Encapsulation and Controlled Release in Polyacrylamide Hydrogels

Mary Joseph,[1] Tessymol Mathew,[1] S. Devipriya,[2] Sunny Kuriakose[2]

[1]*Research and Post Graduate Department of Chemistry, St. Georges College, Aruvithura-686122, Mahatma Gandhi University, Kerala, India*
[2]*Research and Post Graduate Department of Chemistry, St. Thomas College, Pala-686574, Mahatma Gandhi University, Kerala, India*

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ABSTRACT: A novel host–guest system was developed by the encapsulation of simple organic guest molecules in the hydrophilic molecular architecture of crosslinked polyacrylamide hydrogels. The crosslinking agents used for the preparation of the host systems were hexanediol dimethacrylate (HDDMA) and divinyl benzene (DVB). This enabled us to construct hydrogels with different hydrophobic–hydrophilic equilibria. The model guest system used for the studies was benzoic acid. The selections gave simple but excellent host–guest systems with fine polar–apolar balancing. Polyacrylamide hydrogels with encapsulated benzoic acid were prepared with varying crosslink densities (5, 10, 15, and 20 mol %) by the solution polymerization technique. The rate of release of the host from the host–guest assembly was studied in different swelling conditions. The rate of release depended on the interaction forces between the polymer and the solvents. Polar forces, dispersion forces, and hydrogen bonding all played a vital role. The swelling behavior of the host-polymer system and the host–guest assembly was analyzed and compared by the Flory–Rehner method. The amount of benzoic acid encapsulated in the DVB-crosslinked polymer was higher than in the HDDMA-crosslinked polymer, and the rate of release was in the order $5 > 15 > 10 > 20\%$ for the DVB-crosslinked polymer. The rate of release for the HDDMA-crosslinked host–guest assembly was in the order $10 > 5 > 15 > 20\%$. These results were in excellent agreement with those of the Flory–Rehner analysis of the swelling properties. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1816–1824, 2004

Key words: hydrogels; encapsulation; polyacrylamide; host–guest complex

INTRODUCTION

A hydrogel may be described as a polymer material that can absorb a significant amount of water (≥20% of its dry weight) while maintaining its structural integrity. Polymer gels are important materials of both fundamental and technological interest. In recent years, hydrogels have received attention for use as extraction solvents for soft contact lenses, for medical therapeutics and diagnostics and drug-delivery devices, and as support carriers in biomedical engineering.[1,2] To ensure the effective use of these materials and to design one for a particular application, a good understanding of the relationship between the structure and properties of the polymer is essential.

The incorporation of a foreign molecule into the voids of the polymer matrix and its controlled release is of particular interest in this context. In this article, we describe a new type of macromolecular system consisting of a three-dimensional network of a flexible polymer with embedded aromatic units containing polar functional groups. The study of these substances further refines our knowledge of the chemistry and physics of network polymers.[3] As the encapsulation was not covalently attached to the network, we needed to discover the conditions under which the release of the embedded molecule from the gel became negligibly slow. In addition, a study of the kinetics of the release of the encapsulant provided us with useful information about the interaction of the gel with the encapsulant during diffusion and about the structure of the gel. We prepared polyacrylamide (PA) hydrogels with hexanediol dimethacrylate (HDDMA) and divinyl benzene (DVB) as the crosslinking agents and benzoic acid as the encapsulant. We also investigated the factors influencing the release of the encapsulant from the network under different solvation conditions. We also studied the swelling behavior of the free-polymer and host–guest assemblies and com-

Correspondence to: S. Kuriakose, Institut für Organische und Makromolekulare Chemie, Johannes-Gutenberg Universität, Duesbergweg 10-14 D, 55128 Mainz, Germany (sunnykuriakose_30@rediffmail.com or sunnykuriakose30@yahoo.com.in).

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puted the crosslink density of the PA hydrogels with encapsulated guest and that of the PA hydrogels.

EXPERIMENTAL

General

Acrylamide (AA; BDH) and HDDMA (Aldrich) were used as purchased. DVB (Aldrich) was freed from the inhibitor by washing with 1% NaOH and water (30 mL, three times each). All of the low-molecular weight compounds used were commercially available and were purified by literature procedures unless otherwise specified. All of the solvents were used as purchased. A Shimadzu IR-470 spectrometer was used for recording the IR spectra of the samples. Measurements were done with KBr pellets in the range 4000–400 cm^{-1}. Scanning electron microscopy (SEM) studies were conducted on a Jeol JSM 5600 LV scanning electron microscope.

