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Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
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D. Satyanarayana[a]; P. R. Chatterji[a]
[a] Division of Organic Coatings & Polymers, Indian Institute of Chemical Technology, Hyderabad, India

To cite this Article Satyanarayana, D. and Chatterji, P. R.(1992) 'Amphiphilic Graft Copolymer Matrices from Crosslinked Gelatin. I. Synthesis And Characterization', Journal of Macromolecular Science, Part A, 29: 8, 625 — 637
To link to this Article: DOI: 10.1080/10601329208052188
URL: http://dx.doi.org/10.1080/10601329208052188

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J.M.S.—PURE APPL. CHEM., A29(8), pp. 625–637 (1992)

AMPHIPHILIC GRAFT COPOLYMER MATRICES FROM CROSSLINKED GELATIN. I. SYNTHESIS AND CHARACTERIZATION†

D. SATYANARAYANA and P. R. CHATTERJI*

Division of Organic Coatings & Polymers
Indian Institute of Chemical Technology
Hyderabad 500007, India

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ABSTRACT

Amphiphilic matrices are synthesized by sequential graft copolymerization of crosslinked gelatin with methyl methacrylate and acrylic acid. Samples with a varying lipophilic to hydrophilic ratio (L/H values) could be synthesized by adjusting the grafting conditions. The materials have been extensively characterized with respect to their L/H values, frequency of grafting, molecular weights of the grafts, and swelling pattern. DSC and IR data are also presented.

INTRODUCTION

Polymeric amphiphilic matrices have deep implication in fields such as controlled release formulations, chromatographic separations, and multiphase reactions. Synthetic structural and functional aspects of a variety of amphiphilic macromolecular substances have been reported [1–5]. It is apparent that in many special applications an amphiphilic matrix has definite advantage over an exclusively hydrophilic or hydrophobic matrix. Our own earlier investigations included hydrophilic and hydrophobic graft copolymer matrices of crosslinked gelatin [6–9]. Here we report the synthesis and characterization of an amphiphilic matrix, with a crosslinked gelatin core and polymethyl methacrylate (PMMA) and polyacrylic acid

†IICT Communication No. 2725.

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(PAA) as the lipophilic (L) and hydrophilic (H) components. The desired L/H values could be easily achieved by carefully controlling the matrix-to-monomer feed ratio in the grafting medium.

EXPERIMENTAL

Bacteriological gelatin (Gel), methyl methacrylate (MMA), acrylic acid (AA), and glutaraldehyde (25% aqueous solution) were supplied by Loba Chemicals, Bombay. Potassium persulfate (KPS) and A.R. grade solvents were used as such. All reactions were carried out in oxygen-free distilled water.

Preparation of Crosslinked Gelatin (Gelx)

Gelatin was crosslinked by using aqueous glutaraldehyde as reported earlier [6]. The crisp granules were washed thoroughly with water, later with acetone, and then dried at 40°C under vacuum.

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Synthesis of Gelx-*g*-PMMA

Gelx was graft copolymerized with MMA in aqueous medium using KPS initiator at 70°C [6, 8]. The product was subjected to Soxhlet extraction with benzene to remove the homopolymer, PMMA, for 48 h. The material was rinsed with acetone, dried in a vacuum oven at 40°C, and weighed. The process was repeated until the material registered constant weight.

Synthesis of Amphiphilic Matrix (Gelx-$g^{\text{PMMA}}_{\text{PAA}}$)

Gelx-*g*-PMMA was graft copolymerized with acrylic acid in aqueous medium using potassium persulfate (KPS) as the initiator. The product was then freed of homopolymer PAA by continuous extraction in a Soxhlet unit by using water as the solvent for 48 h. The material was rinsed thoroughly with acetone and then dried in a vacuum oven at 40°C and weighed. The process was repeated until constant weight was obtained. These samples were encoded I to IV.

In a parallel set of experiments, Samples A to D were synthesized where the grafting sequence was reversed. That is, Gelx was first grafted with AA to get the Gelx-*g*-PAA matrix. Subsequently this was copolymerized with MMA to yield Gelx-$g^{\text{PAA}}_{\text{PMMA}}$. The other details remained exactly as described above.

Analysis of the Amphiphilic Matrix

This began with the destruction of the Gelx core by acid hydrolysis in 6 *N* HCl at 110°C for 24 h. The free PMMA and PAA grafts were separated by selective solvent extraction by using benzene and water, respectively, precipitated, and estimated gravimetrically. The polymers were purified by reprecipitation for molecular weight determination by viscosity methods [10]. The DSC of the samples were done in a Du Pont 9900 model DSC unit. The FTIR spectra were taken in a Perkin-Elmer 1730 IR spectrophotometer.

