# Swelling characteristics of amphiphilic polymer brushes in pure and mixed solvent systems*

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Amphiphilic polymer brushes are synthesized by the sequential graft copolymerization of crosslinked gelatin with methyl methacrylate and acrylic acid. Samples with varying lipophilic to hydrophilic ratio (L/H values) could be synthesized by adjusting the grafting conditions. Here we report the swelling behaviour of these systems in pure and mixed solvent systems. The swelling ratio is influenced by the L/H value of the material. The brush with L/H value close to 1 exhibits anomalous swelling. Mixed solvents appear to be better swelling media than pure solvents. We discuss these observations in the light of L/H values and the differential solvation of individual chains.

**(Keywords: polymer brushes; amphiphiles; solvent systems; swelling)**

## INTRODUCTION

Polymer brushes connote a unique macromolecular architecture, where long polymer chains are anchored onto interfaces or solid surfaces by physical or chemical means[1]. Our discussions will be exclusively confined to systems where polymer chains are irreversibly and randomly end-grafted to solid surfaces. Such brushes could be planar, cylindrical or spherical, depending upon the morphology of the anchoring surface. The molecular dynamics of the bristles — the grafted chains — in the melt or in the presence of solvent are dictated by several balancing thermodynamic functions[2–5]. The free energy associated with a single bristle has two components: the elastic free energy $F_{\mathrm{el}}$, denoting the flexibility of the chain; and the interaction free energy $F_{\mathrm{int}}$, a cumulative term that includes the interactions between monomer units, chain segments and polymer–solvent pairs. In a good solvent, the extent of stretching is determined by the resultant of the interaction and elastic free energies; whereas in a poor solvent, the unfavourable polymer–solvent interaction free energy overwhelmingly reduces the contours of the chain.

Most of the theoretical treatments on the chain dimensions of polymer brushes in good or poor solvents begin with the basic assumptions that all the bristles are chemically identical and are of equal length, which imply that they respond uniformly to any given solvent. However, it is entirely possible to design a brush in which the bristles are made up of two or more chemically different chains. For such a brush with two different chains A and B, the mutual interaction energies and the differential solvation levels will figure significantly in determining the effective stretching dimensions. Earlier we reported the synthesis and characterization of an amphiphilic polymer brush[6–8]. Structurally, it is a crosslinked gelatin core with poly(methyl methacrylate) and poly(acrylic acid) grafts. The solvent-induced stretching and contraction of the grafted chains are reflected in the macroscopic swelling and shrinking of the polymer matrix. In this paper we discuss the swelling behaviour of this amphiphilic brush in a variety of pure and mixed solvent systems.

## 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 AR-grade solvents were used as received. All reactions were carried out in oxygen-free distilled water.

### *Preparation of crosslinked gelatin (Gelx)*

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

### *Synthesis of Gelx-g-(PMMA, PAA), the amphiphilic brush*

Gelx was graft copolymerized with MMA in aqueous medium using 0.1% potassium persulfate (KPS) at 70°C. At this temperature, KPS decomposes to yield persulfate radicals ($S_2O_8^{-}$), which generate free radical centres on the gelatin network, apart from triggering the homopolymerization of MMA. More details on the kinetics and mechanism of grafting are available in

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refs 7 and 8. The product was subjected to Soxhlet extraction with benzene to remove the homopolymer, PMMA. The graft copolymer, Gelx-*g*-PMMA was rinsed with acetone, dried under vacuum and weighed. This process was repeated till the material registered constant weight. The Gelx-*g*-PMMA thus obtained was graft copolymerized with acrylic acid in aqueous medium using KPS initiator. The product was then freed of the homopolymer, PAA, by continuous extraction with water in a Soxhlet unit till the dry weight of the product remained constant.

### *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 isolated by selective solvent extraction and estimated gravimetrically. Molecular weights of the grafts were determined by viscosity methods[9].

