Host–Guest Phenomena in Polystyrene Networks

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ABSTRACT: A correlation between the extent of crosslinking and the amount of organic substrates encapsulated within organized macromolecular assemblies was established. The encapsulation of benzoic acid in the cavities of styrene-based copolymers and their controlled release in the presence of different solvents were studied. Polystyrene networks with encapsulated benzoic acid were prepared with divinyl benzene (DVB) and hexane diol dimethacrylate (HDDMA) as the crosslinking agents. The amount of benzoic acid released followed the order of 5% > 10% > 20% > 15% in chloroform and toluene for both DVB- and HDDMA-crosslinked polystyrene. However, in methanol and water, the release was in the order of 5% > 10% > 15% > 20% for both systems. As the percentage of the crosslinking agent was increased, the pore size decreased (mesopores), and hence the amount of benzoic acid encapsulated also decreased up to 15%. Beyond 15%, the number, rigidity, and stability of the micropores increased, and more benzoic acid was encapsulated with 20% than 15%. The quantitative interpretation of the experimental results was made in terms of a Flory–Rehner analysis of the swelling measurements of the free polymer and the host–guest system. The theoretical results were in excellent agreement with the experimental results of release studies. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 3602–3611, 2007

Key words: host-guest systems; polystyrene; swelling

INTRODUCTION

The design of self-assembling structures that contain a cavity capable of encapsulating one or more guest molecules has attracted great attention recently because of their novelty and potential applications, including use as drug delivery devices and miniature reaction chambers.[1,2] The design of complex synthetic nanoscale materials is receiving a great deal of attention, and the production of unique structures with desirable functional features is rapidly advancing because of an approach that loosely models the basic construction tools found in nature.[3–5] This approach involves the use of hydrophobic interactions and other relatively weak forces to organize nanoscale structures followed by domain-specific covalent crosslinking to stabilize the preorganized assembly.

In styrene-based copolymers, inner spaces or cavities of definite sizes are produced during the polymerization process, depending on the nature of the crosslinking agent.[6–8] For divinyl benzene (DVB) crosslinked polystyrene (PS), these cavities have a hydrophobic environment, and for hexane diol dimethacrylate (HDDMA) crosslinked PS, they have a hydrophilic environment. Molecules can be trapped in these pockets without recourse to chemical bonding. The method can be used for the functionalization of a polymer if the size and geometry of the functionalized guest molecules are acceptable to the geometry of the cavities.

The establishment of a correlation between the extent of crosslinking and the amount of the organic substrates encapsulated within the organized macromolecular assemblies was carried out. The encapsulation of benzoic acid in the cavities of styrene-based copolymers and their controlled release in the presence of different solvents were studied. These systems are completely immobilized in the cavities. Moreover, the systems can be suggested as alternatives to chemically functionalized polymers. The functionalization of the polymeric backbone is usually carried out through a series of polymer-analogous reactions, which is a laborious and time-consuming process. The loading of the required functional group might be seriously affected by this prolonged treatment even though the initial loading capacity of the resin is high. The problems can be overcome if the required low-molecular-weight species can be introduced directly into the polymer matrix during the process of poly-
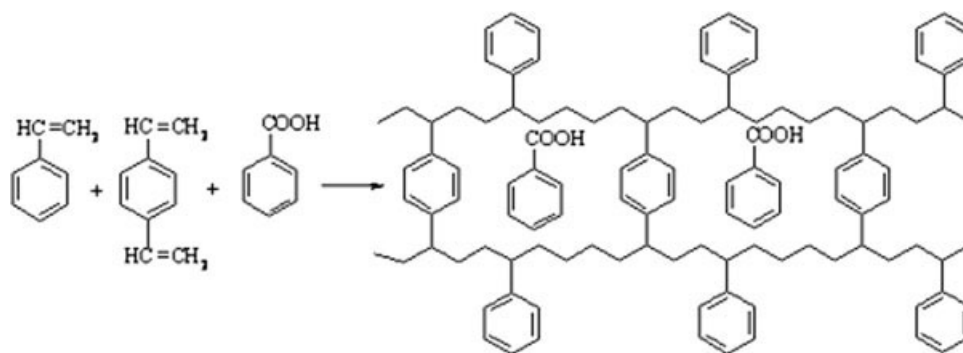
Scheme 1 Synthesis of a benzoic acid encapsulated PS–DVB resin.

merization as a guest molecule. The encapsulation of low-molecular-weight organic molecules in the cavities of three-dimensional polymeric networks without any chemical bonding could lead to low-molecular-weight properties for these molecules. At the same time, the resulting polymer will have physical properties typical of a functionalized polymer.

EXPERIMENTAL

General

Styrene, DVB, and HDDMA were commercial products obtained from Merck (Darmstadt, Germany). The solvents and low-molecular-weight compounds were commercially available samples and were purified by literature procedures. The polymeric products were purified by Soxhlet extraction.

IR spectra were recorded on a Shimadzu IR-470 spectrophotometern (Kyoto, Japan) with KBr pellets in the range 4000–400 cm^{-1}. Scanning electron microscopy (SEM) micrographs were recorded with a Philip scanning electron microscope operated at 10 kV. Thermogravimetric analysis were carried out on a Mettler–Toledo DSC 822e STARe thermal analyzer (Columbus, OH).