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TABLE 1. Structural Details of Amphiphilic Matrices

Sample	Percentage of grafting		L/H values	Molecular weight	Frequency of grafting, ν	Conditions of grafting
	PMMA	PAA				
I	212		1.05	1.3×10^5	6.59	Gelx = 250 g, MMA = 6.08 mol, water = 5 L, KPS = 0.1%, temperature = 70°C, time = 4 h
		202		8.9×10^3	91.92	Gelx-*g*-PMMA = 500 g, AA = 14.56 mol, water = 3 L, KPS = 0.2%, temperature = 70°C, time = 4 h
II	212		2.26	1.8×10^5	4.76	Gelx = 250 g, MMA = 6.08 mol, water = 5 L, KPS = 0.1%, temperature = 70°C, time = 4 h
		94		1.4×10^4	26.81	Gelx-*g*-PMMA = 100 g, AA = 1.46 mol, water = 600 mL, KPS = 0.3%, temperature = 70°C, time = 4 h
III	65		0.76	8.7×10^4	3.01	Gelx = 200 g, MMA = 1.41 mol, water = 2 L, KPS = 0.1%, temperature = 70°C, time = 4 h
		86		1.2×10^4	28.88	Gelx-*g*-PMMA = 125 g, AA = 3.28 mol, water = 600 mL, KPS = 0.375%, temperature = 70°C, time = 4 h
IV	115		1.60	1.1×10^5	4.22	Gelx = 100 g, MMA = 1.225 mol, water = 1 L, KPS = 0.1%, temperature = 70°C, time = 4 h
		72		1.8×10^4	16.00	Gelx-*g*-PMMA = 150 g, AA = 4.16 mol, water = 500 mL, KPS = 0.4%, temperature = 70°C, time = 4 h

TABLE 2. Compositional Analysis of Amphiphilic Matrices (percentages)

			PMMA		PAA				
Sample	L/H	Gelx	Calcd	Obsd	Calcd	Obsd	Residue	Total	Loss
I	1.05	19.4	41.2	25.4	39.2	27.6	15.7	88.1	11.8
II	2.26	24.6	52.2	24.7	22.9	17.5	24.1	90.7	9.2
III	0.76	39.6	25.7	13.1	34.1	26.1	10.1	89.1	10.8
IV	1.60	34.8	40	20.2	25	20	18.6	93.9	6.5

Calculations of Percentage Grafting, Frequency of Grafting, and Composition

Percentages of grafting of PMMA and PAA for samples were calculated with respect to the Gelx as follows:

$$\text{percent PMMA grafted} = \frac{100 \times \text{weight of PMMA grafted}}{\text{weight of Gelx taken}}$$

$$\text{percent PAA grafted} = \frac{100 \times \text{weight of PAA grafted}}{\text{weight of Gelx in the Gelx-}g\text{-PMMA taken}}$$

Appropriate changes were made for reverse grafted samples. L/H values were calculated as the ratio of percent PMMA grafted to percent PAA grafted in all cases.

Frequency of grafting (ν) is defined as the number of chains accommodated on a single gelatin chain length. Even though gelatin is in the crosslinked state, a reasonable approximation of ν can be derived from the following expression:

$$\text{frequency of grafting of PMMA } (\nu_{PMMA}) = \frac{\text{weight of PMMA grafted}}{\text{average molecular weight of PMMA}} \Big/ \frac{\text{weight of Gelx}}{\text{molecular weight of gelatin}}$$

The same calculation also applies to the evaluation of ν_{PAA}.

Compositions were calculated as percentages of Gelx, PMMA, and PAA based on the [Gelx-$g\langle^{PMMA}_{PAA}$] unit.

Solvent Uptake Studies

The swelling studies were monitored gravimetrically [11, 12]. For this, weighed pellets of the samples (ca. 0.3 g each) prepared under uniform hot compression conditions were immersed in different solvents, and the time-dependent increase in weight was recorded. The percent swelling was calculated as the ratio of increase in weight to original weight per 100 g.

