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Notes

Vapor−Liquid Equilibria for Solutions of Brush Poly(methyl methacrylate) in Chloroform

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Introduction

A polymer brush is a small colloidal particle with long polymer chains grafted to a nonabsorbing surface.[1] The properties of brushes in solvents are of technological interest because such systems, by virtue of their unique architecture, can be used for stabilization of colloidal suspensions with application in wastewater treatment or as solvent mops.

Equations for the configuration of terminally anchored polymer chains have been derived by deGennes[2] and Alexander[3] on the basis of concepts originally laid out by Flory[4] for the total change in Gibbs energy upon mixing for constrained chains in solution. Flory divides this total Gibbs energy change of mixing into mixing and elastic contributions:

$$\Delta G = \Delta G_{\mathrm{mix}} + \Delta G_{\mathrm{elast}} \tag{1}$$

Based on the same principles, Birshtein et al.[5] gives μ_S, the chemical potential of the solvent inside the brush relative to that of the pure solvent

$$\frac{\Delta\mu_S}{RT} = \ln a_S = \ln(1 - \Phi_P) + \Phi_P + \chi{\Phi_P}^2 + 3\,(\Phi_P\sigma^2)^{-1} \tag{2}$$

where a_S is the activity of the solvent, Φ_P is the volume fraction of the polymer on a core-free basis, and χ is Flory's polymer−solvent interaction parameter. Birshtein et al.[5] define σ as grafting area per chain, a constant for a given brush. The reciprocal of σ is the grafting density, i.e., the number of chains per unit area based on the size of one monomer unit. Equation 2 assumes that the size of the monomer unit is equal to that of the solvent molecule.

The first three terms in eq 2 account for the mixing contribution, and the last term accounts for the elastic contribution. Conceptually, this expression is similar to the Flory−Rehner equation developed for cross-linked networks.[6,7] Equation 2 assumes that the mixing and elastic terms are separable and that σ is independent of polymer concentration.

We report here some experimental data for testing eq 2. Our data are for PMMA brushes in chloroform at 50 °C.

Experimental Section

Synthesis and characterization of the brushes have been described elsewhere.[8] To recount briefly, glutaraldehyde cross-linked gelatin (Gelx) microspheres of uniform size were first prepared by a two-phase precipitation method. Poly(methyl methacrylate) chains were then grafted onto these microspheres by a suspension-polymerization technique in aqueous media with potassium persulfate as the initiator. At the end of the reaction, the homopolymer was separated from the true graft copolymer by Soxhlet extraction with toluene for 48 h. The graft copolymers were subjected to acid hydrolysis in 6 N HCl at 110 °C for 24 h to destroy the protein core. The linear grafts thus separated were isolated and purified by reprecipitation. The average molecular weight of this sample was determined by GPC equipped with a refractive index detector, against poly(methyl methacrylate) standards in THF using 10^3, 10^4, and 10^5 Å Waters Styragel columns connected in series. A flow rate of 1 mL/min was maintained for all samples. The essential characteristics of the brush polymer such as core size, molecular weight of the grafts, and grafting density are summarized in Table 1.

We monitored the absorption of chloroform vapor by the polymer sample in a classical gravimetric sorption technique described in detail by Panayiotou and Vera[9] and Gupta and Prausnitz.[10] This method has also been used by Neuburger et al.[11] to study vapor−liquid equilibria (VLE) in cross-linked polymer networks. This procedure allows us to vary the activity of the solvent in steps from zero to nearly 1.0. The reliability of the apparatus was established by reproducing published experimental data for polystyrene−chloroform and polystyrene−acetone at 50 °C.[12]

Figure 1 shows a schematic drawing of the apparatus. The entire system is housed in an insulated glass chamber with transparent acrylic panels in the front for cathetometer readings. The temperature inside can be controlled within 0.3 °C. The springs (Ruska Instruments, Houston, TX) have a sensitivity of 1 mg/mm and a maximum load limit of 250 mg. In this range, the elongation of the spring is linear with respect to loading. The elongations are also corrected for the effect of temperature. The experiment begins with loading 15−25 mg of the polymer into the tared aluminum pans. The system is then kept evacuated for several hours (often overnight) at the desired temperature. This step drives away any moisture, oligomers, monomers, or residual solvent present in the polymer sample. This also detects leakages if any. From the calibrated extension of the spring, the dry weight of the polymer is calculated.