Synthesis and characterization of DVB- and HDDMA-crosslinked PS

DVB- and HDDMA-crosslinked PS samples with various crosslink densities (5, 10, 15, and 20 mol %) were prepared by a free-radical-initiated bulk polymerization technique. DVB and styrene were washed with a 1% NaOH solution (30 mL, three times) and with water (30 mL, three times) to remove the inhibitor, and HDDMA was used as received. The monomers in the required ratio were mixed, 200 mg of benzoyl peroxide was added, and the mixture was slowly heated on a water bath at 80°C with stirring. The obtained polymer was filtered and washed with hot water and methanol. The resin was dried in a vacuum at 50°C and characterized by spectroscopic analysis.

Encapsulation of benzoic acid in DVB- and HDDMA-crosslinked PS

Benzoic acid encapsulated PS samples crosslinked with DVB and HDDMA were prepared by bulk polymerization with benzoyl peroxide as the initiator. DVB and styrene were washed with 1% NaOH and water to remove the inhibitor, and HDDMA was used as received. The monomers in the required ratio were mixed. The required amount of benzoic acid (1 : 1 molar ratio with the monomer) and 200 mg of benzoyl peroxide were added to the mixture and slowly heated on a water bath at 80°C with stirring. The precipitated polymer was filtered and washed with hot water, methanol, and acetone. The resin was dried in a vacuum oven at 50°C. Polymers with crosslink densities of 5, 10, 15, and 20 mol % were prepared by the adjustment of the monomer-crosslinker ratio. The products were characterized by spectral analysis.

Controlled release of benzoic acid from guest-encapsulated PS networks

A guest-encapsulated PS resin (200 mg) was accurately weighed and was allowed to swell in a definite amount (20 mL) of a solvent (CHCl$_3$, toluene, water, and methanol) in the presence of a sodium hydroxide solution. The temperature was lowered to 0°C to prevent the hydrolysis of the ester linkage in the polymer network. The mixture was stirred lightly by a magnetic stirrer. The amount of benzoic acid liberated at definite time intervals (5, 10, 15, 30, 45, 60, 75, and 90 min) was estimated by the titration of the unreacted NaOH against standard HCl. A blank experiment was also done, and the weight of benzoic acid released at definite time intervals was calculated.

Swelling studies

To study the swelling characteristics of the guest-encapsulated polymer and the free polymer, about 0.2 g of the polymer was accurately weighed and allowed to swell in the solvent (20 mL for 48 h). The solvent
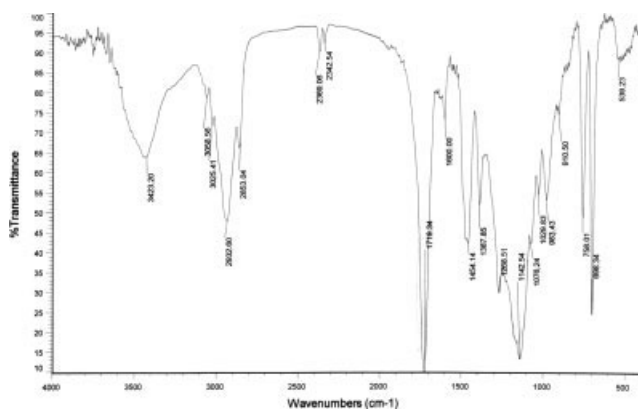
Figure 1 IR spectrum of a benzoic acid encapsulated PS–DVB copolymer.

Figure 2 IR spectrum of benzoic acid encapsulated, HDDMA-crosslinked PS.

was removed by controlled suction, and the weight of the swollen polymer was determined on an electronic balance. From the weight of the swollen polymer, the weight of the dry polymer, and the density of the solvent, the degree of swelling could be determined. The experiment was repeated with various solvents, including chloroform, toluene, cyclohexane, water, and methanol.

RESULTS AND DISCUSSION

The molecular character and extent of crosslinking and other important determinants of the macromolecular structure, such as the structure and chemical nature of the monomers, the polymerization method, and the variables of polymerization, can be varied systematically to provide model macromolecular systems of diverse physical properties.[9–12] The rigidity, swellability, mechanical stability, and so forth are important factors when we design a macromolecular matrix.

Two systems were selected for the investigation. A comparatively rigid, hydrophobic, and mechanically stable host polymer matrix was designed with styrene as the monomer and DVB as the crosslinking agent. A more flexible and hydrophilic host was designed with HDDMA as the crosslinking agent and styrene as the monomer.

Macroporous styrene-based copolymer networks are prepared mainly by the free-radical crosslinking copolymerization (FCC) of styrene and a crosslinking agent in the presence of an inert diluent. The diluent, which is a solvent or nonsolvent, is included in the FCC system as a pore-forming agent.

The crosslinking copolymerization of styrene with a crosslinking agent in the presence of benzoic acid in the dissolved state resulted in the formation of a benzoic acid entrapped PS network (Scheme 1). The free-radical-initiated bulk polymerization technique was used for the polymerization. The guest molecules
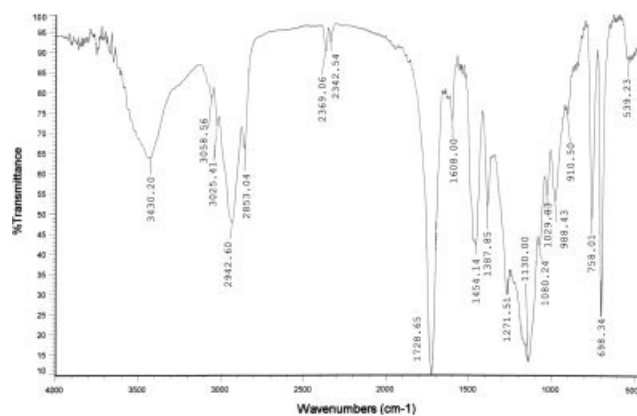
were dissolved in the monomer mixture. Benzoyl peroxide was used as the initiator. The mixture was heated on a water bath at 80°C with stirring. The precipitated polymer was washed with water, methanol, and benzene. DVB- and HDDMA-crosslinked PS samples with different crosslink densities varying from 5 to 20 mol % were prepared in the presence of the guest molecules.

