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PREFERENTIAL SOLVENT ABSORPTION BY POLYMER BRUSHES FROM IMMISCIBLE SOLVENT PAIRS†

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ABSTRACT

Hydrophilic, hydrophobic, and amphiphilic graft polymer brushes are synthesized by grafting polyacrylic acid and/or polymethyl methacrylate onto gelatin granules crosslinked with glutaraldehyde. The ability of these brushes to selectively imbibe a solvent from immiscible pairs of solvents is demonstrated. The enhanced solvent mopping ability of the lipophilic and amphiphilic brushes from mixed solvent systems is interpreted through modified solvent interaction parameters.

INTRODUCTION

Polymer brushes are macromolecular systems in which long polymer chains are endgrafted onto a surface either by physical or chemical means [1, 2]. The dynamics of the bristles in poor, good, and mixed solvent systems has attracted both theoretical and experimental [3–18] attention since these brushes provide excellent working models for several interfacial systems, both chemical and biological. We have been interested in the properties of a special class of brushes synthesized by graft copolymerizing methyl methacrylate (MMA) and/or acrylic acid (AA) onto gelatin granules crosslinked with glutaraldehyde (Gelx) [19, 20]. These graft copoly-

†IICT communication 3539.

mers are conventionally written as *Gelx-graft-(PMMA,PAA)*, *Gelx-graft-(PMMA)* and *Gelx-graft-(PAA)*. Because of the Gelx core, these systems are generally insoluble but, depending upon the chemistry of the grafts, can take up large quantities of appropriate solvents. The efficiency of such mopping action depends on the extent of the three-dimensional stretching and relaxation of the grafted chains in the presence of the solvent because it is the inter- and intrachain spaces that solvent molecules are accommodated and held together by intermolecular forces. However, there is a finite limit beyond which the chains cannot be stretched since they are anchored at one end. This limit is set by the interplay of two forces: the free energy of mixing of the solvent with the polymer and the elastic free energy of the anchored chains.

Theoretical treatments by Alexander [3] and de Gennes [4] predict that under good solvent conditions, the brush height h should scale with the brush chain length N and the grafting density ρ according to

$$h \propto N\rho^{1/3} \quad (1)$$

The stretching of the bristles is a molecular event that is translated into macroscopic swelling of the polymer material. The extent of swelling is directly related to h . A high degree of swelling indicates highly stretched grafts. In this paper we carry out a quantitative analysis of the swelling characteristics of three sets of graft copolymer brushes in immiscible aqueous/organic solvent pairs.

EXPERIMENTAL DETAILS

Details of the synthesis of hydrophilic, lipophilic, and amphiphilic brushes have been reported elsewhere [19, 20]. Briefly, gelatin granules were first cross-linked by treating with 1% aqueous glutaraldehyde solution. The granules were then sieved and those which measured 50–100 μm were subjected to graft copolymerization with methyl methacrylate (MMA) or acrylic acid (AA) to get *Gelx-graft-PMMA* or *Gelx-graft-PAA*. The number tag each sample carries denotes the percentage of grafting. The amphiphilic system *Gelx-graft-(PMMA,PAA)* was synthesised by subjecting *Gelx-graft-PMMA* samples to a second course of grafting with AA.

These samples carry the number code L/H (lipophilic/hydrophilic) ratio, which is defined as

$$\frac{L}{H} = \frac{\text{percentage of PMMA grafted}}{\text{percentage of PAA grafted}} \quad (2)$$

The graft copolymer samples were sieved again, and the lot which measured 80–100 μm were used for swelling studies. The swelling experiments were carried out both gravimetrically and volumetrically, simultaneously. For crosschecking the values and to account for unavoidable errors due to solvent evaporation, in each case the weight and volume occupied by the swollen matrix and the volume and composition of the residual solvents were noted. The solvent compositions within and without the matrix were determined by GC analysis wherever necessary. These data are sufficient for material balances.

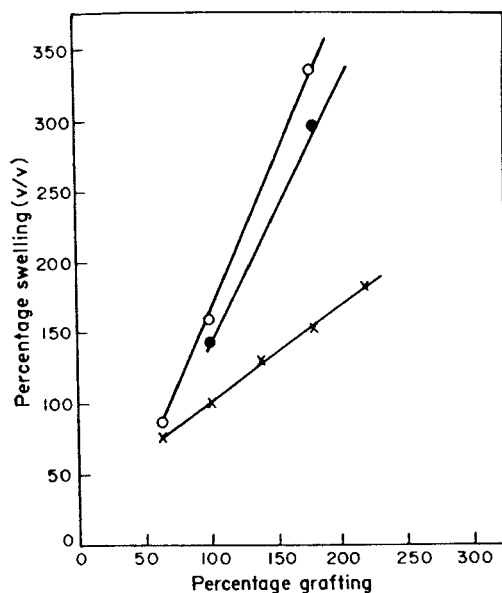


FIG. 1. Swelling behavior of Gelx-graft-PAA samples as a function of percentage grafting in water (\times), ethanol (\bullet), and methanol (\circ).

