

The Synthesis of Nonporous Poly(isobutyl methacrylate) Microspheres by Suspension Polymerization Technique and Investigation of Their Swelling Properties

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ABSTRACT: Poly(isobutyl methacrylate) (PiBMA) microspheres with different crosslinking densities were synthesized by suspension polymerization technique in aqueous medium and their characterization and swelling behaviors in different solvents were investigated. PiBMA spheres with a 800- to 1500- μm -diameter range were obtained by using benzoyl peroxide (BPO) as polymerization initiator, 1/5 ratio of monomer/water in volume, tricalcium phosphate (TCP), and poly(*N* vinyl-2-pyrrolidone) (PVP) as suspension stabilizer with 350 rpm stirring rate in nitrogen atmosphere. The influence of type and amount of crosslinking agent on the swelling properties and diffusional behavior, diffusion coefficient, and network properties of the spheres were examined in pentane, hexane, heptane, and gasoline. Dynamic swelling behaviors of crosslinked spheres were determined by measuring the diameter of the sphere as a function of time by an optical microscope. Swelling behaviors and network properties were found to be dependent on the diameter, crosslinking density of the sphere, and crosslinking agent and solvent. The results of this study indicate that the crosslinked PiBMA microsphere can be swollen in gasoline very well and retains a high ratio (1500% of its volume) of gasoline in their structure. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 349–356, 2002

Key words: microspheres; poly(iso-butyl methacrylate); suspension polymerization; swelling behavior; swelling kinetics; gasoline uptake

INTRODUCTION

Ever since their introduction into the scientific world, microspheres have found large applications in the biomedical field and immobilization of enzymes, for the encapsulation of mammalian cells, immunochemical studies, and the controlled release of pharmaceuticals.^{1–3} Recently, macroporous microspheres were used as sorbents to remove some metal ions.⁴ Wang and his coworkers⁵ produced sodium polyacrylate as superwater-adsorbent.

There are three main methods used for the production of microspheres, suspension, emulsion, and dispersion polymerization. These methods mainly differ from each other by the diameter of the product.⁶ Today, a large variety of techniques that are used in the production of microspheres, such as seed emulsion polymerization, exists that are based on these three main methods.

This large application field prompted us to use these useful beads for the environmental application and we prepared poly(iso-butyl methacrylate) (PiBMA) microspheres to investigate their uptake capacity and swelling behavior in various light-molecular-weight hydrocarbons. We produced spheres with a 800- to 1500- μm -diameter range and having different crosslinking densities by suspension poly-

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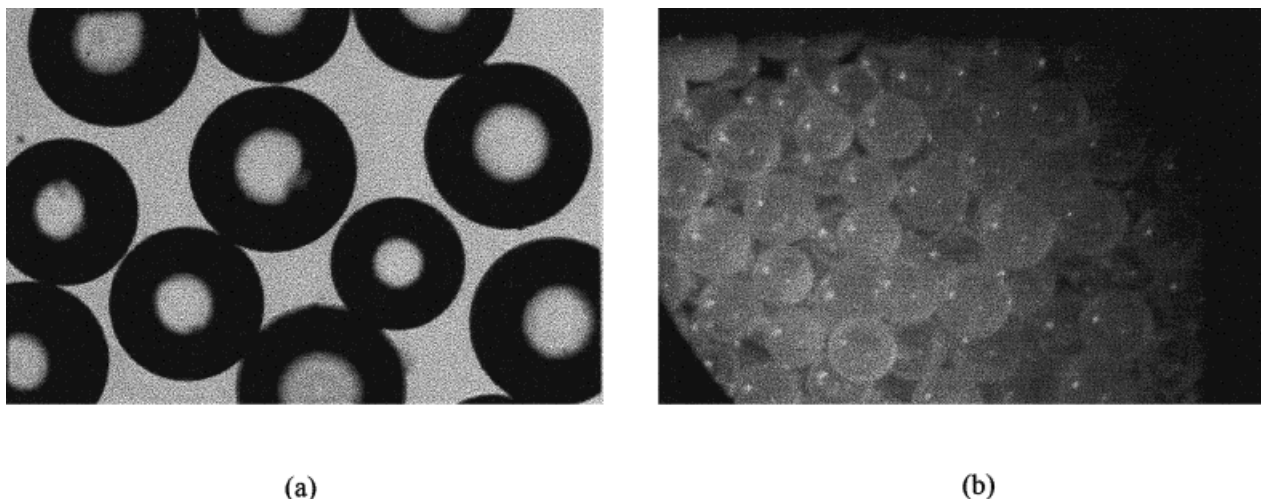