IR spectra

The polymers were characterized by IR spectra. The IR spectra of benzoic acid encapsulated, DVB- and HDDMA-crosslinked PS samples are given in Figures 1–3 and are compared with that of the free polymer network.

The strong peak at 1728.65 cm^{-1} due to the C=O stretching vibration of the carboxylic acid group and the broad peak at 3430.2 cm^{-1} corresponding to the O—H stretching vibration of the carboxyl group of the guest moiety in the guest-encapsulated PS–DVB network are absent in the free polymer.
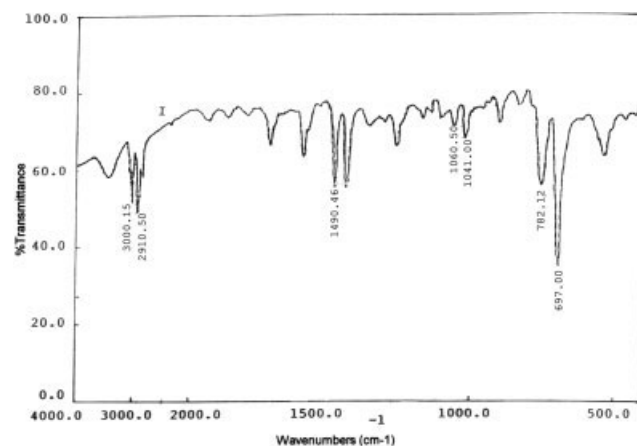

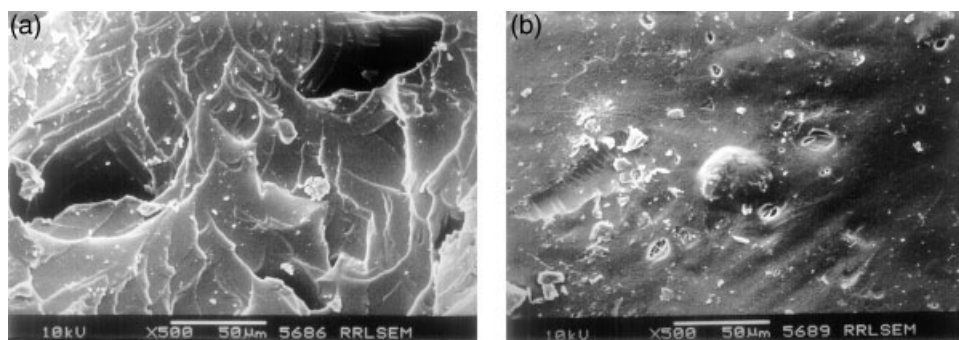**Figure 3** IR spectrum of DVB-crosslinked PS.

Figure 4 SEM micrographs of (a) a PS–DVB resin and (b) a benzoic acid encapsulated PS–DVB resin.

The peak at 1658.3 cm^{-1} in the IR spectrum of HDDMA-crosslinked PS is due to the ester carbonyl of the crosslinks. This is shifted to 1719.34 cm^{-1} for the guest-encapsulated, HDDMA-crosslinked PS because of the mixing of the carbonyl stretching vibration of the ester linkage of the crosslinks and the carbonyl group of the encapsulant. Also, there is an additional broad band at 3423.20 cm^{-1} in guest-encapsulated, HDDMA-crosslinked PS because of the O—H stretching vibrations of the carboxylic functions in comparison with the free polymer.

SEM micrographs

The surface properties of the free polymer and host–guest system are compared and analyzed with SEM micrographs (Figs. 4 and 5). The surface of the free polymer is relatively irregular because of cavities, and that of the host–guest system is smooth and regular.

The foreign molecules (guests) with suitable molecular dimensions are entrapped in the well-defined cavities of the polymer matrix. These cavities are designed by the three-dimensional arrangement of the structural units in the polymer systems. The morphology of the polymer, such as the pore size and pore geometry, is sensitively dependent on the polymerization conditions. With the variations in the temperature, rate of stirring, and distribution of the monomers in the suspension medium, the polymers produced are of variable morphological characteristics. Guest molecules are selectively entrapped in these cavities, and the pore size modification is clearly evident from the SEM photographs.

Release studies of guest-encapsulated PS networks

The effects of the chemical structure and monomer architecture of the host, guest, and host–guest complex on the time-dependent release of the guest from the well-defined cavities of the host were studied. The amounts of benzoic acid encapsulated in PS–DVB and PS–HDDMA resins were measured by a suitable chemical method. The resins were allowed to swell in different solvents for definite time intervals, and the amount of benzoic acid liberated was estimated titrimetrically; the results are given in Figures 6 and 7.

