LBNL-41518
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Chemical Sciences Division

March 1998

Submitted to
Macromolecules

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This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

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Abstract

Vapor -liquid equilibria are reported for solutions of brush polymethyl methacrylate in chloroform. The data indicate that Gibbs energy calculations for the brush/solvent system should include a mixing-elastic crossterm in the elastic contribution.

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.

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Equations for the configuration of terminally anchored polymer chains have been derived by deGennes[2] and Alexander[3] based on 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:

$$\Delta G = \Delta G_{mix} + \Delta G_{elast} \qquad (1)$$

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

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

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 Equation(2) account for the mixing contribution and the last term for the elastic contribution. Conceptually, this expression is similar to the Flory- Rehner equation developed for crosslinked 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 Equation (2). Our data are for PMMA brushes in chloroform at 50°C

Experimental

Synthesis and characterization of the brushes have been described elsewhere.[8] To recount briefly, glutaraldehyde crosslinked gelatin (Gelx) microspheres of uniform size were first prepared by a two-phase precipitation method. Polymethyl 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 hours. The graft copolymers were subjected to acid hydrolysis in 6 N HCl at 110°C for 24 hours to destroy the protein core. The linear grafts thus separated were isolated and purified by reprecipitation. Average molecular weight of this sample was determined by GPC equipped

with a refractive index detector, against polymethylmethacrylate standards in THF using 10^3, 10^4 and 10^5 Angstrom Waters Styragel columns connected in series. A flow rate of 1ml/mn 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 summarised in Table I

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 in crosslinked 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]

Fig.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, Texas) have a sensitivity of 1mg/mm and a maximum load limit of 250mg. In this range, the elongation of the spring is linear with respect to loading. The

elongations are also corrected for 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 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 & discussion

Fig 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 χ = 0.44 in Eq. (2) to calculate the mixing contributions[13] and then the σ values given in Fig.3.

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 Fig 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 I, 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

Eqn.(2). At low volume fractions, our data indicate that the elastic contribution in Eqn.(2) should include the solvent - polymer interaction parameter because that contribution depends on solvent -chain interactions. In its present form Eqn.(2) appears to be limited to brushes dissolved in theta 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 synthesise planar and spherical brushes with uniform bristle size. VLE data of these systems can throw more light into the nature of the mixing-elastic crossterm.

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 crossterm is needed. VLE data on planar and spherical brushes with uniform bristle size could yield more information. Investigations in this direction are in progress.

Acknowledgment

KNJ thanks UGC, India for the award of a junior research fellowship and PRC acknowledges the CSIR, India for Raman Research Fellowship. For financial support, JMP is grateful to the Office of Basic Energy Sciences of the US Dept. of Energy, to the National Science Foundation and to the Donors of the Petroleum Research Fund administered by the American Chemical Society.

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Table I. Properties of Brush, Linear Polymer and Solvent

Brush PMMA

Chemical identity of the brush polymer	Gelx-g-PMMA
Average diameter of the core	17.0 micrometers
*Composition(wt%) (Calculated 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

Supplied by Polymer Source Inc., Quebec, Canada

Mol.Wt. 1.25x10 5(Mw/Mn = 1.05)

Lot No. p93-MMA

Chloroform

Supplied by Fischer scientific

Lot No. 963052

Purity 99.9%

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

Pressure in Torr	Volume fraction of solvent
55.5	0.00335
107	0.01975
158	0.03875
206.5	0.06882
258	0.09980
306	0.1438
360	0.1815
406	0.2282
462.5	0.2552
478	0.2710

Appendix

Calculation of sigma(σ)

Radius of the core = 8.5μm

Volume of the core = $4/3\pi r^3$ = 2571$(\mu m)^3$

Mass of the core = $2571*10^{-6}\mu g$(assuming density=1g/ml)

PMMA content = $2571*10^{-6}*65/35$

$=4775*10^{-12}$ g

Av.Mol.wt of PMMA chains = 10^6

No. of moles of PMMA = $4.775 * 10^{-15}$ moles

Equivalent no. of chains = $4.775 * 10^{-15} * 6.02 *10^{23}$

$= 2.875* 10^9$

Surface area of the core = $4\pi r^2$ = 907$(\mu m)^2$

Chains per $(\mu m)^2$ = $2.875*10^9/907= 3.169*10^6$

Area per chain in $(A°)^2$ = 31.55

Area per monomer unit = 0.895

Figure captions

Figure 1. Schematic drawing of the Gravimetric Sorption apparatus

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 calculated from Equ.2 using $\chi = 0.44$