Figure 1 (a) Optical microscope photograph of PiBMA microspheres. (b) Binocular photograph of PiBMA microspheres.

merization technique. By using two crosslinking agents having same functionality (double) but different chain length, namely, ethylene glycol dimethacrylate (EGDMA) and butanediol dimethacrylate (BDDMA), we investigated the influence of the crosslinking agent on the network structures and swelling behaviors of the spheres.

EXPERIMENTAL

Materials

The iso-butyl methacrylate (i-BMA) monomer, supplied from Merck (Darmstadt, Germany), was puri-

fied by passing it through active alumina. The crosslinking agents (EGDMA and BDDMA) were purified by the same method. Benzoyl peroxide (BPO) initiator supplied from BDH (Poole, England) was purified by recrystallization twice from methanol before use. Poly(2-*N*-vinyl pyrrolidone) (PVP) and tricalcium phosphate (TCP) obtained from BDH and Merck, respectively, were selected as suspension stabilizers and used without further purification. Distilled water was the dispersion medium.

Polymerization Method

PiBMA spheres were produced with the suspension polymerization method described in detail

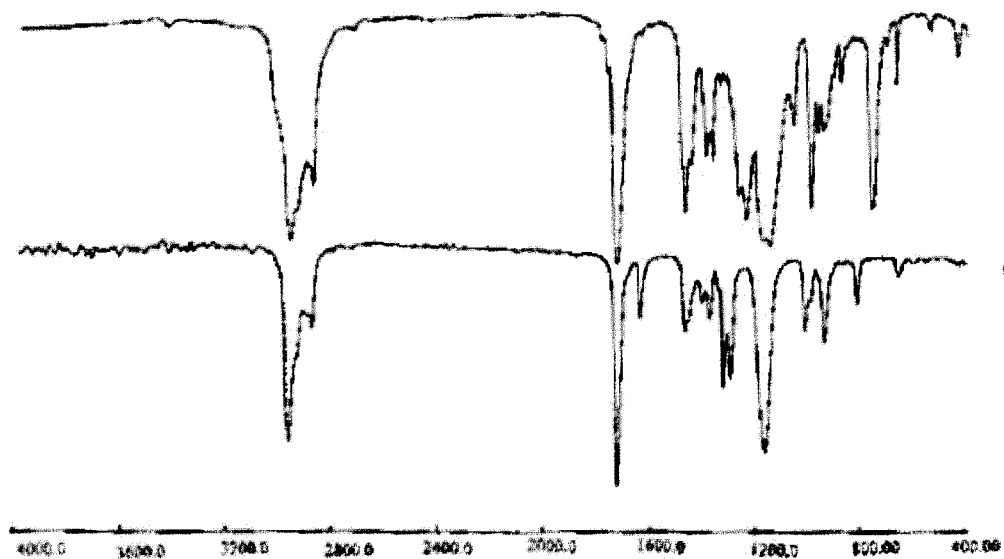


Figure 2 FTIR spectra of isobutyl methacrylate and poly(isobutyl methacrylate).

