therefore, the absorption of a 50/50 vol % Tol/*n*-Hep mixture of these copolymers with an acrylated vinyl comonomer becomes greater than that of the Sty-DVB copolymer, which contains mainly the aromatic portion. It is noted that the diffusion coefficient of the copolymer increased with an increasing chain length of the aliphatic portion. This may be a result of the chemical nature of the long-chain aliphatic portion resembling that of the Hep portion in the mixed solvent, according to the rule of thumb in chemistry "like dissolves like."

The absorption of the copolymers can be considered a result of solvation of the network chains. The extent of network solvation is related to the interaction between solvent molecules and network chains, or the polymer-solvent interaction, which is presented in terms of the solubility parameter, as shown in Table IV. When the difference of these parameters for the polymer and solvent is smaller, the solvation is more favored, which causes an increase in the rate of solvation of the copolymers. As a result, it also leads to an increase in the diffusion coefficient of the terpolymers as shown in Table III.

Absorption of a Mixed Solvent Layer on the Water Surface of Copolymer Beads

Since the copolymer or terpolymer beads can absorb and desorb several organic solvents, they are expected to perform the same absorption/desorption behavior when they are imbibed in a water surface contaminated with organic solvents or spilled oil. As such, the beads were tested for their ability in absorption of spilled organic solvents or spilled oil on a water surface. The terpolymer beads (run E47) were used for absorbing a series of mixed solvents between aromatic and aliphatic or naphthenic portions, Tol/Hep and Tol/cyclohexane at 25/75, 50/50, and 75/25 ratios, floating on the surface of the water. From Table V, when the mixed solvent floats on the water surface because of its lower density, the swelling ratio of the terpolymer beads is slightly larger than that for the mixed solvents without water. Two reasons are given for the swelling behavior: The mixed solvent could form an emulsified mixture with water (emulsification) and it is possible that the emulsified water is partly absorbed because of the presence of a relatively polar ester functionality (acrylate end group), which could penetrate to the interchain vacancies of the expanded terpolymer network during absorption.¹³

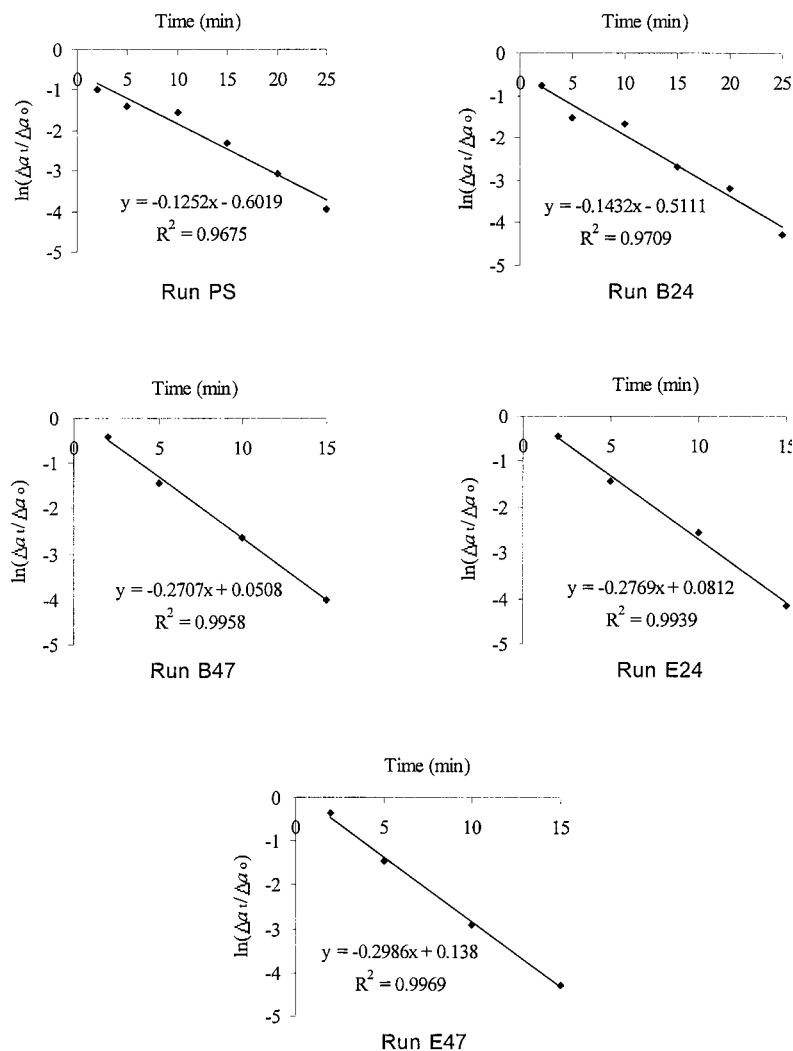


Figure 8 Variation of $\ln(\Delta a_t / \Delta a_0)$ with swelling time.