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

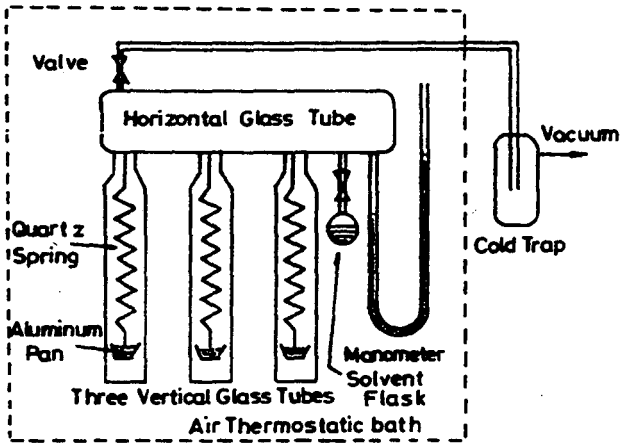
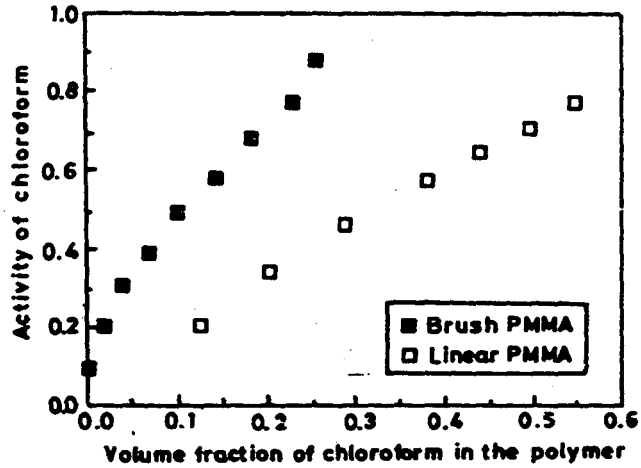

Valve
Horizontal Glass Tube
Vacuum
Quartz Spring
Cold Trap
Aluminum Pan
Manometer
Solvent Flask
Three Vertical Glass Tubes
Air Thermostatic bath

Fig. 2


1.0
0.8
0.6
0.4
0.2
0.0
Activity of chloroform
0.0
0.1
0.2
0.3
0.4
0.5
0.6
Volume fraction of chloroform in the polymer
Brush PMMA
Linear PMMA

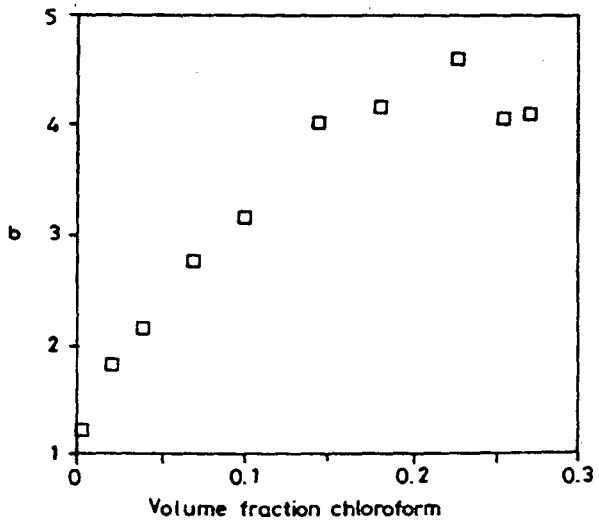
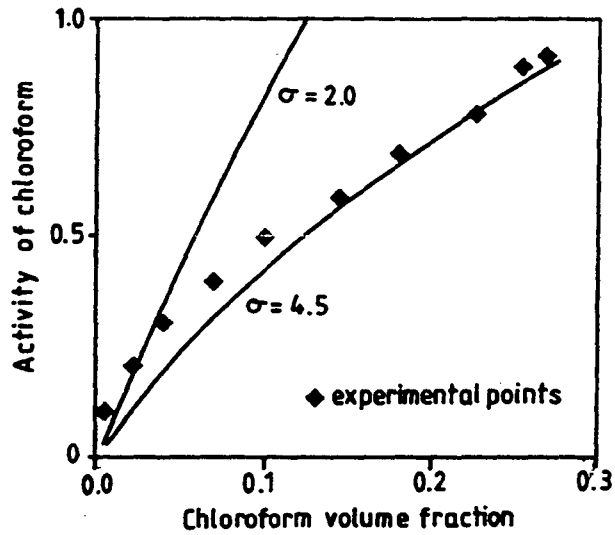

5
4
3
2
1
b
0
0.1
0.2
0.3
Volume fraction chloroform

Fig. 4


1.0
0.5
0
Activity of chloroform
σ = 2.0
σ = 4.5
◆ experimental points
0.0
0.1
0.2
0.3
Chloroform volume fraction

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Prepared for the U.S. Department of Energy under Contract No. DE-AC03-76SF00098