RESULTS AND DISCUSSION

The Gelx-graft-PAA samples are extremely hydrophilic. Figure 1 gives the percentage swelling as a function of percentage grafting in three solvents: water, ethanol, and methanol. Table 1 presents more extensive data including other solvents. The material registers maximum swelling in methanol. When the medium is a

TABLE 1. Equilibrium Swelling (w/w %) of Gelx-graft-PAA Brushes in Different Solvents^a

Sample	Solvent	Percentage grafting		
		180	94	65
1	Water	154	100	78
2	Ethanol	294	145	5.5
3	Methanol	366	158	84
4	Dioxane	144	20	NS
5	0.1 M NaOH	>400	354	340
6	Acetone	NS	NS	NS
7	Benzene	NS	NS	NS
8	Chloroform	NS	NS	NS
9	THF	NS	NS	NS

^aNS = no swelling.

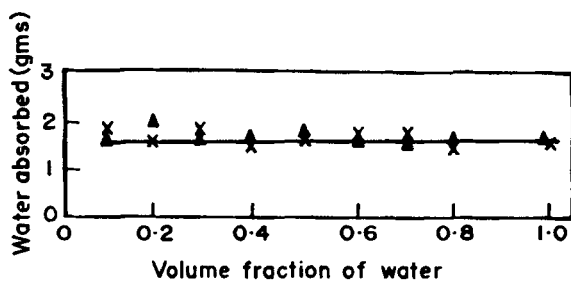


FIG. 2. Preferential absorption of water by 1 gram of Gelx-graft-PAA 180 from water/benzene (▲) and from water/chloroform (×) mixtures.

mixture of water/benzene or water/chloroform, the matrix selectively picks up water (Fig. 2). Irrespective of the composition of the medium, 1 g of Gelx-graft-PAA 180 imbibes about 1.5 g of water and the benzene or chloroform could be quantitatively recovered.

Figure 3 and Table 2 show the swelling pattern of Gelx-graft-PMMA samples in different organic solvents as a function of percentage grafting. We expected this matrix to preferentially absorb benzene and chloroform respectively from water/benzene and water/chloroform mixtures. The results are shown in Fig. 4 (Curves A and B). One gram of Gelx-graft-PMMA 212 can take up either 1 g of benzene or 3.5 g of chloroform.

Let us compare these values with those for pure solvents: 0.38 for benzene (w/w) and 1.58 for chloroform (w/w). This comparison is a clear example of facilitated solvent absorption from a mixed solvent system in comparison to that from pure solvents. A similar trend was observed for amphiphilic matrices as detailed below.

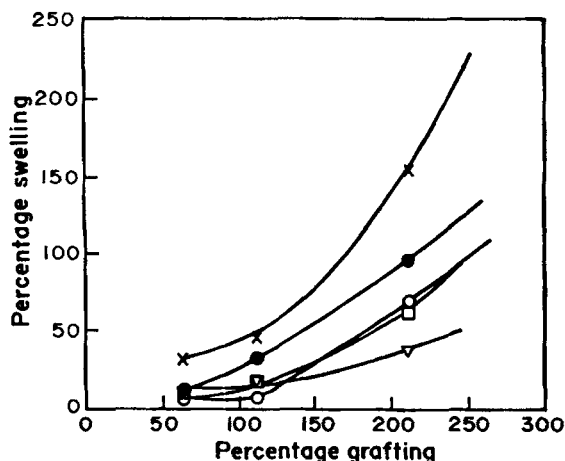


FIG. 3. Swelling behavior of Gelx-graft-PMMA samples as a function of percentage grafting in chloroform (×), THF (○), acetone (□), benzene (▽), and dioxane (●).