Synthesis and characterization of HDDMA- and DVB-crosslinked PAs

HDDMA- and DVB-crosslinked PAs with varying crosslink densities (5, 10, 15, and 20 mol %) were prepared by a free-radical-initiated solution polymerization technique. DVB was washed with a 1% NaOH solution and water to remove the stabilizer, and HDDMA was used as received. Benzoyl peroxide was used as the initiator. A mixture of water and methanol (2:1 v/v) was used as the solvent. The polymerization was carried out at 80°C in a water bath until the precipitation was complete. The polymer was then washed with water and methanol, dried in a vacuum oven at 70°C, and characterized by IR spectroscopic analysis.

PA hydrogels encapsulated with a benzoic acid guest

Benzoic acid encapsulated PAs crosslinked with HDDMA and DVB (5, 10, 15, and 20 mol %) were prepared by solution polymerization with benzoyl peroxide as the initiator. The initiator and benzoic acid (1:1 molar ratio with the monomer) were dissolved in a methanol–water mixture (1:2 v/v) by gentle warming in a water bath. AA and the crosslinking agents were added to the mixture simultaneously from two dropping funnels. The reaction mixture was heated to 80°C with constant magnetic stirring until the polymerization was complete. The guest-encapsulated polymer was then filtered, washed with water and methanol, and dried *in vacuo* at 60°C. The product was characterized by IR spectral analysis.

Controlled release of the guest from the cavities of the PA hydrogels: General procedure

We accurately weighed 200 mg of the guest-encapsulated PA hydrogel, added 50 mL of standard NaOH, and allowed the hydrogel to swell in a solvent, such as water, methanol, chloroform, or toluene, with gentle magnetic stirring at 0°C. A 5-mL sample of the solution was taken after 5 min with a pipette and titrated with a standard HCl solution. The experiment was repeated at different time intervals (15, 20, 25, 30, 45, and 60 min). The concentration and, thus, the amount of acid in the solution were 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 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, we determined the degree of swelling. The experiment was repeated with various solvents, including cyclohexane, chloroform, toluene, acetic acid, water, and solvent mixtures of acetic acid and water.

RESULTS AND DISCUSSION

PA hydrogels with encapsulated guest molecules

Molecules can interact with other molecules through weak interactions (i.e., 0.1–5 kcal/mol), such as hydrogen bonding or van der Waals or dispersive forces, which are collectively known as *noncovalent interactions*. More than 30 years of research in the field of noncovalent interactions has shown that this phenomenon has enormous potential for the construction of chemical structures that exhibit a high degree of structural complexity.[4] In this study, we prepared a simple but novel host–guest assembly by encapsulating benzoic acid in the cavities of the PA hydrogel. Molecular design of the building blocks is an essential element in the successful formation of thermodynamically stable noncovalent capsules. We selected two crosslinking agents, one flexible and hydrophilic (HDDMA) and the other comparatively rigid and hydrophobic (DVB), for the preparation of the hydrogels. The network structure of the polymer gels was obtained by the free-radical crosslinking copolymerization of the monomers.

Several studies have shown that hydrogel structure and, thus, hydrogel properties strongly depend on the initial degree of the dilution of the monomers.[5,6] The diluent, which is a solvent, present in the reaction

TABLE I
Rate of Release of the Guest from Benzoic Acid Encapsulated DVB-Crosslinked PA

Time (min)	Weight of benzoic acid (g) released per gram of polymer															
	Percentage crosslinking for C_6H_5—CH_3 solvent				Percentage crosslinking for $CHCl_3$ solvent				Percentage crosslinking for H_2O solvent				Percentage crosslinking for CH_3OH solvent			
	5	10	15	20	5	10	15	20	5	10	15	20	5	10	15	20
5	.2392	.0903	.1626	.0614	.2057	.0953	.1789	.0526	.1722	.0702	.1431	.0758	.1627	.0716	.1483	.1121
10	.2679	.1003	.2583	.0818	.2105	.1003	.2096	.0670	.2201	.0753	.1873	.0960	.2153	.0870	.1579	.1292
15	.3109	.1204	.2631	.0818	.2870	.1054	.2454	.1005	.2918	.0853	.2064	.1061	.2440	.0953	.1674	.1332
30	.3731	.1254	.3253	.0930	.3205	.1204	.2628	.1238	.3396	.1355	.2352	.1364	.2727	.1022	.1961	.1348
45	.4688	.2006	.4209	.1968	.4353	.1806	.3013	.1435	.4066	.1706	.2965	.1415	.2966	.1022	.2248	.1365
60	.4688	.2006	.4209	.1968	.4353	.1806	.3013	.1435	.4066	.1706	.2965	.1415	.2966	.1022	.2248	.1365

mixture acts as a pore-forming agent and plays an important role in the design of the pore structure of these crosslinked materials.[7] As the amount of solvent increases, the network structure becomes more and more flexible. A continuous network is formed above a critical amount of solvent.[8] The optimum concentration of the solvent system was 2:1 v/v of water and methanol for our polymer network. At this particular concentration, voids formed were an appropriate size so that benzoic acid could be successfully entrapped.