The percentages of grafting of PMMA and PAA were calculated with respect to the Gelx core. The L/H values were deduced as the ratio of percentage PMMA grafted to percentage PAA grafted in all cases. The synthesis and

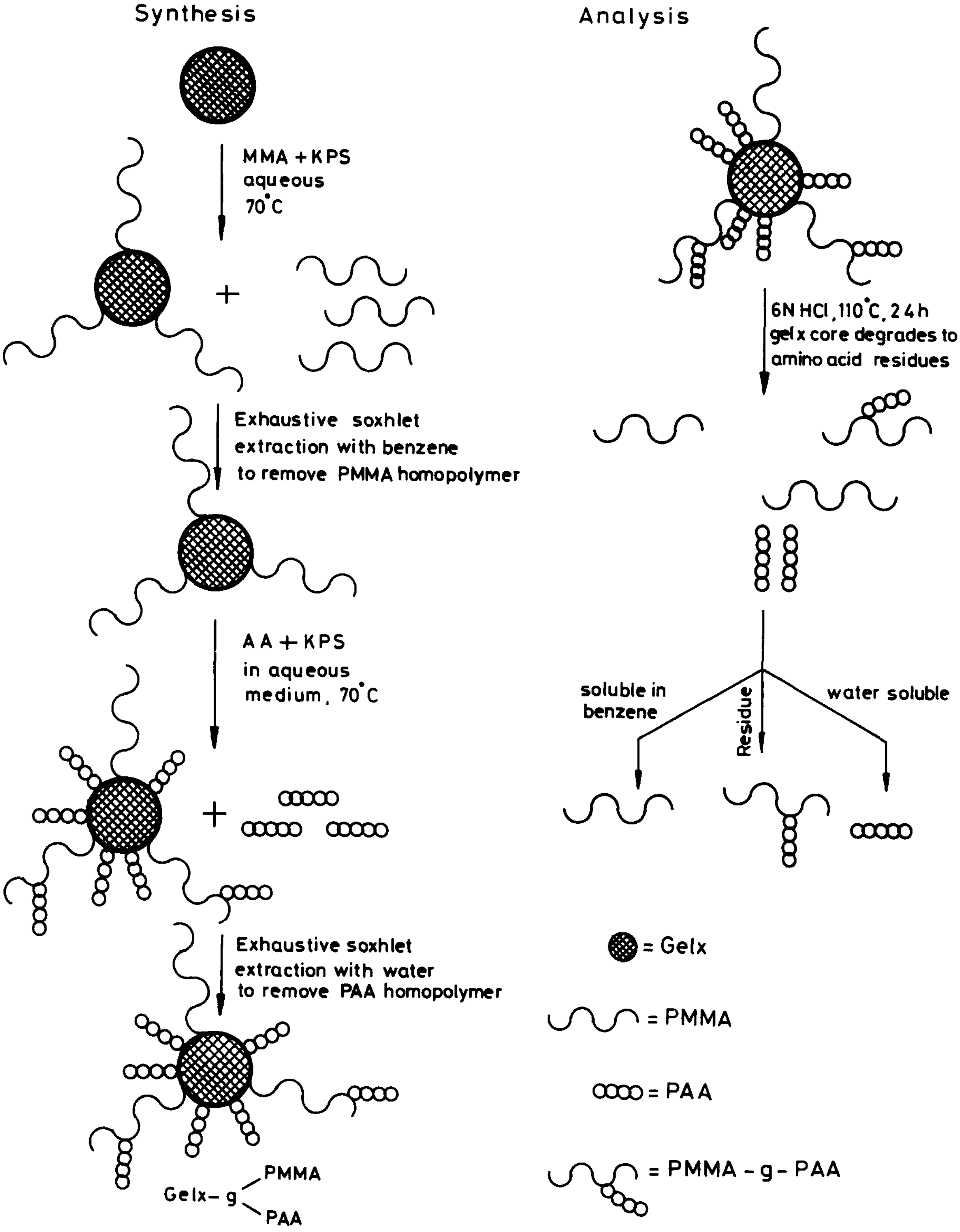

**Figure 1** Synthesis and analysis of amphiphilic graft copolymers

analysis procedures are illustrated in *Figure 1*. More details on these are available in *Table 1* and ref. 8.

### *Solvent uptake studies*

The swelling studies were monitored gravimetrically[10,11]. For this, weighed pellets of the samples (10 mm diameter × 4 mm thickness, approx. 300 mg each) prepared under uniform hot compression conditions were immersed in different solvents and the time-dependent increase in weight recorded till equilibrium swelling was reached. The swelling ratio was calculated as the ratio of the increase in weight to the original weight. All solvents were degassed by passing through a Millipore filter in a degassing assembly (Advantec, Toyo KG 47).