RESULTS AND DISCUSSION

We earlier reported the grafting of crosslinked gelatin with hydrophilic and hydrophobic monomers [6-9], and there we discussed in detail the various factors affecting the percentage of grafting and grafting efficiency. These were taken as

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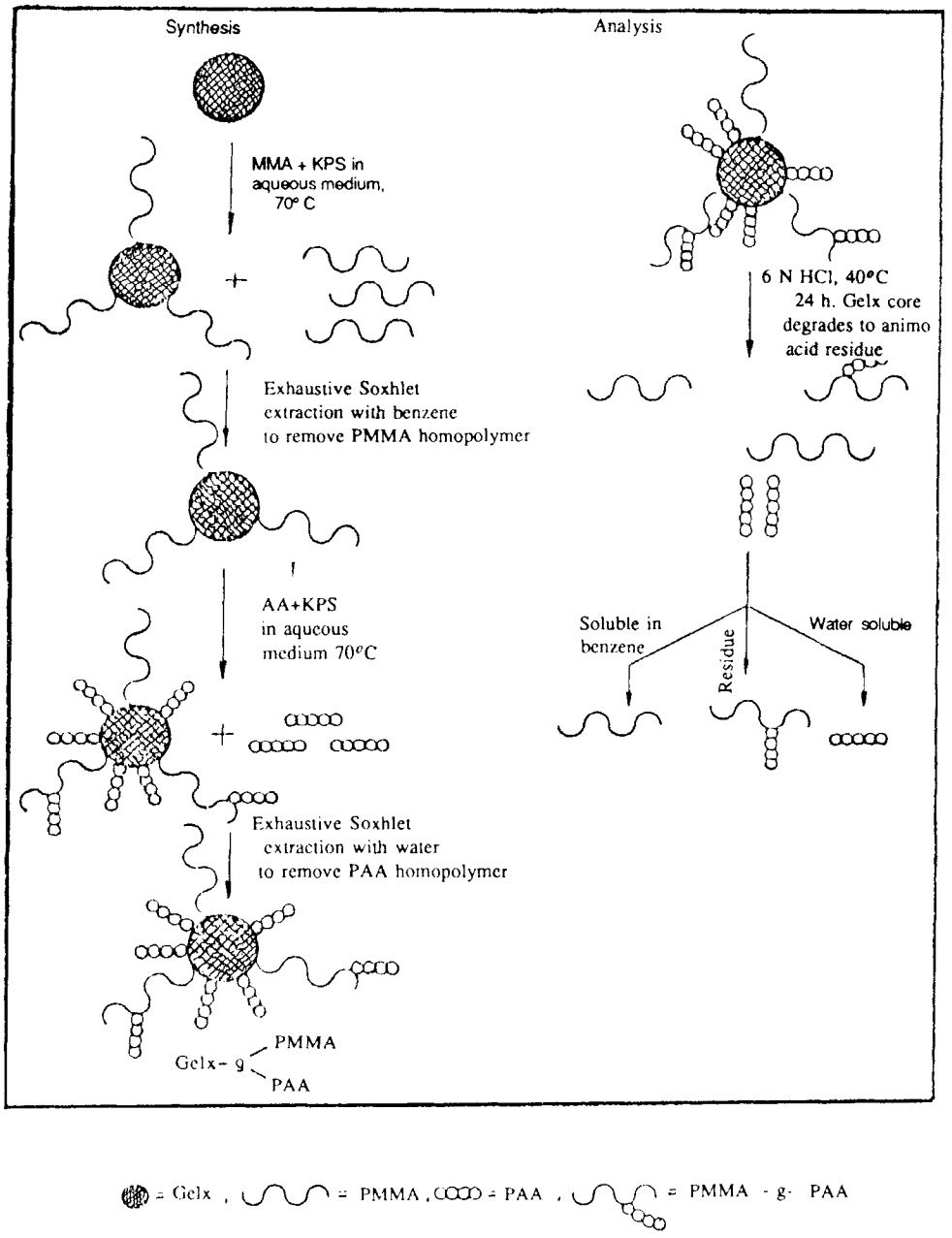

FIG. 1. Synthesis and analysis of amphiphilic graft copolymers.