IR spectra

The polymers were characterized by IR spectroscopic analysis in the solid state with KBr pellets. The crosslinked PA showed the characteristic absorption of the amide group. The absorption obtained at 1670 cm^{-1} was characteristic of the C═O stretching vibration of the amide bond. A broad band was obtained around 3350–3400 cm^{-1} with a shoulder at 3208 cm^{-1} due to the merging of O—H (moisture) and amide N—H stretching vibrations.

PA hydrogels with benzoic acid guest moieties were also characterized by IR analysis. The strong absorption obtained at 1692.82 cm^{-1} was assigned to the C═O stretching vibration. A notable shift to a higher wave number region was observed, and this indicated the presence of acid carbonyl stretching coupled with amide carbonyl stretching. A strong and broad band was observed at 3429.83 cm^{-1}; this may have arisen from the merging of amide N—H and the O—H stretching vibration of the carboxylic function of benzoic acid.

Controlled release of benzoic acid from the network polymer

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 PA hydrogels with encapsulated benzoic acid molecules were allowed to swell in the solvents (chloroform, toluene, methanol, and water). The temperature was lowered to 0°C to prevent the hydrolysis of ester linkages in the polymer network. The released guest was estimated by titrimetric methods.

The release was at a maximum in $CHCl_3$ and decreased in the order toluene > water > methanol for the HDDMA-crosslinked polymer (Table I), and the order of release was toluene > chloroform > water > methanol for the DVB-crosslinked polymer (Table II).

SEM analysis showed interesting changes in the structural patterns before and after the release of the guest from the host–guest assembly. The benzoic acid

TABLE II
Rate of Release of the Guest from HDDMA-Crosslinked PA Encapsulated with Benzoic Acid

Time (min)	Weight of benzoic acid (g) released per gram of polymer															
	Percentage crosslinking for $CHCl_3$ solvent				Percentage crosslinking for C_6H_5—CH_3 solvent				Percentage crosslinking for H_2O solvent				Percentage crosslinking for CH_3OH solvent			
	5	10	15	20	5	10	15	20	5	10	15	20	5	10	15	20
5	.1744	.1668	.1164	.1238	.1403	.1458	.1215	.0983	.1164	.1250	.1180	.0769	.0680	.1258	.1008	.0639
10	.1876	.1830	.1232	.1342	.1806	.1632	.1241	.1085	.1958	.1406	.1238	.0935	.1485	.1667	.1114	.0783
15	.2395	.2206	.1368	.1388	.2014	.1858	.1388	.1111	.2227	.1771	.1399	.0992	.1490	.1739	.1167	.0935
30	.2483	.2374	.1585	.1432	.2353	.2116	.1532	.1239	.2275	.2139	.1507	.1092	.1497	.1752	.1273	.1011
45	.2509	.2988	.1738	.1599	.2408	.2502	.1687	.1355	.2308	.2408	.1659	.1104	.1622	.1856	.1326	.1054
60	.2509	.3044	.1738	.1599	.2481	.2505	.1687	.1355	.2308	.2408	.1659	.1104	.1632	.1856	.1326	.1054

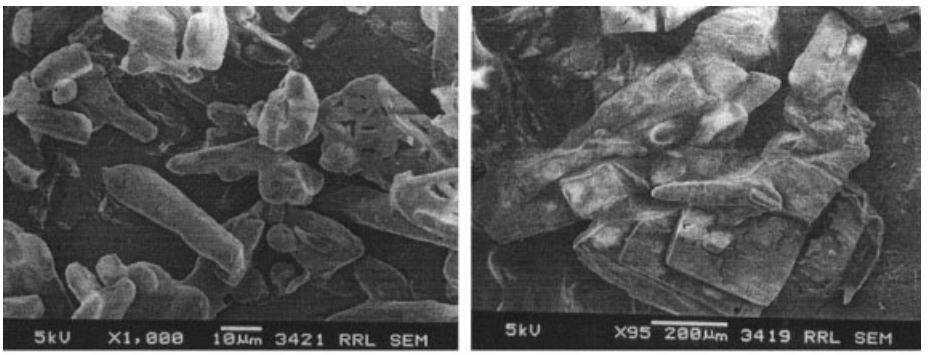

Figure 1 Benzoic acid encapsulated in HDDMA-crosslinked PA matrix (a) before and (b) after release.

encapsulated PA hydrogel (HDDMA-crosslinked) showed a regular and smooth surface [Fig. 1(a)]. The surface of the hydrogel after the release of the guest in chloroform was relatively irregular [Fig. 1(b)]. This was due to the free space available within the cavities of the polymer network. Comparable results were obtained for the benzoic acid encapsulated in DVB-crosslinked PA hydrogels. Figure 2(a) shows the SEM micrographs of the host–guest system, and Figure 2(b) shows the SEM micrographs after the release of the guest.