## RESULTS AND DISCUSSION

By virtue of its structure, an amphiphile always tends to orient itself in any medium. There have been many attempts to study the molecular organization of amphiphilic assemblies at interfaces[12–15]. Malmsten *et al.*[12] point out that, for an amphiphilic system, owing to segmental orientational effects, the local solvency conditions become more pertinent than generalized interaction parameters. The Gelx-*g*-(PMMA, PAA) system considered here has a very interesting structure, with the hydrophobic PMMA chains and hydrophilic PAA chains randomly and irreversibly grafted to the gelatin core. We felt that the contradictory solvency requirements for the PMMA and PAA chains could give rise to a solvent-induced, yet perfectly synchronized, stretching–shrinking process. Furthermore, we felt that a qualitative glimpse of this phenomenon could be obtained by monitoring the swelling behaviour of this matrix in a variety of solvents.

Considerations of chemical structure and solvent power with respect to PMMA and PAA form the basis for selecting specific solvents and solvent pairs for swelling studies. For example, water and ethanol are solvents for PAA, whereas acetone, benzene, chloroform and tetrahydrofuran (THF) are solvents for PMMA. We were handicapped by the limited number of solvents for the extremely hydrophilic PAA. In the series of mixed solvents we have used ethanol/water, acetone/water, ethanol/chloroform, ethanol/benzene and dioxane/THF. In *Figure 2* we have plotted the swelling ratio as a function of the L/H values for various solvents. While practically no swelling is observed in either pure dioxane or benzene, the swelling in the other solvents is in the following order:

$$\text{acetone} = \text{THF} < \text{chloroform} < \text{water} < \text{ethanol}$$

Both dioxane and benzene have very low dipole moments, 0.45 and 0 respectively. The inability of the amphiphilic matrices to swell in these solvents could be due to their non-polar nature. Another salient feature that becomes apparent from *Figure 2* is the unusual swelling behaviour of the sample with L/H = 1.05. The sample exhibits maximum swelling in all the solvents tested. The

**Table 1** Structural details of amphiphilic matrices

| | Percentage of grafting | | | | |
|---|---|---|---|---|---|
| Sample | PMMA | PAA | L/H values | Mol. wt | Conditions of grafting |
| I | 212 | | 1.05 | $1.3 \times 10^5$ | Gelx = 250 g, MMA = 6.08 mol, water = 5 l, KPS = 0.1%, temp. = 70°C, time = 4 h |
| | | 202 | | $8.9 \times 10^3$ | Gelx-*g*-PMMA = 500 g, AA = 14.56 mol, water = 3 l, KPS = 0.2%, temp. = 70°C, time = 4 h |
| II | 212 | | 2.26 | $1.8 \times 10^5$ | Gelx = 250 g, MMA = 6.08 mol, water = 5 l, KPS = 0.1%, temp. = 70°C, time = 4 h |
| | | 94 | | $1.4 \times 10^4$ | Gelx-*g*-PMMA = 100 g, AA = 1.46 mol, water = 600 ml, KPS = 0.3%, temp. = 70°C, time = 4 h |
| III | 65 | | 0.76 | $8.7 \times 10^4$ | Gelx = 200 g, MMA = 1.41 mol, water = 2 l, KPS = 0.1%, temp. = 70°C, time = 4 h |
| | | 86 | | $1.2 \times 10^4$ | Gelx-*g*-PMMA = 125 g, AA = 3.28 mol, water = 600 ml, KPS = 0.375%, temp. = 70°C, time = 4 h |
| IV | 115 | | 1.60 | $1.1 \times 10^5$ | Gelx = 100 g, MMA = 1.225 mol, water = 1 l, KPS = 0.1%, temp. = 70°C, time = 4 h |
| | | 72 | | $1.8 \times 10^4$ | Gelx-*g*-PMMA = 150 g, AA = 4.16 mol, water = 500 ml, KPS = 0.4%, temp. = 70°C, time = 4 h |