TABLE 2. Equilibrium Swelling (w/w %) of Gelx-graft-PMMA, Brushes in Different Solvents

Sample	Solvent	Percentage grafting		
		212	115	65
1	Chloroform	153	41	33
2	THF	69	6	6
3	Acetone	60	18	6
4	Benzene	38	18	13
5	Dioxane	94	19	11
6	Rectified spirit	42	17	12

The swelling behavior of Gelx-graft-(PMMA,PAA) samples is shown in Table 3. Because of its two-in-one structure, the amphiphilic matrix Gelx-graft-(PMMA,PAA) can imbibe both water and organic solvents. We infer from Fig. 5 that 1 g of the matrix takes up a total of 3.5 g of the chloroform/water mixture of which nearly 1.5 g is water. The results with benzene/water are slightly different. One gram of the matrix picks up just 1.5 g of water, and the amount of benzene imbibed is negligibly low, about 0.15 g/g of matrix. When treated with pure water, chloroform, or benzene, 1 g of this matrix ($L/H = 1.05$) picks up 0.85 g of water, 0.89 g of chloroform, and 0.06 g of benzene.

The second set of experiments was a follow-up on the first: to establish the matrix weight and the quantity of solvent it could soak up. The trend is shown in Figs. 6 and 7. The slope corresponds to the mopping capacity of the matrix in terms of grams of solvent per gram of matrix.

By weight or by volume, the amount of solvent imbibed by the lipophilic and amphiphilic matrices from a mixed solvent system is more than that from a pure solvent. What could be the reason for this differential behavior? One plausible reason could be that the events are assessed with respect to the swelling of a polymer brush and not its dissolution. The polymer chains grafted onto the Gelx core do not

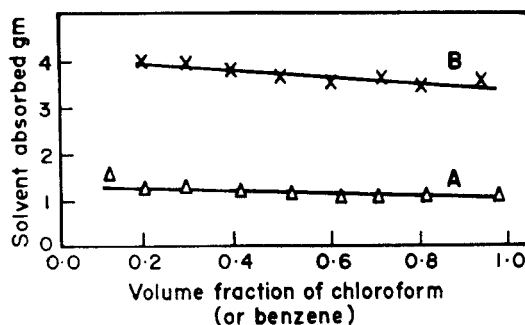


FIG. 4. Preferential absorption of benzene (A) and chloroform (B) by 1 gram of Gelx-graft-PMMA 212 from water/benzene (Δ) and water/chloroform (\times) mixtures.

TABLE 3. Equilibrium Swelling (w/w %) of Gelx-graft-(PMMA,PAA) Brushes in Different Solvents

Sample	Solvent	Sample			
		I	II	III	IV
		L/H			
		1.05	2.26	0.76	1.60
1	Water	83	30	60	33
2	Ethanol	214	104	50	80
3	Methanol	291	170	95	127
4	Acetone	62	30	10	70
5	Benzene	6	7	6	12
6	Chloroform	89	83	28	50
7	THF	144	94	22	113
8	0.01 M NaOH	270	100	88	55

possess the translational entropy of linear chains, but then they are not constrained on both ends as in a crosslinked network. Their status is somewhere intermediate but closer to the latter system. At equilibrium the chemical potentials of the solvent within and outside the brush should be equal:

$$\mu_{\text{solvent (brush)}} = \mu_{\text{solvent (bath)}} \quad (3)$$

The chemical potential of the solvent in the bath is no longer that of the pure solvent because of the presence of a second solvent. Because this is an immiscible companion, we have a three-phase system: the polymer, solvent 1, and solvent 2.

Certain abnormalities in the swelling behavior of polymer brushes in mixed solvents have been observed. For instance, Auroy et al. [11] and Marko [21] reported that there exist conditions when the polymer brush preferentially solvated with a good solvent remains collapsed in a binary mixture of good and poor sol-

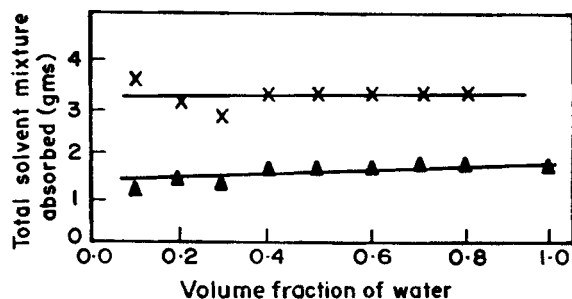


FIG. 5. Total solvent absorption by 1 gram of Gelx-graft-(PMMA,PAA) samples from water/benzene (▲) and water/chloroform (×) mixtures.