The degree of crosslinking, the concentration of the monomer (AA), and the nature of the solvent (i.e., molecular size and polarity) influenced the release of the host molecule from the host–guest complex. The results of the release studies could be explained only when the different interaction energies and interacting surfaces of the crosslinks and chain segments were considered.

Although swelling was higher in water than in chloroform or toluene, the release was higher in $CHCl_3$ for the HDDMA-crosslinked polymer and in toluene for the DVB-crosslinked polymer (Figs. 3 and 4). The solubility parameter[9] is a useful criterion for the characterization of the strength of 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. Thus, for $CHCl_3$ and toluene, the dispersion force was higher[10] (Table III) and the polar and hydrogen-bonding interactions were negligible. For water and methanol, hydrogen bonding and polar forces between the polymer and solvent were much higher. According to Quinn et al.,[11] some very peculiar complicating factors may affect the visual behavior of hydrogels. Among them are the following:

1. Water may act as a plasticizer or antiplasticizer, depending on the concentration, temperature, and pH.
2. The structural organization of absorbed water is sensitive to polymer mobility.
3. Polymer conformational changes can accompany hydration.
4. The presence of a third component, such as salt, can alter the way in which water behaves.

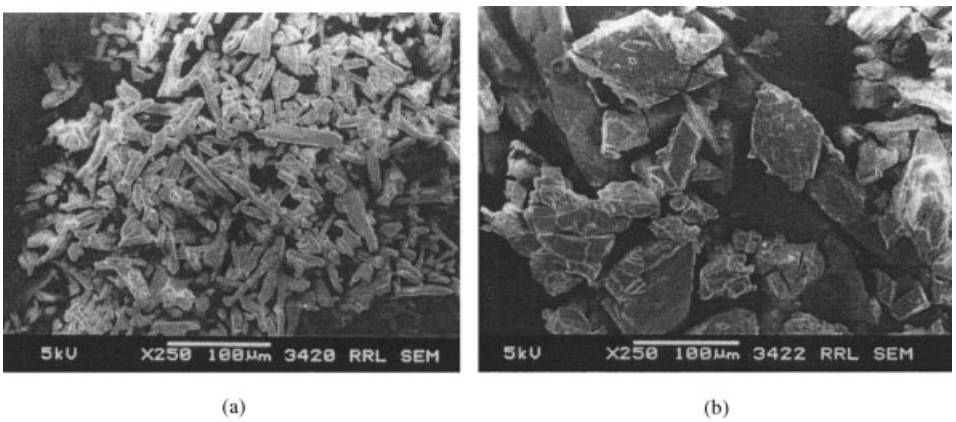

Figure 2 Benzoic acid encapsulated in DVB-crosslinked PA matrix (a) before and (b) after release.