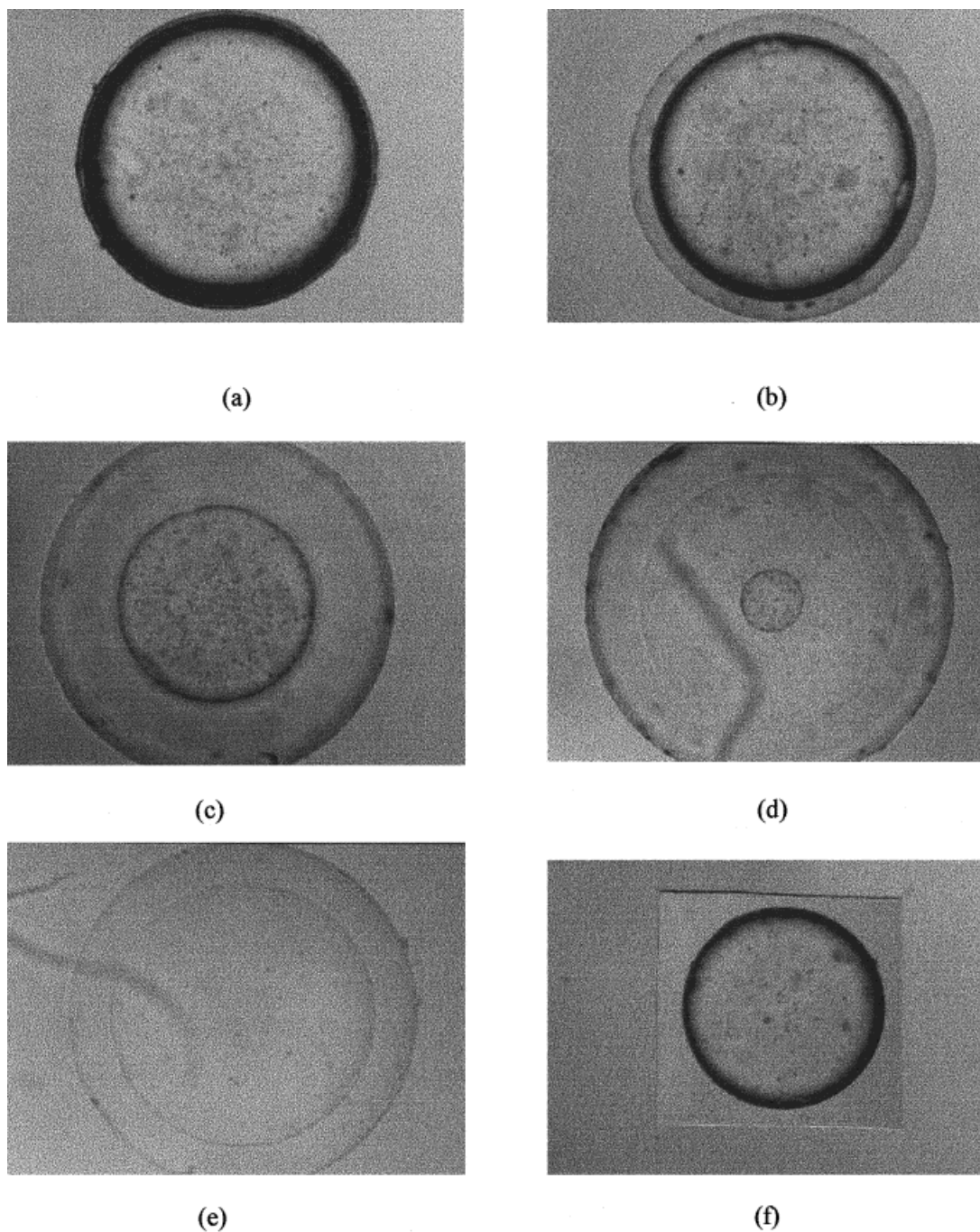


Figure 3 Optical microscope photographs of solvent diffusion into PiBMA spheres. (a) Before swelling; (b) 10 min; (c) 30 min; (d) 120 min; (e) equilibrium; (f) after solvent release (solvent; *n*-hexane).

elsewhere.⁷⁻⁸ To obtain PiBMA spheres with an average diameter of 800-1500 μm , the following procedure was applied. The monomer/water ratio selected as 1/5 by volume and dispersion medium was prepared by dissolving predetermined amounts of PVP and TCP in distilled water. The

initiator concentration was selected as 1 g BPO/100 g i-BMA, and then crosslinking agent was added to monomer phase. The monomer phase was then transferred into dispersion medium placed in a mechanically stirred (at a constant stirring rate) round-bottom cylindrical reactor