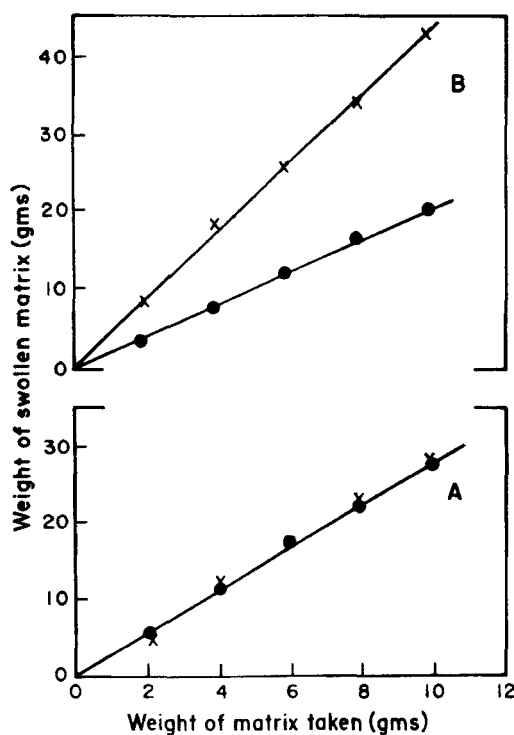


FIG. 6. Preferential solvent absorption by (A) Gelx-graft-PAA 180 from 4:1 compositions of water/benzene (●) and water/chloroform (×), and (B) Gelx-graft-PMMA 212 from 1:4 mixtures of water/benzene (●) and water/chloroform (×). Total volume, 100 mL; temperature, 30°C; time 24 hours.

vents. Investigating this aspect, recently Birshtein et al. [5] carried out a detailed analysis of the collapse and stretching of a polymer brush in a mixture of solvent A and precipitant B of volume fractions ϕ and $(1 - \phi)$, respectively. The unusual swelling patterns were explained in terms of a modified interaction parameter. In the presence of a second solvent B, the expression for the chemical potentials of both solvents are altered, and the effective interaction parameter χ is modified to

$$\chi = \chi_A \phi + \chi_B (1 - \phi) - \chi_{AB} \phi (1 - \phi) \quad (4)$$

This expression has been derived for a pair of miscible solvents. The present case is slightly more complicated because of several additional factors. First, the brush itself: its protein core could influence the behavior of the grafts. Second, the immiscibility of the solvent system introduces an additional solvent phase.

But the issue remains: Why are the effects more pronounced for chloroform than for benzene? Both have similar solubility parameter values (9.27 and 9.17 cal/cm³, respectively), and similar solvent interaction parameter values (about 0.48 for each with respect to PMMA); yet, the matrix mops up more chloroform than benzene. Even the molar volumes are not very different (80 and 89 mL/mol, respectively). But there is a great difference in the solubilities of these solvents in water. We believe this settles the issue. For benzene the solubility is a mere 0.07 parts/100

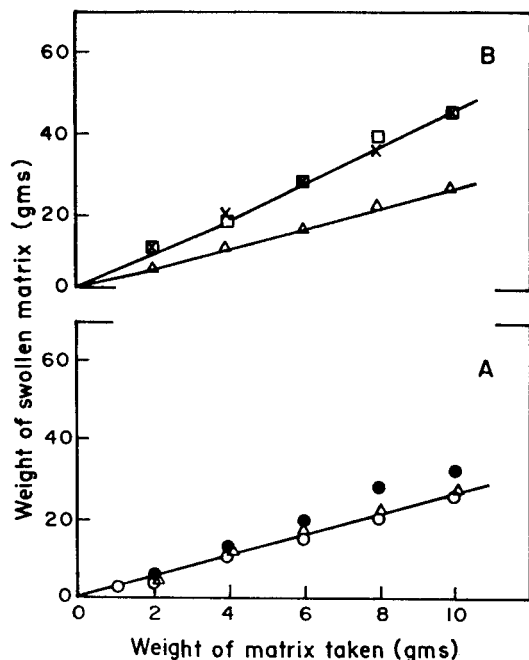


FIG. 7. Preferential solvent absorption by an amphiphilic matrix *Gelx-graft*-(PMMA,PAA). L/H = 1.05 from solvent mixtures. (A) Water/benzene; (●) 1:1, (○) 1:4, (△) 4:1. (B) Water/chloroform: (□) 1:1, (×) 1:4, (△) 4:1. Total volume, 100 mL; temperature, 30°C; time, 24 hours.

parts of water, but for chloroform it is 10 times higher: 0.8 parts/100 parts of water. This difference could contribute toward the enhanced polymer-solvent interaction for *Gelx-graft*-PMMA and [*Gelx-graft*-(PMMA,PAA)] with the water-chloroform system.

CONCLUSION

Polymer-solvent interaction parameters (χ) are modified in mixed solvent systems, and these modified values determine the ability of the polymer to preferentially imbibe one component from the solvent mixture.

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