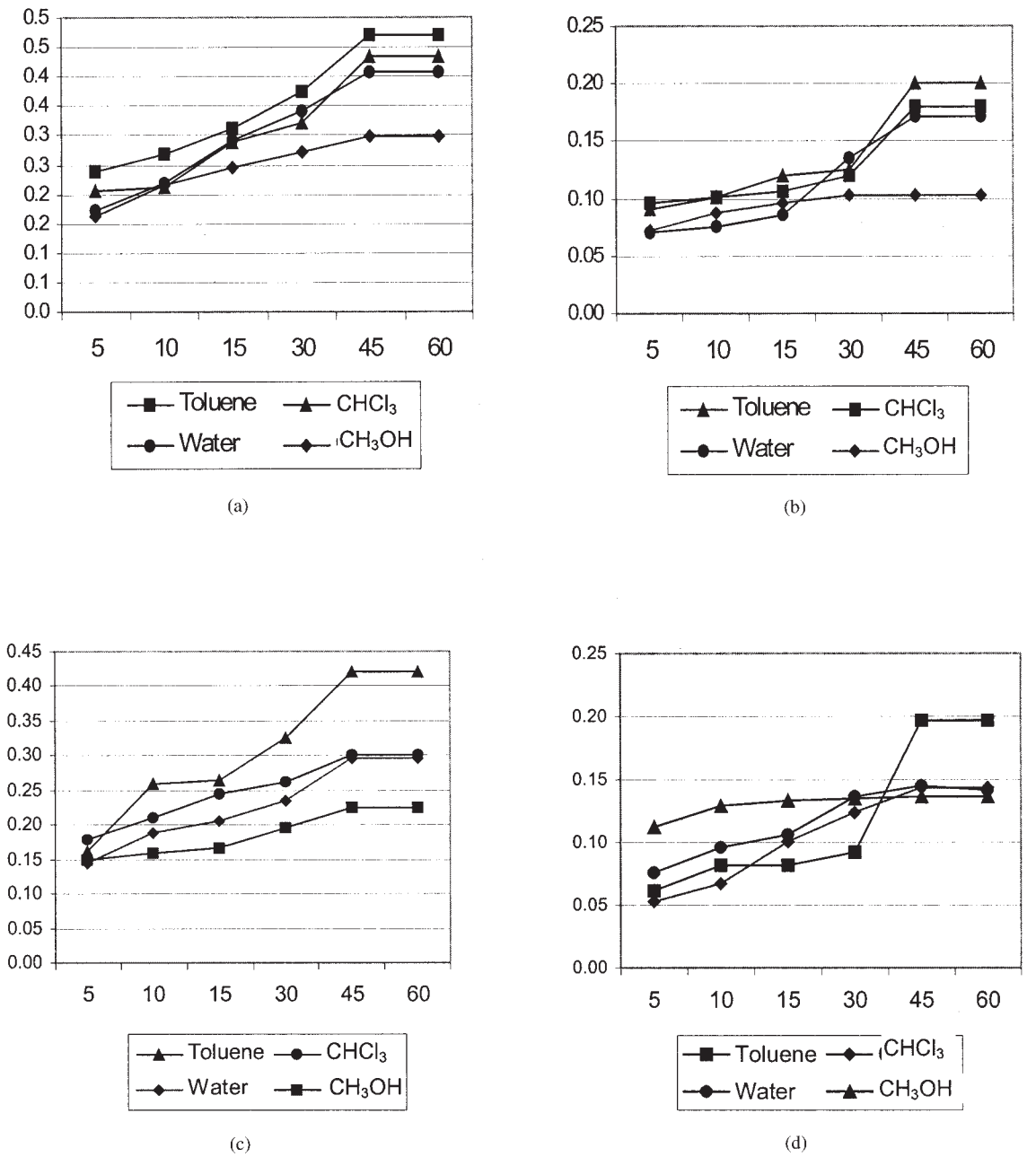

Figure 3 Rate of release of benzoic acid from DVB-crosslinked PA encapsulated with benzoic acid. The *X* axis represents time in minutes, and the *Y* axis represents the weight of benzoic acid in grams released per gram of polymer. AA–DVB–C_6H_5COOH = (a) 5, (b) 10, (c) 15, and (d) 20%.

Thus, water and methanol may not have penetrated into the cavities, but they were absorbed by means of hydrogen bonds and polar forces. However, $CHCl_3$ and toluene selectively penetrated into the cavities by means of dispersion forces, and the release of benzoic acid was higher in these solvents. Also, the mesh size and the size of the solvent molecules played important roles. The aromatic solvents and guest molecules were comparable in size and could easily displace the benzoic acid molecules.

The amount of benzoic acid encapsulated in the DVB-crosslinked polymer was much higher than in the HDDMA-crosslinked polymer. Only when the coils of the macromolecules formed well-defined cavities could the small molecules be selectively trapped within these cavities. A primary criterion for the inclusion of guests within the host cavities was obviously their size.

Another interesting feature we observed was that the amount of benzoic acid released (and hence encapsulated) in the 10 mol % guest-encapsulated HDDMA-crosslinked PA was higher than in 5% guest-encapsulated polymer; this value decreased in the order 15 to 20 mol % for all of the solvents we