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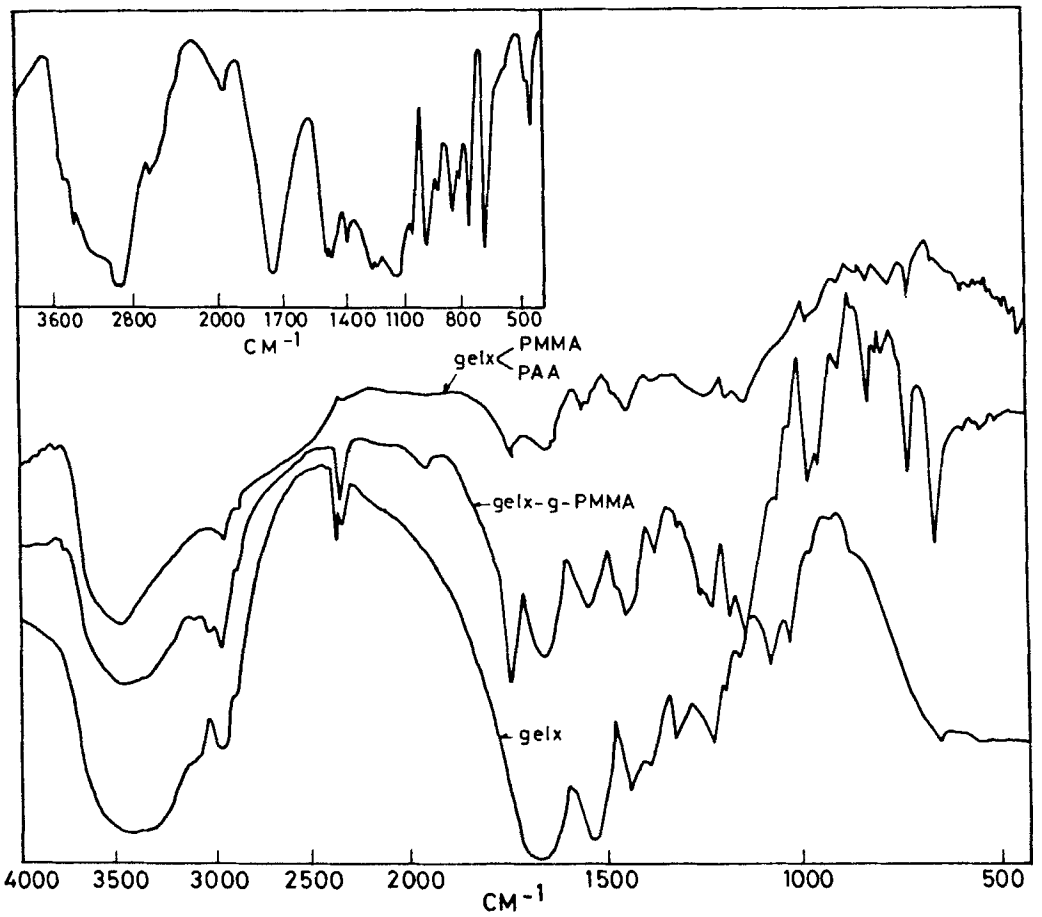

FIG. 2. FTIR spectra of graft copolymer samples. The inset shows the IR of the residue.

guidelines in fixing the appropriate reaction conditions to achieve specific L/H values. However, during the course of our investigations, we observed that the reaction conditions established for the (Gelx-KPS-AA) graft copolymerization system [9] were not directly applicable to the [(Gelx-*g*-PMMA)-KPS-AA] system. This is not surprising because Gelx and Gelx-*g*-PMMA have drastic functional differences. While Gelx is a hydrophilic system, Gelx-*g*-PMMA is predominantly hydrophobic, due to the introduction of the PMMA grafts. This necessitated modifications in the relative concentrations of Gelx-*g*-PMMA and the acrylic acid depending upon the extent of PMMA grafting.

Table 1 lists the percentage of grafting and grafting conditions together with other structural details like the L/H values, frequency of grafting, and the molecular weight of the grafts. While PMMA registers lower frequencies of grafting and higher average molecular weights, PAA registers comparatively higher frequencies of grafting and slightly lower average molecular weights. Though it is beyond our scope to provide an elaborate and convincing explanation for this at present, it