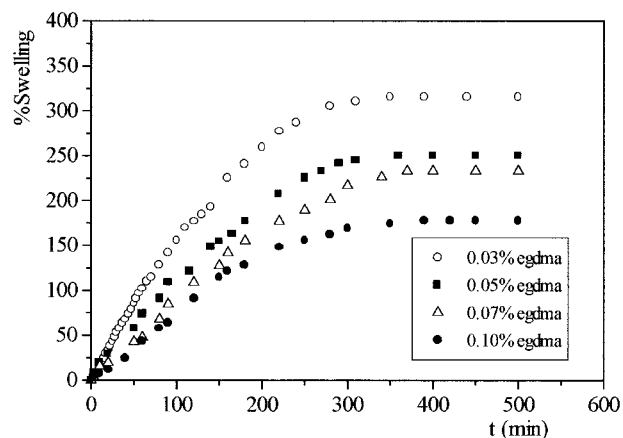


Figure 4 Dynamic swelling curves of crosslinked PiBMA spheres in *n*-hexane (crosslinking agent; EGDMA).

which was thermostatically controlled to $\pm 1^\circ\text{C}$. All experiments were carried out in nitrogen atmosphere at 70°C . The experimental conditions described above were set after some preliminary trials of different conditions to achieve an average sphere size of $800\text{--}1500\ \mu\text{m}$.⁹ After completion of the polymerization, the spheres were cleaned by several washing steps with water and alcohol and then dried in a vacuum oven.

Characterization of PiBMA Spheres

FTIR spectra of the noncrosslinked and crosslinked PiBMA particles were obtained by using a Nicolet 520 FTIR spectrophotometer. The microspheres and KBr were thoroughly mixed and

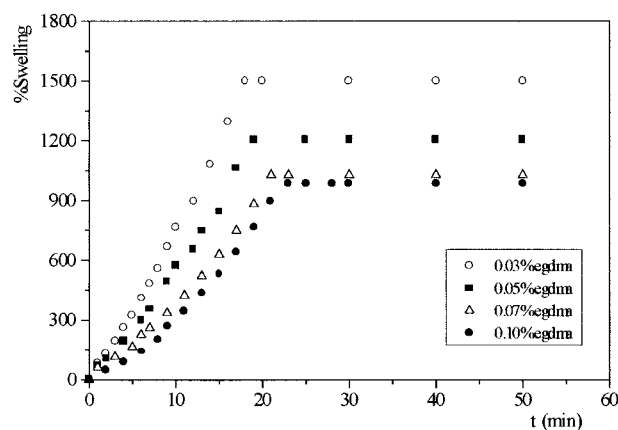


Figure 5 Dynamic swelling curves of crosslinked PiBMA spheres in gasoline (crosslinking agent; EGDMA).

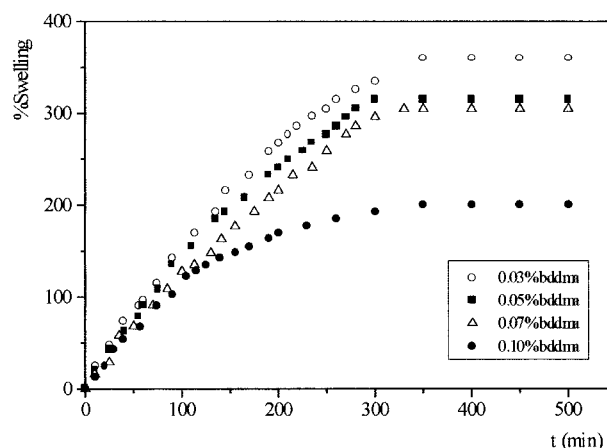


Figure 6 Dynamic swelling curves of crosslinked PiBMA spheres in *n*-hexane (crosslinking agent; BD-DMA).

this mixture was pressed to form a disk and the spectrum was recorded.