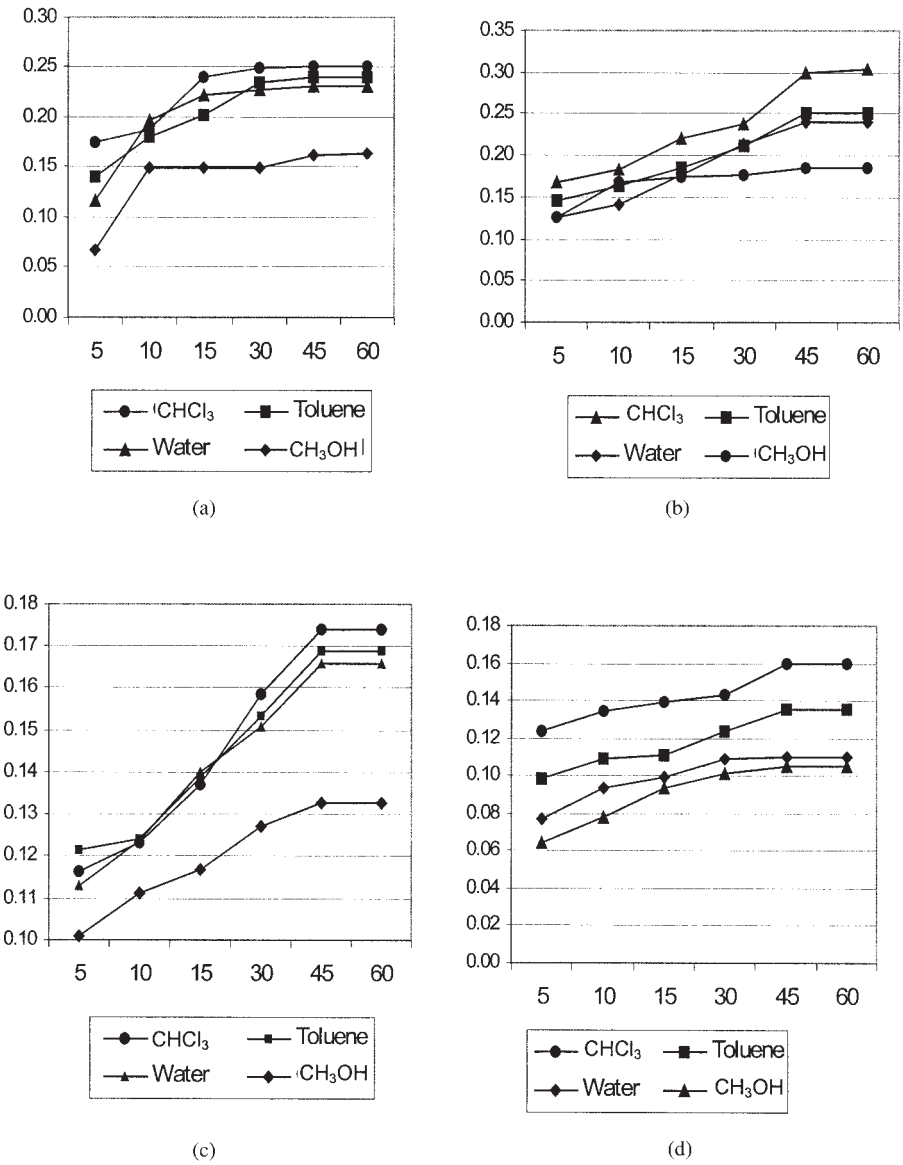

Figure 4 Rate of release of benzoic acid from HDDMA-crosslinked PA encapsulated with benzoic acid. The *X* axis represents time in minutes, and the *Y* axis represents the weight of benzoic acid in grams released per gram of polymer. AA–HDDMA–C_6H_5COOH = (a) 5, (b) 10, (c) 15, and (d) 20%.

investigated (i.e., chloroform, toluene, water, and methanol).

For the guest-encapsulated DVB-crosslinked PA, the amount of benzoic acid released (and hence encapsulated) was higher for the 15 mol % sample than for the 10 mol % sample; this value decreased in the 20 mol % sample in the presence of the four solvents we investigated. These phenomena could be best explained on the basis of a Flory–Rehner analysis of the swelling data of the free-polymer and guest-encapsulated polymer systems.

TABLE III
Solubility Parameters of the Solvents

Solvent	δ_d	δ_P	δ_h	$\delta = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2}$
$CHCl_3$	8.65	1.5	2.8	9.21
C_6H_5—CH_3	8.82	0.7	1.0	8.90
H_2O	7.42	6.0	10.9	14.48
CH_3OH	6.0	15.3	16.7	23.43

δ_d = dispersive force; δ_p = polar force; δ_h = hydrogen bonding.