Furthermore, the swelling of the terpolymer beads (run E47) in pure solvents and mixed solvents is also shown in Table V. The result shows that the swelling ratio of the terpolymer beads (run E47) in pure Tol was higher than those in the mixed solvents containing Tol-to-Hep ratios and Tol-to-cyclohexane ratios of 25/75, 50/50, and 75/

25. Based on the concept of the solubility parameter, pure Tol is a good solvent for the copolymer beads; when a poor solvent (Hep or cyclohexane) was added into the good solvent (Tol), the solubility parameter of the mixed solvent decreased. This effect leads to a decrease in the swelling ratio.

Table III Absorption Kinetics of Imbiber Beads

Parameter	PS	B24	B47	E24	E47
Initial bead radius, a_0 (mm)	0.336	0.400	0.293	0.268	0.293
Bead radius at saturation, a (mm)	0.554	0.664	0.489	0.493	0.553
a/a_0	1.65	1.66	1.67	1.84	1.89
τ (min)	8.0	7.0	3.7	3.6	3.3
D ($\text{cm}^2 \text{s}^{-1}$) $\times 10^5$	0.64	1.05	1.08	1.12	1.52

Table IV Interaction of the Solvent-Synthetic Copolymers

Runs	Solubility Parameter ^a (MPa) ^{1/2}	$ \delta_1 - \delta_2 ^b$
PS	19.0	2.2
B24	18.8	2.0
B47	18.6	1.8
E24	18.3	1.5
E47	18.2	1.4

^a From swelling experiment (see Fig. 5).

^b δ_1 and δ_2 are the solubility parameters of the solvent and copolymer, respectively. The 50/50 vol % of toluene/heptane mixed solvent is 16.8 (MPa)^{1/2}.

CONCLUSIONS

A series of imbiber terpolymer beads was prepared by suspension copolymerization of Sty-DVB and two acrylated vinyl monomers, *n*-BA and 2-EHA, as the third comonomer in the presence of a Tol/*n*-Hep mixture as the diluent. The thermal properties, surface appearance, and swelling efficiency of imbiber beads varied with the third comonomer species. An increase in the acrylated vinyl monomer content led to a decrease in the glass transition temperature of the terpolymer due to the low glass transition temperature of these acrylated vinyl polymers, *n*-BA and 2-EHA, with elastomeric characteristics. The surface appearance of terpolymer beads shows that the porous structure increases with increasing acrylated vinyl comonomer content. This has been related to the polarity of the third comonomers, the presence of acrylated vinyl groups in the poly-

mer chains increasing the hydrogen and dipole interactions, and their decreasing thermodynamic affinity between the copolymers and the diluent. This behavior promoted the formation of beads with porous surfaces. This swelling efficiency, swelling time, and diffusion coefficient of the beads depended on their chemical structure and solubility. The imbiber beads can absorb organic solvents having solubility parameters of 14.9–20.9 (MPa)^{1/2} and can be also used to absorb many mixed solvents or petroleum on a water surface. As for the absorption and desorption kinetics of the imbiber terpolymer beads in a 50/50 vol% Tol/*n*-Hep mixture, the diffusion coefficients of copolymers prepared with various amounts of the third comonomer, *n*-BA or 2-EHA, were in the range of 6.40×10^{-6} to 1.52×10^{-5} cm² s⁻¹. Furthermore, the imbiber beads could be used to absorb and desorb a Tol/Hep mixture for many cycles (up to at least three cycles) while still retaining their spherical shape. Increasing the number of carbon atoms of the acrylated vinyl monomer incorporated in the Sty/DVB copolymer beads from 4 (*n*-BA) to 6 (2-EHA) enhances the absorption of the aliphatic hydrocarbon solvents of hexane, Hep, and cyclohexane. This is an advantage of the inclusion of the third acrylated vinyl comonomer to the Sty/DVB copolymer.

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Table V Swelling Ratio of Imbiber Beads (E47) in Solvent Mixtures in Water

Solvent Composition	Solubility Parameter ^a	Swelling Ratio	
		Without Water	With Water
Toluene	18.2	8.2	9.1
Heptane	15.3	2.7	3.2
Cyclohexane	16.8	5.1	5.8
Toluene : heptane 0.25 : 0.75	16.0	6.8	7.3
Toluene : heptane 0.5 : 0.5	16.8	7.2	7.8
Toluene : heptane 0.75 : 0.25	17.5	7.4	8.5
Toluene : cyclohexane 0.25 : 0.75	17.2	7.5	8.0
Toluene : cyclohexane 0.5 : 0.5	17.5	7.6	8.4
Toluene : cyclohexane 0.75 : 0.25	17.9	7.8	8.8

^a The solubility parameter of a mixed solvent was calculated from $\delta_t = V_1\delta_1 + V_2\delta_2$, where V_1 and V_2 are the volume fractions of solvents 1 and 2, respectively, and δ_1 and δ_2 are the solubility parameters of solvents 1 and 2, respectively.

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