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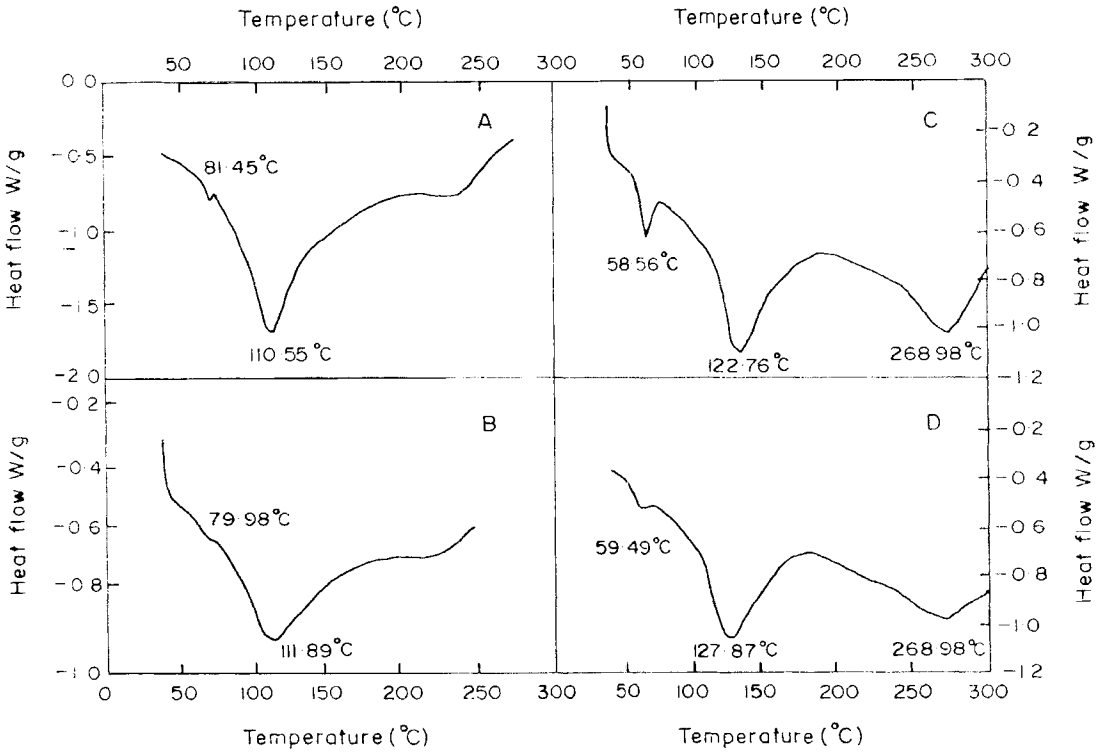

FIG. 3. DSC scan of (A) Gelx, (B) Gelx-*g*-PMMA, (C) Gelx-*g*-PAA, and (D) Gelx-$g\begin{smallmatrix}\text{PMMA}\\\text{PAA}\end{smallmatrix}$.

could be reasonably presumed that the solubility characteristics of the monomers and initiators as well as the extent of swellability of the matrix could be influencing factors [7, 8].

There is a finite possibility for some amount of PAA grafting onto the dangling PMMA chains. The compositional analysis of the graft copolymers reveals that this indeed is so (Table 2). Here we compare the theoretical PMMA and PAA contents of samples calculated on the basis of percentage of grafting with the values obtained from the actual analysis of the Gelx-$g\begin{smallmatrix}\text{PMMA}\\\text{PAA}\end{smallmatrix}$ matrix. The quantitative estimation of PMMA and PAA always left behind a considerable amount (10–25%) of residue insoluble in water, acetone, benzene, or THF, but swellable in these systems to different extents. Since the Gelx portion of the matrix, being a protein, suffers exhaustive degradation to the level of amino acid residues, the logical conclusion is that this residue is PMMA-*g*-PAA. This conclusion derives strong experimental support from the IR spectrum of the residue shown as the inset in Fig. 2. The absence of characteristic absorptions of Gelx, i.e., amide carbonyl ($\sim$1650 cm^{-1}) and —NH— (1550 cm^{-1} and above 3400–3500 cm^{-1} due to deformation and stretching), substantiates the total destruction of the protein core. This possibility is schematically represented in Fig. 1.

The FTIR and DSC data of typical samples are presented in Figs. 2 and 3. The FTIR spectra is mostly qualitative and not particularly informative. The

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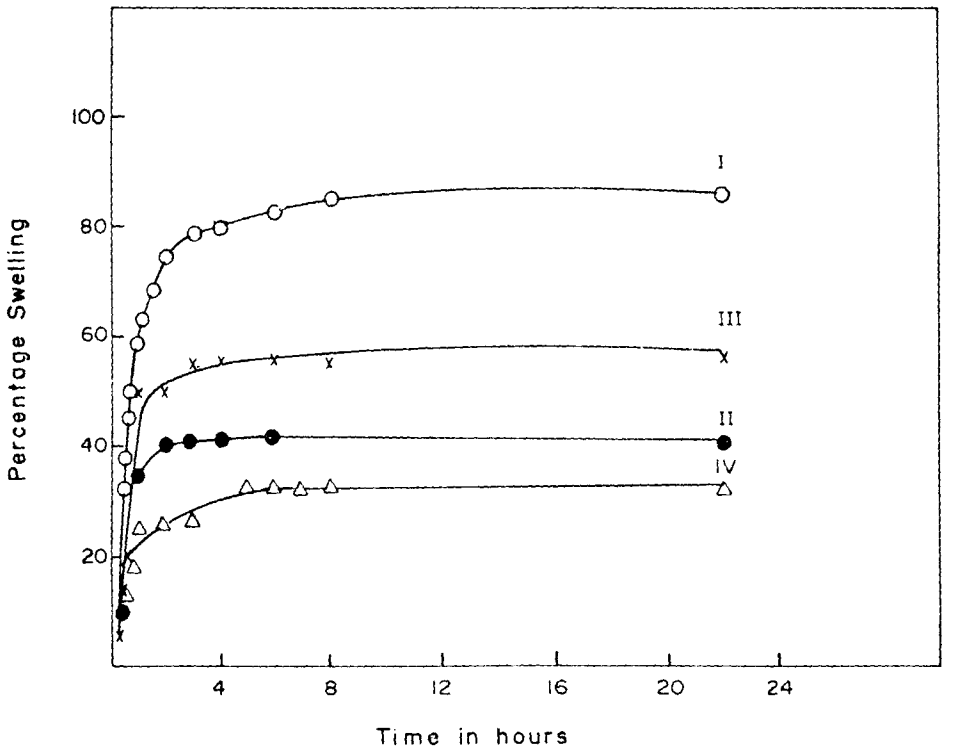