Swelling behavior: Flory–Rehner analysis

The phenomenon of gel swelling has been the subject of numerous studies in polymer physics. It has been demonstrated that minute changes in the external conditions, including temperature, solvent condition, ionic strength, and external electric field, can induce

TABLE IV
Swelling Behavior of DVB-Crosslinked PA Hydrogels Encapsulated with Benzoic Acid

Solvent	Weight of the swollen polymer (g) with various crosslink densities							
	5%		10%		15%		20%	
	Free polymer	Host–guest system	Free polymer	Host–guest system	Free polymer	Host–guest system	Free polymer	Host–guest system
Cyclohexane	0.2138	0.2100	0.2180	0.2100	0.2200	0.2000	0.2186	0.2000
Chloroform	0.2200	0.2200	0.2200	0.2180	0.2317	0.2100	0.2256	0.2100
Toluene	0.2400	0.2110	0.2320	0.2100	0.2178	0.2008	0.2103	0.2009
90% CH_3COOH + 10% H_2O	6.8325	2.1600	4.0060	2.3148	4.6382	1.3122	3.5002	0.4730
80% CH_3COOH + 20% H_2O	6.7681	2.1520	3.9382	2.2360	4.7862	1.2486	3.5218	0.5068
60% CH_3COOH + 40% H_2O	5.2538	1.8700	3.8560	1.7728	4.9380	1.0550	3.1010	0.5760
40% CH_3COOH + 60% H_2O	4.8938	1.5552	2.1313	1.4128	3.8930	1.0280	2.9816	0.6458
CH_3COOH	6.5320	1.7120	3.7881	2.1888	3.9816	1.3460	3.5138	0.6321
HCOOH	7.3400	2.4060	4.1800	2.4190	5.2650	1.3770	3.6304	0.5638
H_2O	2.7360	1.0120	2.8931	1.1502	2.3160	0.6822	2.1818	0.4798

Mass of dry polymer = 0.2 g.

drastic changes in the state of the swollen network.[12–15]

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

The analysis of the swelling data (Tables IV and V) was done with the help of Flory–Rehner theory.[16,17] The Flory–Rehner treatment of the swelling of a polymer network based on the assumption of additivity of the free energy of mixing and the free energy of elasticity leads to the expression

$$M_c = \frac{\rho_p \rho_s V_s V_r^{1/3}}{\ln(1 - V_r) + V_r + \chi V_r^2}$$

for a phantom model[4,18] network, where ρ_p is the density of the polymer, ρ_s is the density of the solvent, V_s is the molar volume of the solvent, V_r is the volume fraction of the polymer in the swollen gel at equilibrium, and χ is the polymer–solvent interaction parameter. The density of the polymer was determined by the pycnometric method. The polymer–solvent interaction parameter for the free polymer was taken from the literature.[19] The molecular weight between crosslinks (M_c) was calculated for each polymer, and the results show that for HDDMA-crosslinked PA, the M_c value for the 10% crosslinked polymer was higher than for the 20% crosslinked polymer (Table VI). The molecular weight decreased in the order 15 > 20%; that is, the free space available for the 10 mol % sample was the maximum. It has been pointed out experimentally[20,21] and theoretically[22,23] that AA-based hydrogels exhibit inhomogeneous crosslink distribution. A significant fraction of the pendant vinyl groups is consumed by cyclization and multiple

TABLE V
Swelling Behavior of HDDMA-Crosslinked PA Hydrogels Encapsulated with Benzoic Acid

Solvent	Weight of the swollen polymer (g) with various crosslink densities							
	5%		10%		15%		20%	
	Free polymer	Host–guest system	Free polymer	Host–guest system	Free polymer	Host–guest system	Free polymer	Host–guest system
Cyclohexane	0.2320	0.2120	0.2320	0.2200	0.2500	0.2044	0.2320	0.2230
Chloroform	0.2110	0.2100	0.2068	0.2030	0.4300	0.2200	0.2300	0.2100
Toluene	0.2400	0.2000	0.2300	0.2000	0.3000	0.2100	0.2200	0.2008
90% CH_3COOH + 10% H_2O	5.0000	1.8800	4.7746	1.4810	1.4800	1.1066	1.9852	0.8536
80% CH_3COOH + 20% H_2O	5.3400	1.9016	5.4112	1.3520	1.2100	1.0490	1.7730	0.9964
60% CH_3COOH + 40% H_2O	4.7700	1.5700	4.7264	1.3110	1.0870	1.0070	1.3600	1.0868
40% CH_3COOH + 60% H_2O	3.4550	1.2580	3.9498	1.0200	1.0090	0.5840	1.1638	0.7012
CH_3COOH	5.1500	1.5532	5.9648	1.1800	1.2500	1.0278	1.7400	0.8654
HCOOH	6.0600	2.1010	6.3512	1.5318	1.3700	1.1412	2.4122	0.9274
H_2O	2.7760	0.7104	2.6904	0.7201	0.7090	0.6368	0.7440	0.8880

Mass of dry polymer = 0.2 g.