Dynamic swelling behaviors of crosslinked spheres were determined by measuring the diameter of spheres as a function of time by an optical microscope at room temperature.

RESULTS AND DISCUSSION

Structural Characterization

At the end of the polymerization procedure described above, we obtained PiBMA spheres with perfect spherical geometry. Figure 1 shows the optical photograph of these spheres. Achievement

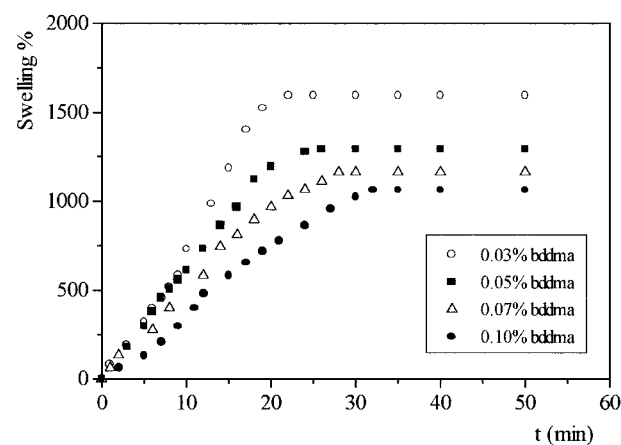


Figure 7 Dynamic swelling curves of crosslinked PiBMA spheres in gasoline (crosslinking agent; BD-DMA).

of complete conversion of monomer into polymer and thorough rinsing with water and alcohol have led to the formation of nonsticking microspheres. FTIR spectra of the i-BMA and PiBMA spheres showed the disappearance of the C=C band observed at 1630 cm^{-1} in the spectra of monomer, in the spectra of polymer (Fig. 2).

Swelling

The PiBMA spheres prepared in this study had a crosslinked network structure. Therefore, the matrix does not dissolve in a typical solvent of the base polymer but swells depending on the degree of crosslinking density. The swelling behavior is also dependent on the chain length of the crosslinking agent, so we used EGDMA and BDDMA as crosslinking agents to investigate swelling behaviors of spheres. Four solvents, *n*-pentane, *n*-hexane, *n*-heptane, and gasoline, were used to determine the swelling behaviors of the spheres having different crosslinking densities. The kinetics of volume swelling was followed by measuring the radius of the spheres with time in the particular solvent. The following equation was used to calculate the percentage volume swelling:

$$\begin{aligned} \% \text{ Swelling} &= [(V_t - V_i)/V_i] \times 100 \\ &= [(R_t^3/R_i^3) - 1] \times 100 \quad (1) \end{aligned}$$

Here, V_i , V_t , R_i , and R_t show the volume and diameter of spheres initially and at time t , respectively. Optical microscope photographs which illustrate the solvent diffusion into PiBMA spheres with time are given in Figure 3.

Figure 4-7 show the swelling behaviors of the PiBMA spheres crosslinked with EGDMA and BDDMA swollen in gasoline and *n*-hexane. The

Table I Variation of Maximum Swelling Values of PiBMA Microspheres with the Concentration of Crosslinking Agent (EGDMA)

Amount of Crosslinking Agent (wt %)	Equilibrium Swelling			
	Pentane	Hexane	Heptane	Gasoline
0.03	185	315	366	1498
0.05	170	250	305	1205
0.07	163	233	250	1025
0.1	155	178	185	987

Table II Variation of Maximum Swelling Values of PiBMA Microspheres with the Concentration of Crosslinking Agent (BDDMA)