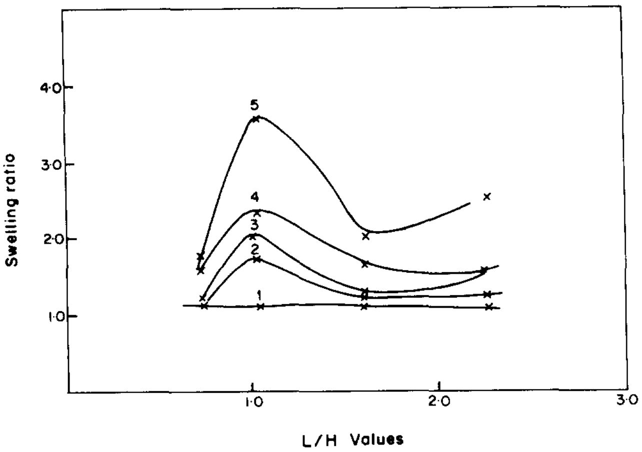

**Figure 2** Swelling ratio of amphiphilic matrices in different solvents as a function of L/H values: 1, dioxane; 2, acetone; 3, chloroform; 4, water; 5, ethanol. Benzene is superimposed on the dioxane curve and THF on the acetone curve respectively

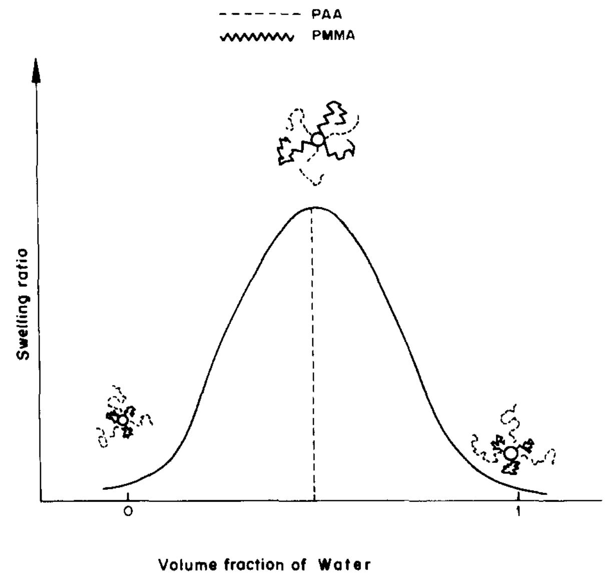

**Figure 3** Visualizing the behaviour of Gelx-*g*-(PMMA, PAA) in ethanol/water mixed solvent system: (○) Gelx core; (- - -) PAA grafts; (——) PMMA grafts

obvious temptation is to rationalize this observation by invoking the principles of a lipophilic/hydrophilic balance. However, we are hesitant to speculate because we feel that this could be just one of the many factors operating. PAA is known to interact with other responsive macromolecules like poly(oxyethylene) through the carboxylic acid functionality, yielding 1:1 complexes[16]. At present we do not have any evidence to predict a similar situation in the PAA–PMMA system.

Of the mixed solvent pairs, the ethanol/water system merits special discussion. While PAA is soluble in both these solvents, PMMA is not soluble in either, but is soluble in a mixture of the two. This is a typical case of cosolvency, where a mixture of two non-solvents turns out to be a solvent. The interactions between the PMMA segments and the mixed solvent clusters could induce thermodynamically favourable orientations leading to better solvation. This particular behaviour has immense significance in the present study. Here we start with a solvent (say ethanol) which preferentially interacts with the PAA chains alone. The PMMA chains are in the contracted state. As the water content in ethanol is increased, at a given water/ethanol composition, a situation is reached where both PAA and PMMA chains interact equally well with the mixed solvent medium. The non-solvents in the mixture act as cosolvents and the coil expansion of PMMA chains takes place in spite of the negative excluded-volume effects of the individual solvent components. As the water content is increased further and the pure water stage is reached, PMMA chains contract and PAA chains alone remain stretched. Conceptually this is a case of solvent-induced coil–globule transition of PMMA chains against the backdrop of stretched PAA chains. Our attempt to visualize this is schematically represented in *Figure 3*. The actual experimental results given in *Figure 4* substantiate our hypothetical model. Moreover, it provides the additional information that the maximum swelling occurs at about the same ethanol/water ratio for all samples.