The release is maximum in chloroform and decreases in the order of toluene > CH$_3$OH > H$_2$O. The solubility parameter is a useful quantity for the characterization of the strength of the interactions in polymer–solvent systems. The various types of forces existing between polymer segments and solvents can be obtained from the three-dimensional solubility parameter concept.[13] Thus, for CHCl$_3$ and toluene, the dispersion force is higher, and polar and hydrogen-bonding interactions are negligible. For water and methanol, hydrogen-bonding and polar forces are higher (Table I). Thus, CHCl$_3$ and toluene can selec-
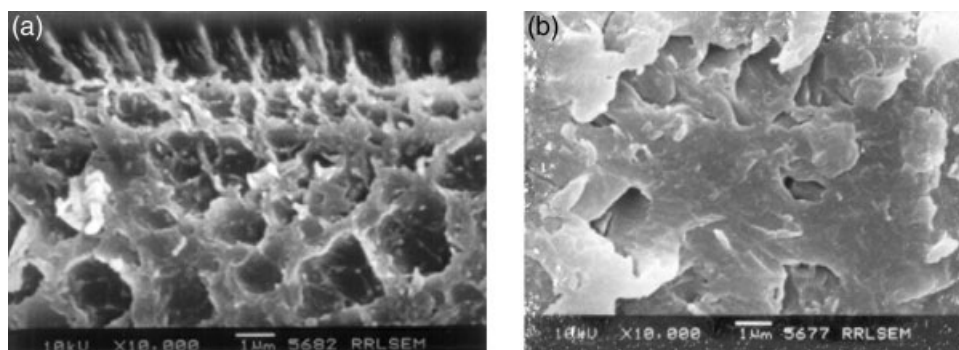

Figure 5 SEM micrographs of (a) HDDMA-crosslinked PS and (b) a host–guest system.
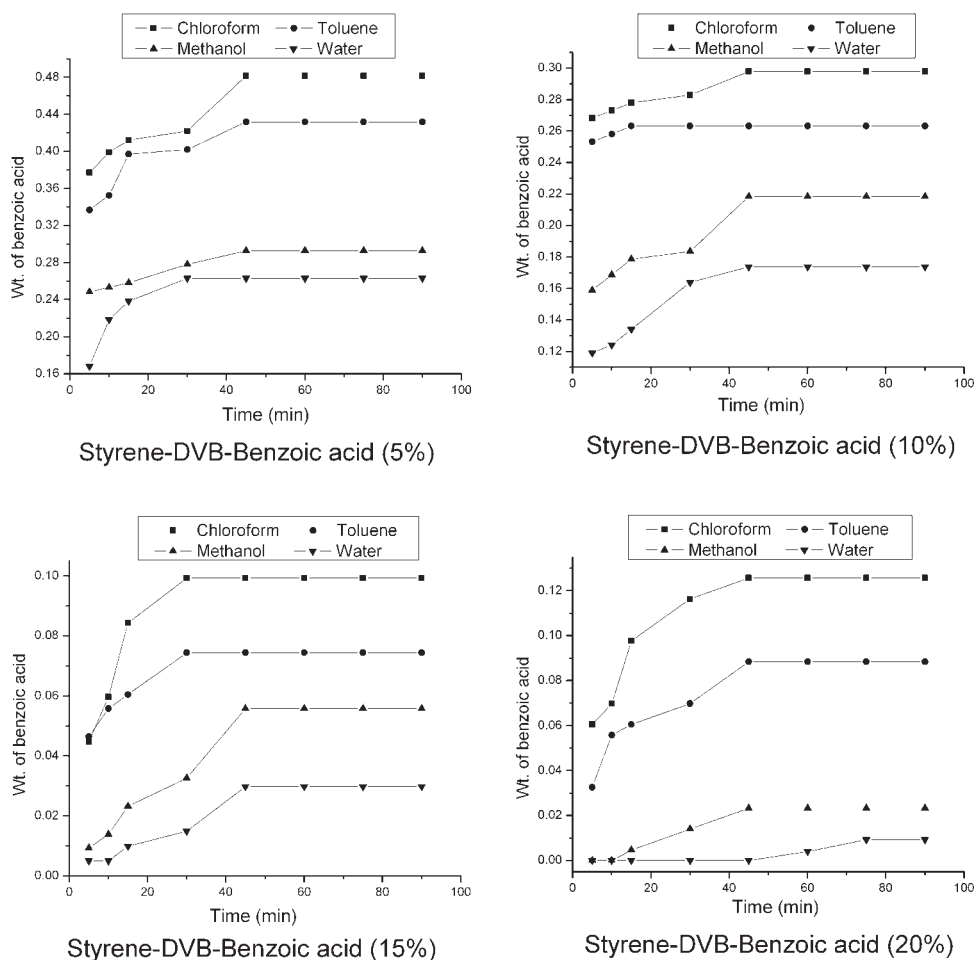
Figure 6 Rate of release of benzoic acid from guest-encapsulated, DVB-crosslinked PS.

tively penetrate cavities by means of dispersion forces, and the release of benzoic acid is higher in these solvents. Also, $CHCl_3$ and toluene are solvating diluents, so they can penetrate the micropores more easily, and benzoic acid can be easily released. However, water and methanol cannot penetrate the pores of the guest-encapsulated PS–HDDMA network by hydrogen-bonding and polar forces, and benzoic acid cannot be released in these media.

The amount of benzoic acid released is maximum in the 5% crosslinked polymer and decreases in the order of 10% > 15%. However, the amount of benzoic acid released from the 20% crosslinked polymer is slightly higher than that from the 15% crosslinked polymer in the presence of $CHCl_3$ and toluene (Figs. 8 and 9) for both systems.