Amount of Crosslinking Agent (wt %)	Equilibrium Swelling			
	Pentane	Hexane	Heptane	Gasoline
0.03	208	345	381	1596
0.05	193	315	342	1291
0.07	185	305	315	1161
0.1	163	200	250	1063

maximum % swelling values obtained from these curves are collected in Table I and II for all solvents. As is seen from these figures and tables, by increasing the amount of crosslinking agent, % swelling decreases. Initial rates of swelling also decrease with increasing concentration of crosslinking agent. It is also observed that the equilibrium swelling increases in the order *n*-pentane < *n*-hexane < *n*-heptane < gasoline. This can be explained by considering the solubility parameter of the PiBMA for the solvents used in the swelling experiments, which is a measure of hydrophobic interaction between PiBMA polymers and the solvents used in this work. It is well known that the swelling occurs more easily when the solubility parameters of a solvent and polymer matrix are close to each other. The solubility parameters of solvents used here are as follows: 7.0, 7.3, 7.4 (cal/cm^3)^{1/2} for pentane, hexane, and heptane, and 8.5–11.1 (cal/cm^3)^{1/2} for PiBMA.¹⁰ Because the value of heptane and PiBMA are closer to each other, maximum swelling is observed in heptane rather than pentane and hexane. However, the highest value of % swelling was obtained in gasoline, 1500% of original dry volume. Furthermore, equilibrium swelling time of microspheres in gasoline is almost 10 times shorter than in other solvents used. This unique and unexpected behavior of PiBMA microspheres for uptaking very large volumes of gasoline seemed to be a promising application for removing gasoline from aqueous mixtures. No solubility parameter value is available for gasoline in the literature. It is well known that gasoline is composed of a mixture of many organic aliphatic and aromatic compounds. So, the total value of solubility parameters becomes closer to PiBMA.

Diffusion

The following equations are used to determine the nature of diffusion of the selected model solvents

Table III Diffusional Exponent and Diffusion Mechanism

Diffusion Type	$n_{\text{thin film}}$	n_{cylinder}	n_{sphere}
Fickian	0.5	0.45	0.43
Anormal (non-Fickian)	$0.50 < n < 1.00$	$0.45 < n < 1.00$	$0.43 < n < 1.00$
Zero order	1.00	1.00	1.00

(pentane, hexane, heptane, and gasoline) into PiBMA spheres:

$$M_t/M_\infty = kt^n \quad (2)$$

where M_t is the amount of solvent diffused in the spheres at time t and M_∞ is the amount of solvent at equilibrium. k is the constant incorporating characteristic of the macromolecular network system and penetrant. n is the diffusional exponent, which indicates the transport mechanism. This equation is valid for the first 60% of the fractional uptake¹¹⁻¹² and is determined by using the equation given below for the spheres:

$$M_t/M_\infty = (r_e^3 - r_i^3)/r_{e,\infty}^3 = kt^n \quad (3)$$

where r_e is the external radius, r_i is the inner radius, and $r_{e,\infty}$ is the maximum radius reached at equilibrium. By plotting $\ln M_t/M_\infty$ versus $\ln t$ graphs, n exponent can be calculated from the slope of the line. The value of n varies with the shape of the material. Table III shows the relationship between n and the geometry of the system.

For all systems $\ln M_t/M_\infty$ versus $\ln t$ graphs were constructed and the value of n was calculated. Table IV and V show the value of n for the systems containing different types and amounts of crosslinking agent. As it can be seen from the

table, the diffusion of the solvent into PiBMA spheres shows generally non-Fickian character and also zero order for the spheres containing relatively higher amounts of crosslinking agent, which implies that relaxation and diffusion times are of the same order of magnitude.

The diffusion coefficient of the selected solvent into PiBMA spheres were calculated from the following equation by short-time approximation:

$$M_t/M_\infty = 6[Dt/\pi a^2]^{1/2} - 3Dt/a^2 \quad (4)$$

where D is the diffusion coefficient in cm^2/min , t is the time of diffusion, and a is the radius of the sphere. By ignoring the second term, M_t/M_∞ versus $t^{1/2}$ graphs were plotted for the first 60% of swelling and D values were calculated from the slope of the lines. The values of diffusion coefficients determined for the PiBMA spheres containing different amounts and types of crosslinking agents are given in Tables VI and VII. As can be seen from these tables, the diffusion coefficient is inversely proportional to the molecular weight of the penetrant. As the mesh size of crosslinked network is reduced through higher concentrations of crosslinking agents, the diffusion coefficient of all three solvents showed considerable decreases. We were not able to identify the exact composition of gasoline used in this work; however, because gasoline contains many kinds of