FIG. 4. Swelling profile of amphiphilic matrices in water. The compositions (PMMA: PAA) of I, II, III, and IV are 1.05, 2.26, 0.76, and 1.6, respectively.

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absorptions at 1652 cm^{-1} (amide carbonyl of Gelx), 3400–3500 and 1550 cm^{-1} (N—H stretching and deformation), 2952 and 1450 cm^{-1} (C—H stretching and deformation), and 1733 cm^{-1} (carbonyl moiety of ester/acid) conspicuously indicate grafting. However, it is difficult to independently identify the presence of PMMA and PAA segments in the double grafts because the carbonyl absorption is the characteristic of each moiety and they occur in close proximity, leading to overlapping.

The thermograms presented in Fig. 3 (A–D) should be considered together with the fact that the species are being identified at Gelx, Gelx-*g*-PMMA, and Gelx-$g\langle^{\text{PMMA}}_{\text{PAA}}$ stage. For comparison, we have included Gelx-*g*-PAA (Fig. 3C). Gelx-*g*-PMMA does not show any low temperature transition; hence the Gelx and Gelx-*g*-PMMA thermograms are virtually identical. Gelx-*g*-PAA suffers two prominent low temperature transitions which are the only conspicuous features of the Gelx-$g\langle^{\text{PMMA}}_{\text{PAA}}$ thermogram. Block and graft copolymers with sufficiently long chain segments tend to exhibit independent homopolymer behaviors [13]. Hence it is not surprising that in the temperature range studied in the thermogram of Gelx-$g\langle^{\text{PMMA}}_{\text{PAA}}$ includes the characteristics of PAA.

The coexistence of hydrophobic PMMA chains and hydrophilic PAA chains on a common scaffold enables the matrix to swell in both nonaqueous and aqueous media (Figs. 4 and 5, Table 3).

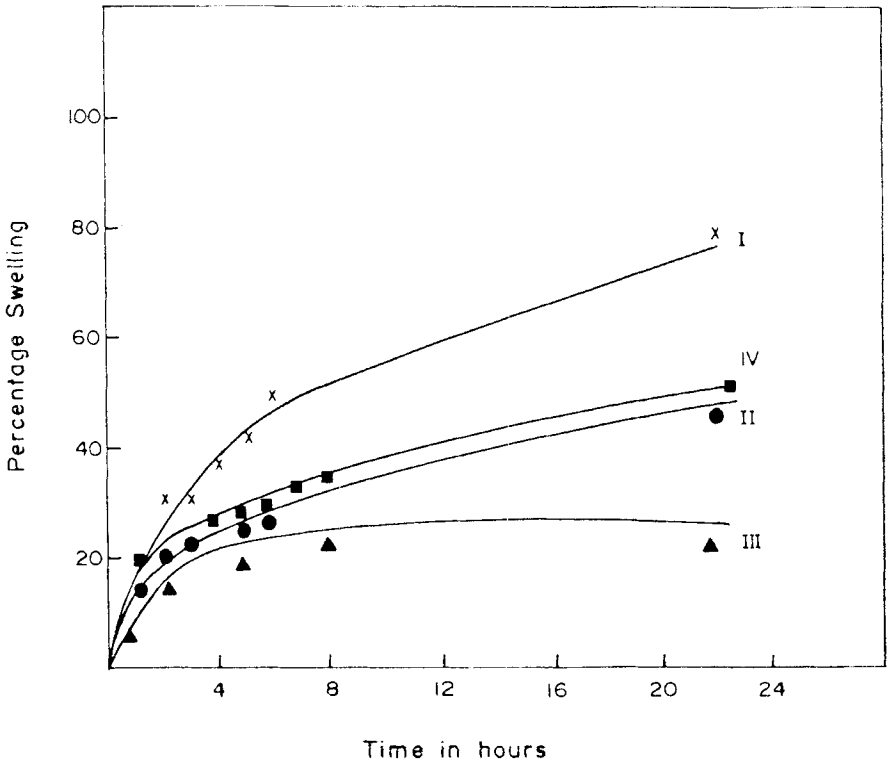

FIG. 5. Swelling of amphiphilic matrices in THF. The compositions (PMMA:PPA) of I, II, III, and IV are 1.05, 2.26, 0.76, and 1.6, respectively.