The degree of crosslinking, the concentrations of the monomer and crosslinking agent, and the nature of the solvent influence the release of the guest molecule from the host–guest complex. The result of the release studies can be explained only when the mechanism of porosity formation during polymerization and the different interaction energies between network polymers

and solvents and between different chain segments are considered. During the FCC of a network, a porous structure is formed because of phase separation during the network formation.[14–16] Because of different mechanisms of porosity formation (microsyneresis or macrosyneresis) during FCC, the final copolymer consists of agglomerates of particles of various sizes.[15,16] Thus, pores of different dimensions are formed during the network formation; that is, micropores (width up to 20 Å) appear between nuclei, and mesopores (width in the range of 20–500 Å) appear in the interstices between microspheres and macropores (width > 500 Å). Mesopores and macropores appear between the agglomerates of microspheres.

In the FCC of styrene, a crosslinking agent, and benzoic acid, during polymerization, benzoic acid is entrapped in the pores of the network. The possibility of entrapment is maximum in micropores and mesopores. The benzoic acid entrapped in macropores may be removed during washing and drying.

At the beginning of the copolymerization, much more crosslinking agent (DVB or HDDMA) is incorporated into the copolymer than is expected on the basis
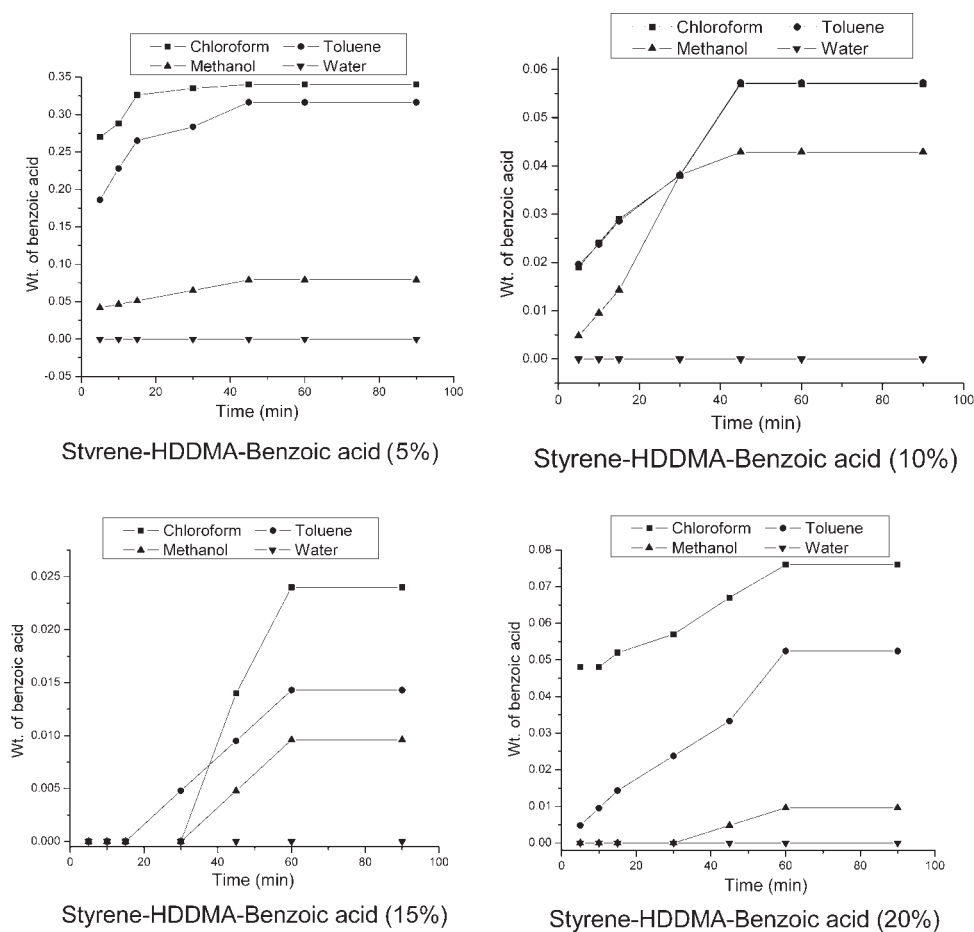
Figure 7 Rate of release of benzoic acid from a guest-encapsulated PS–HDDMA resin.

of the initial composition of the monomer mixture because of the greater reactivity of the crosslinker. Accordingly, the earlier formed and phase-separated nuclei and their agglomerates (microspheres) are more highly crosslinked than those formed in a later stage of copolymerization when the major part of the DVB monomer has been used up. The early formed gel regions will constitute the interior of the microspheres, whereas the latter formed and loosely crosslinked regions will be located at the surface of the microspheres.

Thus, the pores and hence benzoic acid encapsulated in these pores within the first formed regions of the network remain stable during the drying process because these regions will have a higher crosslink density. Because the macropores form the interstices of the microspheres and agglomerates that form in later stages of the reactions, these network regions are loosely crosslinked, so the pores in these regions collapse upon drying in the rubbery state.

The inhomogeneity in the networks increases with an increasing DVB or HDDMA concentration.[17] Also, the crosslink density of the less crosslinked regions of the network decreases with an increasing DVB or HDDMA concentration. Thus, benzoic acid encapsu-

lated in the micropores is more tightly held than in the mesopores and macropores because of increased crosslink density in the microspheres.

As the crosslinker content increases, the crosslinking density increases, the pore size also decreases (mesopores and macropores), and the amount of benzoic acid also decreases. However, as the crosslinker content increases beyond 15%, the inhomogeneity and hence number of micropores also increases, the rigidity and stability of the pores increases, and the amount of benzoic acid entrapped in the pores increases.