Table IV Variation of n With the Amount of Crosslinking Agent (EGDMA) and Type of Solvent

Amount of Crosslinking Agent (wt %)	Diffusional Exponent			
	Pentane	Hexane	Heptane	Gasoline
0.03	0.62	0.68	0.69	0.73
0.05	0.82	0.84	0.86	0.89
0.07	0.85	0.87	0.89	0.91
0.1	0.90	0.91	0.99	1.01

Table V Variation of n With the Amount of Crosslinking Agent (BDDMA) and Type of Solvent

Amount of Crosslinking Agent (wt %)	Diffusional Exponent			
	Pentane	Hexane	Heptane	Gasoline
0.03	0.48	0.51	0.55	0.63
0.05	0.59	0.63	0.69	0.75
0.07	0.66	0.70	0.78	0.86
0.1	0.72	0.79	0.87	0.97

Table VI Variation of D with the Amount of Crosslinking Agent (EGDMA) and Type of Solvent

Amount of Crosslinking Agent (wt %)	Diffusion Coefficient $\times 10^5$ (cm ² /min)			
	Pentane	Hexane	Heptane	Gasoline
0.03	4.65	4.38	3.97	9.92
0.05	3.41	3.10	2.76	8.99
0.07	2.53	2.36	2.32	8.68
0.1	2.12	2.12	1.98	7.13

aliphatic and aromatic compounds, there is a strong cooperative interaction between PiBMA and gasoline. This interaction causes an enhancement in the swelling in gasoline.

The diameter of the sphere is also effective in the diffusion of any solvent into the network structure. To investigate the effect of the diameter, PiBMA spheres having the same crosslinking density (0.03% EGDMA) but different diameters were swollen in pentane and values of n and D were calculated. Table VIII shows these values. As can be seen from these values, as the diameter of the sphere increases, the rate of the solvent diffusion coefficient decreases and the value of n increases.

Network Structure

Molecular weight between crosslinks (\bar{M}_c) is an important characteristic of crosslinked polymers. The average molecular weight between crosslinks is directly related to crosslinking density. There are several methods used in the determination of \bar{M}_c . One of them is the equilibrium swelling

Table VII Variation of D with the Amount of Crosslinking Agent (BDDMA) and Type of Solvent

Amount of Crosslinking Agent (wt %)	Diffusion Coefficient $\times 10^5$ (cm ² /min)			
	Pentane	Hexane	Heptane	Gasoline
0.03	5.06	4.55	4.25	10.15
0.05	4.65	4.21	3.71	9.55
0.07	3.35	2.70	2.44	9.16
0.1	2.62	2.40	2.18	7.85

Table VIII Variation of Diffusional Exponent and Diffusion Coefficient with Respect to Diameter of the PiBMA Sphere^a

Diameter (μm)	n	$D \times 10^5$ (cm ² /min)
700	0.49	12.1
1250	0.61	1.9
2500	0.69	1.1

^a PiBMA spheres that were used in this experiment contain 0.03% EGDMA and the experiment carried out in the pentane.

method. The Flory–Rehner equation is used to calculate \bar{M}_c according to the following equation:

$$\bar{M}_c = -V_1 \rho_p (\phi_p^{1/3} - \phi_p/2) / [\ln(1 - \phi_p) + \phi_p + \chi_1 \phi_p^2] \quad (5)$$

where \bar{M}_c is the number of average molecular weight between crosslinks, V_1 is the molar volume of solvent, ρ_p is the density of polymer, ϕ_p is volume fraction of polymer in swollen gel, and χ_1 is the Flory–Huggins polymer–solvent interaction parameter. The following equation is used to calculate

$$\phi_p := \frac{\text{volume of dry microsphere}}{\text{volume of swollen microsphere}} \quad (6)$$