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In order to check whether the sequence of grafting influences the swelling profiles, we synthesized another set of samples (coded A to D) in which the grafting sequence was reversed; that is, PMMA was grafted onto the Gelx-*g*-PAA matrix. The structural and swelling details of four compositions, A to D, which match well with Samples I to IV, are given in Table 4 and Fig. 6. These studies suggest that the sequence of grafting together with the extent of grafting of each component could exert a synergistic influence on the swelling profile of the matrix. Solubility patterns

TABLE 3. Maximum Swelling (percentage)

		Solvent	
Sample	L/H	Ethanol	Chloroform
I	1.05	214	88
II	2.26	104	83
III	0.76	50	27
IV	1.6	80	50

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TABLE 4. Structural Details of Reverse Grafted Amphiphilic Matrices

Sample code	Percentage of grafting		L/H values	Molecular weight of grafts	Frequency of grafting	Conditions of grafting
	PAA	PMMA				
A	180		1.28	1.30×10^4	55.97	Gelx = 100 g, AA = 4.15 mol, water = 1.4 L, KPS = 0.3%, temperature = 70°C, time = 4 h
		231		2.65×10^5	3.52	Gelx-*g*-PAA = 200 g, MMA = 1.69 mol, water = 1.5 L, KPS = 0.1%, temperature = 70°C, time = 4 h
B	94		2.35	8.60×10^3	44.31	Gelx = 175 g, AA = 4.01 mol, water = 1.5 L, KPS = 0.2%, temperature = 70°C, time = 4 h
		222		3.57×10^5	2.51	Gelx-*g*-PAA = 105 g, MMA = 1.27 mol, water = 1.5 L, KPS = 0.1%, temperature = 70°C, time = 4 h
C	94		0.68	9.16×10^3	41.60	Gelx = 175 g, AA = 4.01 mol, water = 1.5 L, KPS = 0.2%, temperature = 70°C, time = 4 h
		65		2.16×10^5	1.21	Gelx-*g*-PAA = 150 g, MMA = 0.61 mol, water = 1 L, KPS = 0.1%, temperature = 70°C, time = 3 h
D	65		1.72	4.90×10^3	53.6	Gelx = 100 g, AA = 1.53 mol, water = 1.5 L, KPS = 0.2%, temperature = 70°C, time = 4 h
		112		3.30×10^5	1.37	Gelx-*g*-PAA = 125 g, MMA = 0.94 mol, water = 1.5 L, KPS = 0.1%, temperature = 70°C, time = 4 h