TABLE I
Solubility Parameters of the Solvents

Solvent	δ_d	δ_p	δ_h	$\delta = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2}$
Chloroform	8.65	1.5	2.8	9.21
Toluene	8.82	0.7	1.0	8.90
Water	6.00	15.3	16.7	23.43
Cyclohexane	8.18	0.0	0.0	8.18
Methanol	7.42	6.0	10.9	14.48

δ, three dimensional solubility parameter; δ_d, contribution of solubility parameter from dispersion forces; δ_p, contribution of solubility parameter from polar forres; δ_h, contribution of solubility parameter from hydrogen bonding.
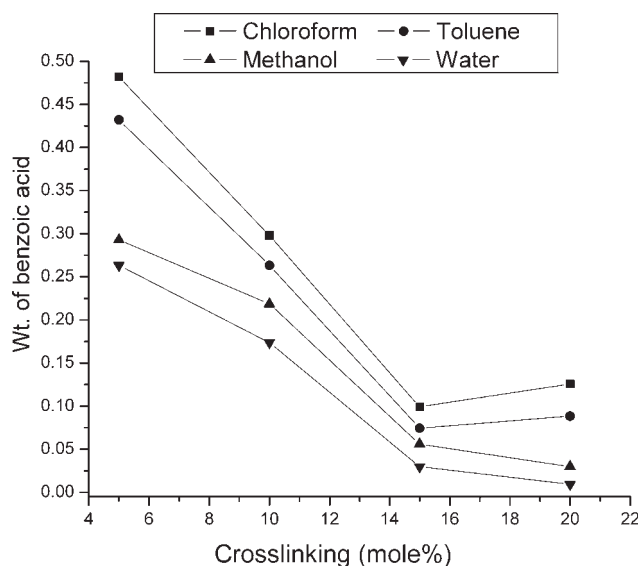
Figure 8 Weight of benzoic acid released from a guest-encapsulated PS–DVB resin.

In the presence of $CHCl_3$, the expansion of the pores (or formation of new pores) occurs, and this must be accompanied by either deformation of the polymer matrix or the relaxation of the crosslinking network.

Moreover, for the guest-encapsulated PS–DVB and PS–HDDMA copolymer, the amount of benzoic acid released in CH_3OH and water for the 20% crosslinked polymer is lesser than that for the 15% crosslinked polymer, in contrast to the behavior in $CHCl_3$ (Fig. 9). This gives a clear indication that CH_3OH and H_2O cannot penetrate the rigid micropores (which are filled by an encapsulant) by polar and hydrogen-bonding forces and cannot extend the polymer matrix so that the benzoic acid in the rigid micropores is released.

As the percentage of the crosslinker is increased from 10 to 15% and then to 20%, the number of micropores is increased, and most of the benzoic acid encapsulated is in the micropores; therefore, the amount of benzoic acid released is less in CH_3OH and H_2O (for the 15 and 20% crosslinked resins) than for the 5 and 10% crosslinked polymers.

The amount of benzoic acid encapsulated in the PS–HDDMA-crosslinked resin is much less than in the PS–DVB-crosslinked resin for the same percentage of the crosslinker. HDDMA is more flexible and hydrophilic, and the length of the crosslinker unit is higher than that of the DVB crosslinker. Hence, the pore size (macropore) of the PS–HDDMA polymer network will be higher than that of the PS–DVB network, and benzoic acid cannot be successfully encapsulated in the macropores of the PS–HDDMA resin. Thus, benzoic acid in macropores may not be fitted, and most of the benzoic acid encapsulated is in micropores and mesopores. Hence, the amount of benzoic acid released in

the presence of CH_3OH and H_2O is very low compared with that of the PS–DVB resin.

Swelling studies

The physical and chemical properties of the base polymer (e.g., the solvent affinity, molecular weight distribution, and density) provide the reference point to characterize the network. Important microscopic parameters in a network are the average strand length, functionality of crosslinks (and a suitable description of the overall network connectivity), topological defects (e.g., free ends), and entanglements. These properties are often difficult (or impossible) to measure experimentally. They can be indirectly evaluated from their effect on the macroscopic properties of the network, such as the elastic modulus and equilibrium swelling.

In the dissolution or swelling of a linear or crosslinked polymer, the driving force is due to the contribution of normal entropy and enthalpy changes associated with the mixing of the solvent and solute molecules added to configurational entropy resulting from the dilution of flexible chain molecules. In the case of crosslinked polymers, the tendency to disperse is opposed by a decreased configurational entropy of the polymer chains held between crosslink points, where they are forced to assume a more elongated, less probable configuration as the networks expand. Thus, at a higher crosslink ratio, the swollen volume is lower.

The difference between the solubility parameters of the diluent (δ_1) and the copolymer (δ_2), that is, $\delta_1 - \delta_2$, or its square, $(\delta_1 - \delta_2)^2$, is generally used to represent the solvating power of a diluent in a network forma-
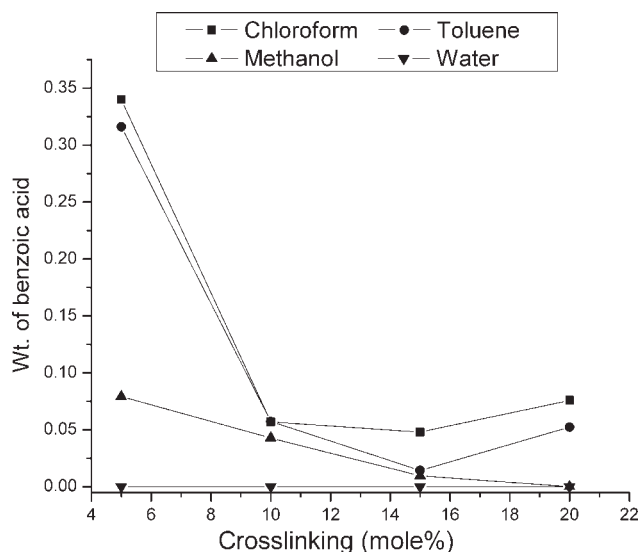

Figure 9 Weight of benzoic acid released with the crosslinker percentage from a guest-encapsulated PS–HDDMA resin.