Swelling ratio and crosslinking density are other important parameters used in the characterization of crosslinked polymers. The swelling ratio (S) is equal to $1/\phi_p$ and the crosslinking density is defined as the mole fraction of crosslinked units

$$q = M_0 / \bar{M}_c \quad (7)$$

Table IX Variation of Network Structure Parameters with the Amount of Crosslinking Agent (EGDMA)

Amount Crosslinking Agent (wt %)	ϕ	S	\bar{M}_c	Q	ρ
0.03	0.35	2.80	910	0.15	0.99
0.05	0.37	2.70	765	0.19	1.02
0.07	0.38	2.63	650	0.22	1.05
0.1	0.39	2.54	588	0.24	1.06

Table X Variation of Network Structure Parameters with the Amount of Crosslinking Agent (BDDMA)

Amount Crosslinking Agent (wt %)	ϕ	S	\bar{M}_c	Q	ρ
0.03	0.32	3.12	2100	0.06	0.99
0.05	0.34	2.94	1975	0.07	1.07
0.07	0.35	2.85	1755	0.08	1.09
0.1	0.38	2.59	1450	0.09	1.09

where M_0 is the molar mass of repeating units. By using eqs. (5), (6), and (7), \bar{M}_c , S , q , and ϕ_p values were calculated for selected solvents and the average values are given in Tables IX and X. As can be seen from these tables, the increase in the percentage of the crosslinking agent cause the \bar{M}_c to be decreased. Also, it can be observed that the \bar{M}_c values which were determined for the BDDMA have higher values than that of EGDMA. The reason for this observation is the relatively longer chain length of BDDMA.

CONCLUSION

PiBMA microspheres were synthesized by suspension polymerization technique. The influence of the structure of crosslinking agent and the solvent on the swelling behavior and properties were determined. It was also observed that all spheres resumed their original size and shape after swelling and deswelling in all solvents. This indicates that the same spheres can be used for the same purpose more than once. Swelling of

xerogels were investigated in three homologous light-weight hydrocarbons, namely, *n*-pentane, *n*-hexane, and *n*-heptane. Equilibrium swelling degrees display a direct relation with respect to molecular sizes of these hydrocarbons. The same microspheres were observed to swell 1500% of their original volumes when immersed in gasoline, which is an unexpected extent of swelling in this medium. Because of their rapid swelling to very high volumes in contact with gasoline, the microspheres are planned to be used in gasoline recovery from aqueous systems.

REFERENCES

1. Ugelstad, L.; Stenstad, P.; Kliaas, L.; Rian, A. *Macromol Symp* 1996, 101, 491–500.
2. Coutinho, F. M. B.; Cid, R. C. A. *Eur Polym J* 1990, 26, 1185–1188.
3. Kun, K. A.; Kunin, R. *J Polym Sci* 1968, 6, 2689.
4. Egawa, H.; Kabay, N.; Shuto, T.; Jyo, A. *J Appl Polym Sci* 1992, 46, 129.
5. Wang, G.; Li, M.; Chen, X. *J Appl Polym Sci* 1997, 65, 789.
6. Trommsdorf, E.; Munzer, M. *Polymerization Process*; Schildknecht, C. E., Skeist, I., Eds.; Wiley: New York, 1977.
7. Hohenstein, W. P.; Mark, H. *J Polym Sci* 1946, 1(6), 548.
8. Mendizabal, E.; Puig, J. E. *Polymeric Materials Encyclopedia*; Solomon, J. C., Ed.; Vol. 9, CRC Press: Boca Raton, FL, 1996; p 8215.
9. Bodugöz, H. M.S. Thesis, Hacettepe University, Ankara, Turkey, 1997.
10. Brandrup, J.; Immergut, E. H. *Polymer Handbook*, Third ed.; Wiley: New York, VII/517, V/126, 1989.
11. Peppas, N. A.; Colombo, P. *J Controlled Release* 1997, 45, 35–40.
12. Crank, J.; Park, G. S. *Diffusion in Polymers*; Academic Press: New York, 1968.