Solvent vapor from a deaerated solvent reservoir is then introduced into the chamber to achieve the desired pressure as read from the mercury manometer. The system reaches equilibrium when the extension of the spring remains constant. The pressure of the system is read from the manometer with the precision 1 Torr. All experiments were conducted below or slightly above 1 bar, where no polymer is in the vapor phase. The pressure was also kept below 90% of the solvent

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Table 1. Properties of Brush, Linear Polymer, and Solvent

Brush PMMA

chemical identity of the brush polymer: Gelx-*g*-PMMA
av diameter of the core: 17.0 μm
composition (wt %) (calcd from % grafting): gelatin, 35; PMMA, 65
av mol wt of PMMA (from GPC): 10^6
grafting density (no. of chains/μm^2) calculated from the above data assuming a density of unity for the core): 3.2×10^6

Linear PMMA

supplier: Polymer Source Inc., Quebec, Canada
mol wt: 1.25×10^5 ($M_w/M_n = 1.05$)
lot no.: p93-MMA

Chloroform

supplier: Fischer Scientific
lot no.: 963052
purity: 99.9%

Table 2. Total Pressure for Brush PMMA in Chloroform at 50 °C

pressure (Torr)	vol fraction of solvent	pressure (Torr)	vol fraction of solvent
55.5	0.003 35	306	0.143 8
107	0.019 75	360	0.181 5
158	0.038 75	406	0.228 2
206.5	0.068 82	462.5	0.255 2
258	0.099 80	478	0.271 0

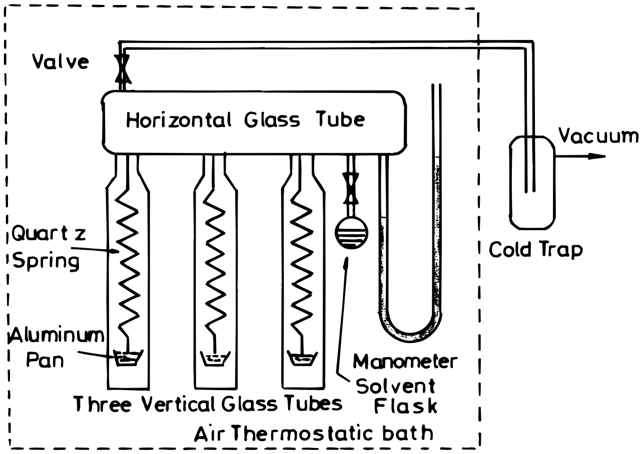

Figure 1. Schematic drawing of the gravimetric sorption apparatus.

vapor pressure at the operating temperature to prevent condensation in the system. The activity of the solvent is obtained upon dividing the observed pressure by the vapor pressure of the pure solvent.

Results and Discussion

Figure 2 shows solvent activity as a function of solvent volume fraction in the polymer. For comparison we have included results for linear PMMA. Similar experiments with Gelx showed no absorption by the core. At the same solvent activity, brush PMMA absorbs less solvent than linear polymer. We have used $\chi = 0.44$ in eq 2 to calculate the mixing contributions[13] and then the σ values given in Figure 3.

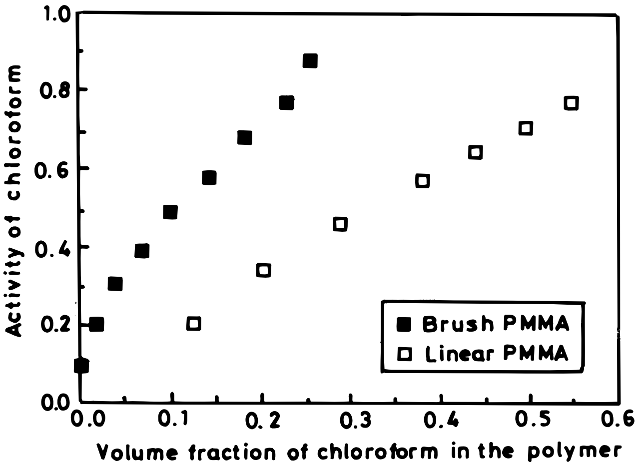

Figure 2. Vapor–liquid equilibria for chloroform–PMMA. Results for linear and brush PMMA at 50 °C.