TABLE II
Swelling Behavior of Guest-Encapsulated, DVB-Crosslinked Styrene Resins

| | Mass of the swollen polymer (g) | | | | | | | |
| | 5% crosslink density | | 10% crosslink density | | 15% crosslink density | | 20% crosslink density | |
Solvent	Free polymer	Host–guest system	Free polymer	Host–guest system	Free polymer	Host–guest system	Free polymer	Host–guest system
Chloroform	0.6988	1.321	0.648	1.04	0.6448	0.863	0.6724	0.84
Toluene	0.501	0.5102	0.36	0.4946	0.321	0.4824	0.334	0.419
Water	0.3542	0.421	0.3462	0.398	0.345	0.3848	0.3492	0.35
Cyclohexane	0.341	0.3674	0.3368	0.358	0.3252	0.23	0.3252	0.217
Methanol	0.2854	0.36	0.2636	0.3078	0.2604	0.217	0.2604	0.26

tion system. According to Hildebrand and Scott's theory,[18] the solubility of a polymer in a solvent is favored when $(\delta_1 - \delta_2)^2$ is minimized. It has also been shown that instead of the Hildebrand solubility parameter, the three-dimensional solubility parameter of Hansen[19] is a better predictor for the diluent–polymer affinity.

The swelling capacities of the gel samples (both the free polymer and host–guest system) were measured in various solvents. For comparison with the free polymer, DVB- and HDDMA-crosslinked PS samples with different crosslink densities (5, 10, 15, and 20 mol %) were prepared under the same experimental conditions as the guest-encapsulated polymer, and the swelling behavior was analyzed.

The quantitative interpretation of the experimental results are given in terms of a Flory–Rehner analysis[20,21] of the swelling measurements of the free polymer and host–guest system. The theoretical results are in excellent agreement with the experimental results of release studies, confirming the qualitative view given previously.

The swelling studies of the guest-encapsulated, DVB- and HDDMA-crosslinked PS samples were carried out by the placement of a definite amount of a dry sample in solvents such as $CHCl_3$, toluene, cyclohexane, methanol, and H_2O for 48 h. The weight of the swollen samples were taken after the removal of the solvent. The results are given in Tables II and III.

The extent of swelling is maximum in $CHCl_3$ and decreases in the order of toluene → cyclohexane →

water → methanol; this is similar to that of the free polymer. In the swollen state, polymer chains are elongated in the network, pore dimensions are increased, and the release of benzoic acid becomes easier.

However, the extent of swelling is higher for the guest-encapsulated PS–HDDMA resin than for the guest-encapsulated PS–DVB resin. (The reverse is the case for the free polymer.) The reason is that the amount of benzoic acid encapsulated in the PS–DVB resin is higher than that in the PS–HDDMA resin. Hence, the voids available in the guest-encapsulated PS–HDDMA resin are higher than those in the guest-encapsulated PS–DVB resin.

Quantitative interpretation of the results

The swelling of polymeric networks by organic solvents has been the subject of research for some 60 years, with many theories and modifications to existing theories being proposed to explain swelling behavior. The Flory–Rehner theory can be successfully used to describe the swelling of networks by small-molecule solvents. It is very often used to provide an estimation of the actual degree of crosslinking in the network from the total swelling.

The molecular weight between crosslinks (M_c) of the host–guest system has been calculated with the Flory–Rehner theory and is compared with M_c for the free polymer (Tables IV and V).

The Flory–Rehner treatment of the swelling of a polymer network, based on the assumption of the

TABLE III
Swelling Behavior of Guest-Encapsulated, HDDMA-Crosslinked Styrene Resins

| | Mass of the swollen polymer (g) | | | | | | | |
| | 5% crosslink density | | 10% crosslink density | | 15% crosslink density | | 20% crosslink density | |
Solvent	Free polymer	Host–guest system	Free polymer	Host–guest system	Free polymer	Host–guest system	Free polymer	Host–guest system
Chloroform	0.97	1.276	0.9348	1.225	0.8496	1.09	0.841	0.95
Toluene	0.4814	0.8958	0.45	0.56	0.4103	0.503	0.3866	0.457
Water	0.3986	0.3714	0.373	0.329	0.332	0.3432	0.3638	0.3272
Cyclohexane	0.253	0.3112	0.2628	0.3002	0.2694	0.3	0.3538	0.2926
Methanol	0.2938	0.2756	0.2812	0.276	0.26	0.294	0.256	0.2768

TABLE IV
M_c Values for PS–DVB Resins and Host–Guest Systems

Crosslinking (mol %)	M_c	
	Free polymer	Host–guest system
5	4.972×10^3	3.450×10^3
10	8.260×10^2	2.319×10^3
15	7.960×10^2	3.840×10^3
20	8.030×10^2	1.736×10^3

additivity of the free energy of mixing and free energy of elasticity, leads to an expression for a phantom network model[22,23] of swelling:

$$\therefore \overline{M}_c = \frac{-\rho V_1 \varphi_m^{1/3}}{\ln[1 - \varphi_m] + \varphi_m + \chi \varphi_m^2}$$

where ρ is the density of the polymers, V_1 is the molar volume of the solvent and χ is the polymer–solvent interaction parameter. ϕ_m is the polymer volume fraction in the swollen gel:

$$\phi_m = \frac{w_1/\rho_1}{w_1/\rho_1 + w_2/\rho_2}$$

where w_1 and ρ_1 are the weight and density of the polymer sample, respectively, and w_2 and ρ_2 are the weight and density of the solvent, respectively.