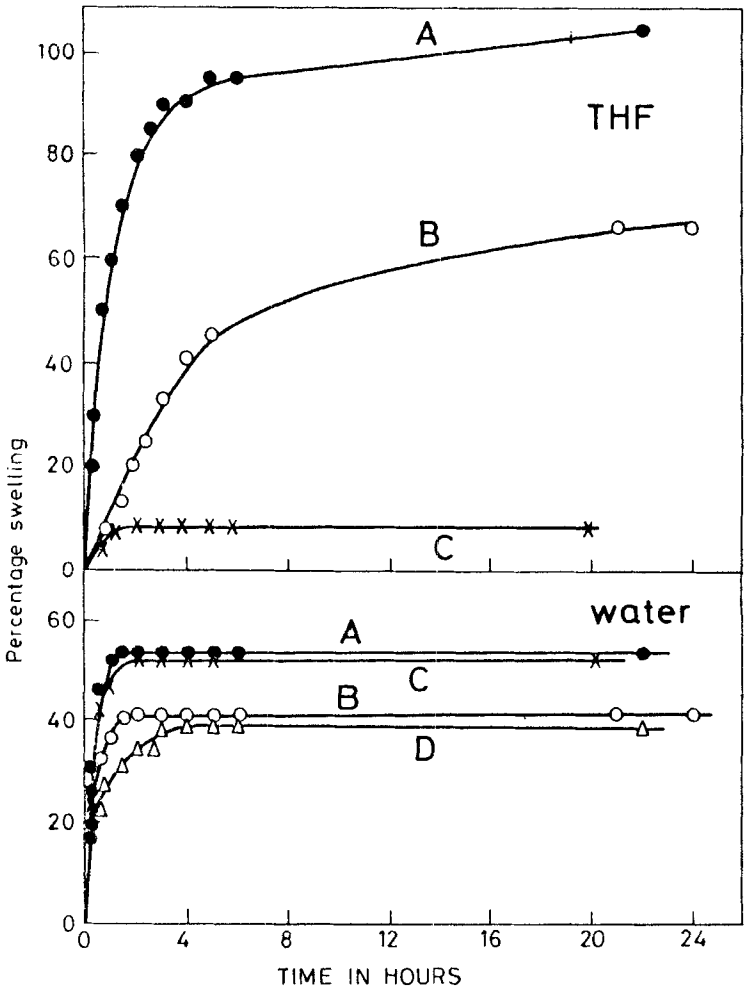

FIG. 6. Swelling of reverse grafted amphiphilic matrices in water and THF. The compositions (PMMA:PAA) of A, B, C, and D are 1.28, 2.35, 0.68, and 1.72, respectively.

of polymers often show inexplicable deviations. In this specific case, the contiguous hydrophilic and lipophilic segments could introduce a new dimension to the effective polymer/solvent interaction parameter for the system.

We attempted to gain some insight into this aspect by monitoring the swelling of the samples in ethanol–water mixtures. We calculated the solubility parameter of the mixed solvent according to the equation [14]

$$\delta_{mix} = \frac{X_A V_A \delta_A + X_W V_W \delta_W}{X_A V_A + X_W V_W} \tag{1}$$

where δ = solubility parameter, X = mole fraction of the solvent, V = volume of the solvent, the subscripts A and W denote alcohol and water, respectively. The equilibrium swelling values are plotted as a function of the δ values in Fig. 7. Both

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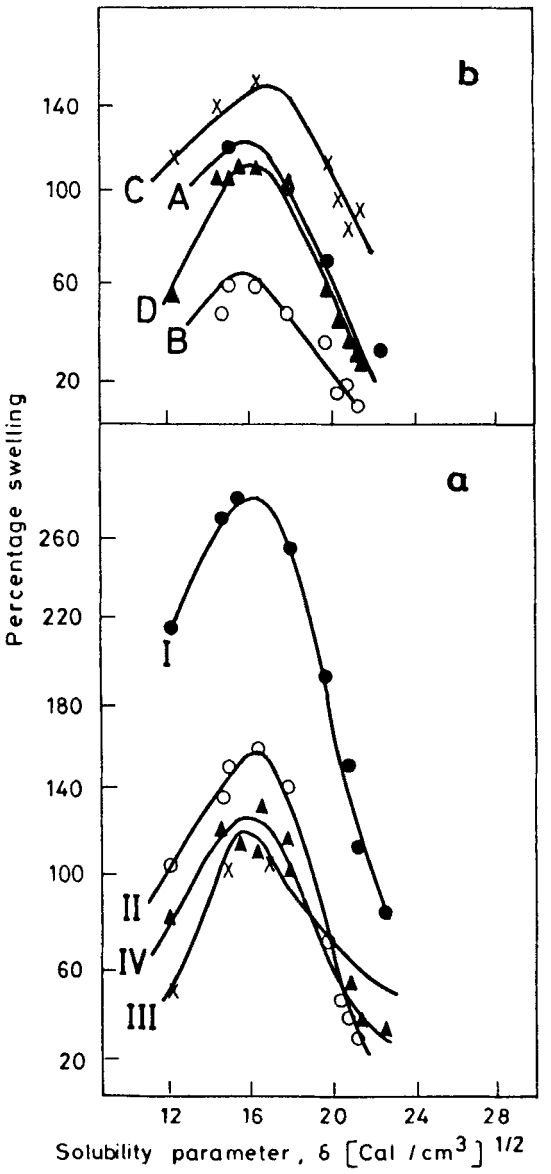

FIG. 7. Swelling behavior of amphiphilic matrices as a function of the solubility parameter of ethanol/water systems. (a) Samples I–IV. (b) Samples A–D. Details of the samples are given in Tables 1 and 4.

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sets (with minor variations) depend on the peak L/H values in the vicinity of δ = 16, which corresponds to an ethanol-water composition of 70/30. More extensive studies along these lines are underway.

ACKNOWLEDGMENT

One of us (D.S.) acknowledges financial assistance in the form of a junior research fellowship from the Council of Scientific and Industrial Research, India.

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Received November 15, 1991

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