*Figure 5* correlates the swelling ratio to the solubility parameter $\delta$ of the solvent system. A value close to 14.0 could be attributed to the Gelx-*g*-(PMMA, PAA) matrix with L/H value 1.0. The observation that solvent pairs are better swelling agents than pure solvents is not surprising since it is impossible to satisfy the solvency

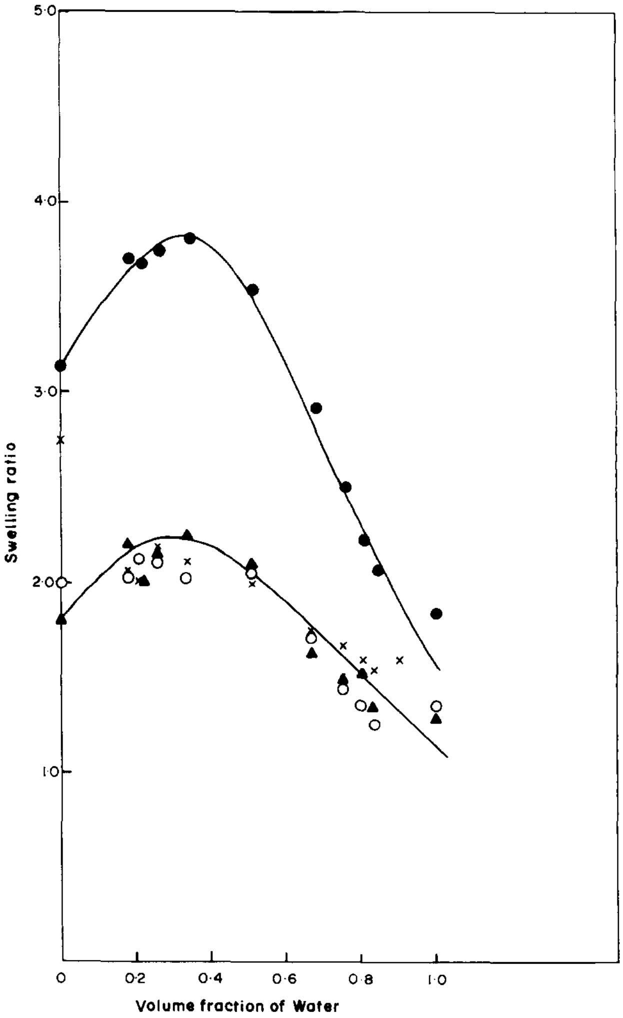

**Figure 4** Swelling profile of amphiphilic matrices in water/ethanol. L/H values of samples are: (●) 1.05, (○) 2.26, (×) 0.76), (▲) 1.60

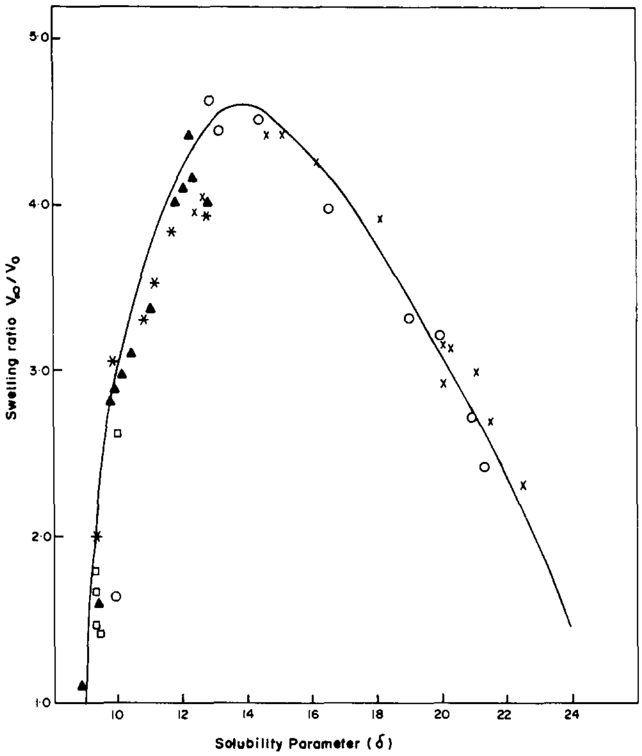

**Figure 5** Swelling behaviour of the amphiphilic matrix (L/H = 1.05) as a function of the solubility parameter (δ) of the solvent system: (○) acetone/water; (×) ethanol/water; (▲) benzene/ethanol; (*) chloroform/ethanol; (□) THF/dioxane

requirements of both PAA and PMMA with a single solvent. Moreover, the proximity of hydrophilic PAA and hydrophobic PMMA could introduce a new dimension to the polymer–solvent interaction parameter. The possibility of preferential solvent absorption cannot be disregarded either. Currently we are trying to determine the composition of the solvent mixture imbibed by the matrix, which we strongly feel would improve the clarity of the present picture.

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