As the crosslinking density increases, the molecular weight between crosslinks (M_c) decreases, as expected. An interesting feature that is observed is that except for the 5% crosslinked polymer, M_c for the guest-encapsulated resin is higher than that for the free polymer for the PS–DVB resin. The amount of benzoic acid encapsulated in the 5% crosslinked polymer is much higher than that in the 10% crosslinked polymer. Hence, it is less for the 5% guest-encapsulated resin than for the free polymer.

Depending on the distribution of the diluent in the network structure after its formation, networks can be classified into three groups: expanded (pre-swollen) networks, heterogeneous dry networks, and heterogeneous swollen networks. In the encapsulated PS networks, heterogeneous swollen networks may be formed. For the guest-encapsulated, DVB- and

TABLE V
M_c Values for PS–HDDMA Resins and Host–Guest Systems

Crosslinking (mol %)	M_c	
	Free polymer	Host–guest system
5	4.944×10^3	3.166×10^4
10	2.333×10^3	4.90×10^3
15	1.157×10^3	1.08×10^4
20	6.89×10^2	4.766×10^3

HDDMA-crosslinked PS, it is higher for 15% than for 20%. This is in excellent agreement with what we have observed in release studies. The amount of benzoic acid encapsulated in the 20% crosslinked polymer is higher than that in the 15% crosslinked polymer. Because the amount of benzoic acid encapsulated in the 15% crosslinked polymer is very low compared with that in the 10 and 20% copolymers, M_c will be higher for it on account of the free pores.

CONCLUSIONS

The physical encapsulation and controlled release of benzoic acid within the organized cavities of PS networks have been carried out. The free-radical-initiated bulk polymerization of styrene with a crosslinking agent in the presence of benzoic acid in the dissolved state results in the formation of benzoic acid entrapped, styrene-based polymeric systems. A series of resins with DVB and HDDMA as the crosslinking agents with various crosslink densities (5, 10, 15, and 20 mol %) have been prepared by a bulk polymerization technique. The products have been characterized by IR spectra and SEM. It has been found that benzoic acid can be successfully encapsulated in styrene-based copolymer networks by a bulk polymerization technique. The morphology of the polymer, such as the pore size and pore geometry, is sensitively dependent on the polymerization conditions.

The nature of the forces and bonding existing between the polymer and encapsulant and the amount of guest that can be encapsulated in the host have been studied with release experiments. The release is maximum in chloroform and decreases in the order of toluene > methanol > water for guest-encapsulated, DVB-crosslinked PS and guest-encapsulated, HDDMA-crosslinked PS. For chloroform and toluene, the dispersion force is higher, and the polar and hydrogen-bonding interactions are negligible. The amount of benzoic acid released follows the order of 5 > 10 > 20 > 15% in chloroform and toluene for both DVB-crosslinked PS and HDDMA-crosslinked PS. However, in methanol and water, the release is in the order of 5 > 10 > 15 > 20% for both systems. A qualitative interpretation of the results has been given.

As the percentage of the crosslinking agent is increased, the pore size decreases (mesopores), and hence the amount of benzoic acid encapsulated also decreases up to 15%. Beyond 15%, the number, rigidity, and stability of the micropores increase, and more benzoic acid is encapsulated in 20% than in 15%. This idea has been confirmed by the fact that CH_3OH and H_2O cannot penetrate the micropores by their polar and hydrogen-bonding forces, and hence the release of benzoic acid is very difficult in the presence of these solvents, especially at higher percentages.

The amount of benzoic acid encapsulated in the PS–HDDMA-crosslinked resin is much less than that in the PS–DVB-crosslinked resin for the same percentage of the crosslinker. The pore size (macropore) of the PS–HDDMA polymer network is higher than that of the PS–DVB network, and thus benzoic acid in the macropores may not fit, and most of the benzoic acid encapsulated is in micropores and mesopores. Hence, the amount of benzoic acid released in the presence of CH_3OH and H_2O is very low in comparison with the PS–DVB resin.

The quantitative interpretation of the experimental results has been given in terms of a Flory–Rehner analysis of the swelling measurements of the free polymer and host–guest system. The theoretical results are in excellent agreement with the experimental results of the release studies, confirming the qualitative view. Swelling studies of the guest-encapsulated, DVB- and HDDMA-crosslinked PS samples have revealed that the extent of swelling is maximum in chloroform and decreases in the order of toluene → cyclohexane → water → methanol; this is similar to the free polymer.

M_c for the host–guest system decreases in the order of 5 > 10 > 20 > 15%. This is in excellent agreement with what we have observed in the release studies. The amount of benzoic acid encapsulated in the 20% crosslinked polymer is higher than that in the 15% crosslinked polymer. Because the amount of benzoic acid encapsulated in the 15% crosslinked polymer is very low compared with that in the 10 and 20% crosslinked polymers, M_c is higher for this system on account of the presence of free pores in the system.

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