TABLE VI
M_c Values of PA Hydrogels and the Host–Guest Systems

Crosslinking (mol %)	M_c			
	HDDMA-crosslinked PA		DVB-crosslinked PA	
	Free polymer	Host–guest system	Free polymer	Host–guest system
5	2.338×10^5	1.0213×10^4	1.0936×10^5	1.58×10^3
10	2.451×10^5	5.127×10^3	5.9587×10^4	1.3426×10^4
15	1.4712×10^4	3.4021×10^3	8.5077×10^4	8.5858×10^3
20	1.4127×10^4	2.4629×10^3	3.5836×10^4	1.3214×10^3

crosslinking reactions; this must have been responsible for the inhomogeneous crosslink distribution in the PA hydrogels.[24] Also, as shown in the release studies, the amount of benzoic acid released was at a maximum for the 10 mol % sample and then decreased in the order 5 > 15 > 20%.

For DVB-crosslinked PA, the M_c value for the 15 mol % crosslinked polymer was higher than for the 10 mol % polymer; then, M_c decreased for the 20 mol % crosslinked polymer. As shown in the release studies, the amount of benzoic acid released was higher for the 15 mol % crosslinked polymer than for the 10 mol % crosslinked polymer.

M_c for the DVB-crosslinked polymer was higher than for the HDDMA-crosslinked PA; that is, the number of voids available for the DVB-crosslinked polymer was higher than for the HDDMA-crosslinked PA. Hence, more benzoic acid could be encapsulated in the DVB-crosslinked PA, and the experimental results confirm this. The amount of benzoic acid released was higher for the guest-encapsulated DVB-crosslinked PA than for the guest-encapsulated HDDMA-crosslinked PA. Thus, the mesh widths were suitable for the DVB-crosslinked polymer to incorporated the benzoic acid molecule.

M_c for the guest-encapsulated HDDMA-crosslinked PA decreased in the order 5 > 10 > 15 > 20 mol % as expected. As the percentage of crosslinking agent increased, the crosslink density increased and M_c decreased as expected. For the guest-encapsulated DVB-crosslinked PA, M_c was higher for the 10 mol % sample than for the 5 mol % sample. This was because the amount of benzoic acid encapsulated in the 10 mol % polymer was much smaller than that in the 5 mol % polymer.

The amount of benzoic acid encapsulated in 10% DVB-crosslinked PA was very low compared to that in the 5 and 10% crosslinked polymers. Hence, M_c for the encapsulated polymer followed the order 10 > 15 > 5 > 20%.

CONCLUSIONS

Encapsulation studies were carried out on PA hydrogels. Simple but novel guest-encapsulated PA hydrogels were prepared with AA as the monomer, HDDMA and DVB as the crosslinking agents with varying crosslink densities (i.e., 5, 10, 15, and 20 mol %), and benzoic acid as the encapsulant. Polymerization was done by the solution polymerization method, and the products were characterized by IR spectral analysis. During polymerization, the solvent (2:1 v/v of water and methanol) acted as the pore-forming agent for a proper mesh width, and the guest was successfully encapsulated in the voids of the network polymer.

The release of encapsulated benzoic acid was studied in different solvents, including chloroform, toluene, water, and methanol. The rate of release of benzoic acid depended on the different types of interaction between the solvent and the polymer. The release was at a maximum in chloroform and decreased in the order toluene > water > methanol for the HDDMA-crosslinked polymer; the order of release was toluene > chloroform > water > methanol for the DVB-crosslinked polymer. Chloroform and toluene selectively penetrated into the cavities of the host–guest assembly by dispersion forces, and the release was higher in these solvents.

Flory–Rehner analysis of the swelling data of the free polymer and the HDDMA-crosslinked encapsulated polymer revealed that a phase change occurred in the 10% crosslinked free polymer in the presence of solvent and that M_c decreased in the order 10 > 5 > 15 > 20%. The amount of benzoic acid released followed the same order: 10 > 5 > 15 > 20% for all of the solvents. For the DVB-crosslinked polymer, the phase change occurred at 15%, and M_c decreased in the order 5 > 15 > 10 > 20%; the release of benzoic acid was also in the same order.

This study revealed that the entrapment of suitable guest molecules in the cavities of crosslinked polymers is possible and is similar to the formation of supramolecular assemblies. The structural architecture of the network polymers, its solvophobic–solvophilic interactions with various solvents and solvent mixtures, the release of the encapsulated guests under suitable conditions, and so on are the themes of this article. In an extension of this study, the functional and isomerizational changes of the guest within the

cavities, their mechanisms, the rejection of the guest by the host during these changes, and so on, will be examined.

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