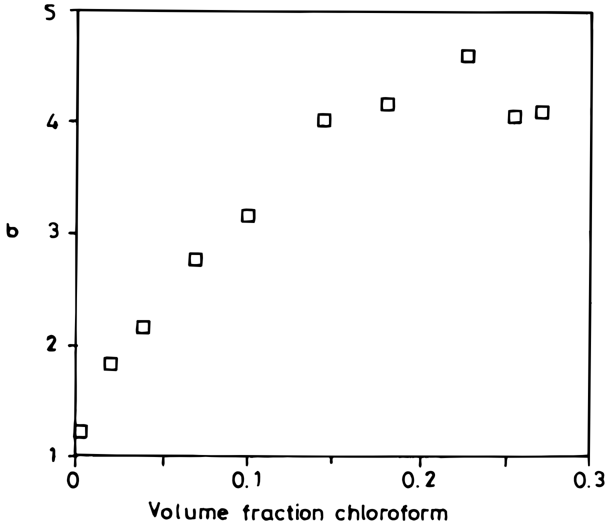

Figure 3. PMMA brush in chloroform at 50 °C. σ was calculated from eq 2 by using $\chi = 0.44$.

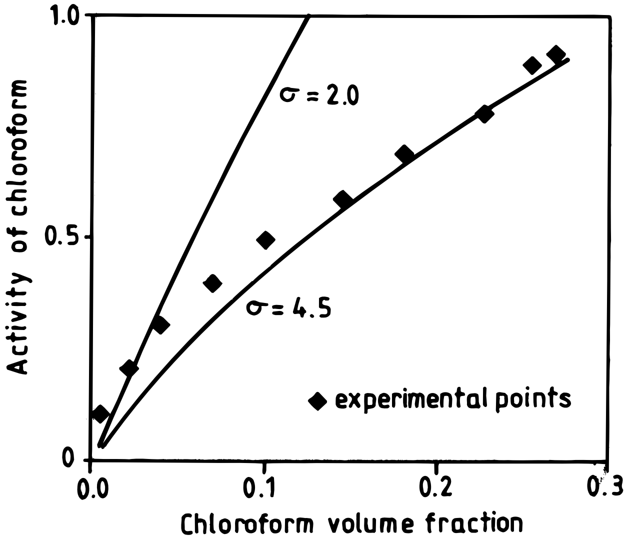

Figure 4. Solvent activity using two different values of σ with $\chi = 0.44$.

Because the effective σ depends on volume fraction, the theoretical elastic contribution does not agree with experiment. Attempts to fit the measured activity to a constant value of sigma were not successful. As shown in Figure 4, deviations between theoretical and observed results become increasingly evident when the volume fraction of the solvent is low. Neuburger et al.[11] reported a similar observation upon performing similar experiments with polymer networks. From the structural parameters of the brush in Table 1, we calculated the value of σ in terms of the area occupied by one monomer unit. Details of the calculation are given in the Appendix.

Our data support the conclusion of Neuberger et al.,[11] and more recently by Sommer et al.,[14] that the theoretical elastic term is in error due to neglect of a mixing-elastic cross term in eq 2. At low volume fractions, our data indicate that the elastic contribution in eq 2 should include the solvent−polymer interaction parameter because that contribution depends on solvent−chain interactions. In its present form, eq 2 appears to be limited to brushes dissolved in Θ solvents where $\chi \cong 0$.

It is also possible that the curvature of the anchoring surface introduces additional complexities. Currently, work is in progress to synthesize planar and spherical brushes with uniform bristle size. VLE data of these systems can throw more light onto the nature of the mixing-elastic cross term.

Conclusions

Vapor−liquid equilibria for solutions of brush polymers are qualitatively similar to those for linear polymers. However, there is a large difference in magnitude because the chains are anchored at one terminal and hence the elastic contribution is significant. Attempts to apply existing theories show that the theoretical elastic term is inadequate; it appears that a mixing-elastic cross term is needed. VLE data on planar and spherical brushes with uniform bristle size could yield more information. Investigations in this direction are in progress.

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Appendix. Calculation of σ

radius of the core = 8.5 μm

volume of the core = $4/3\pi r^3 = 2571\ (\mu\mathrm{m})^3$

mass of the core = $2571 \times 10^{-6}\ \mu$g (assuming density = 1 g/mL)

PMMA content = $2571 \times 10^{-6} \times 65/35 = 4775 \times 10^{-12}$ g

av mol wt of PMMA chains = 10^6

no. of moles of PMMA = 4.775×10^{-15} mol

equivalent no. of chains = $4.775 \times 10^{-15} \times 6.02 \times 10^{23} = 2.875 \times 10^9$

surface area of the core = $4\pi r^2 = 907\ (\mu\mathrm{m})^2$

chains per $(\mu\mathrm{m})^2 = 2.875 \times 10^9/907 = 3.169 \times 10^6$

area per chain (Å)^2 = 31.55

area per monomer unit = 0.895

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