Macromolecules 1994, *27*, 1256–1266

Theory of the Collapse–Stretching Transition of a Polymer Brush in a Mixed Solvent

T. M. Birshtein* and Yu. V. Lyatskaya

Institute of Macromolecular Compounds, Academy of Sciences of Russia,
St. Petersburg 199004, Russia

Received June 11, 1993; Revised Manuscript Received November 15, 1993⊗

ABSTRACT: The collapse–stretching transition of a polymer brush in a binary solvent was considered on the basis of mean-field theory. The transition is found to be roughly guided by a single parameter χ and to differ slightly from that in the one-component solvent. The peculiarities of the good solvent/precipitant mixture were considered. An analogy between the collapse–stretching transition of a polymer brush in a binary solvent and the well-known effect of polymer precipitation in the mixed solvent was shown.

Introduction

The pioneering analysis of the layers of grafted polymer chains, carried out by Alexander[1] and de Gennes[2] about 15 years ago, gave rise to a great number of investigations (see, for example, refs 3–5 and also the review in ref 6 and references therein) of the structure and properties of such a system referred to as polymer brushes. Polymer brushes are interesting for a set of reasons. They are adequate models of the elements of polymer structures with complicated architecture such as block copolymer micelles and superstructures, regularly branched chains, etc.[4] Polyelectrolyte brushes function in living systems (glycocalix).[7] The possibility of practical implementation of polymer brushes in colloid systems and membranes is also of great interest. Last, but not least, polymer brushes are quite interesting objects from the point of view of statistical physics, especially that of phase separation and phase transitions.

This paper concerns the theory of collapse of planar polymer brushes in a binary solvent, with one of the components being a precipitant. The work was stimulated by the experimental investigations of the collapse–stretching transition of polymer brushes in a binary mixture of solvent/precipitant carried out by Auroy and Auvray[8] where some peculiarities of the system behavior were demonstrated. For example, it was shown,[8] that the polymer brush with preferential solvation of good solvent remains collapsed even in the case when the volume fraction of the good solvent in the brush is much greater than that of the precipitant. This problem has already been discussed by Lai and Halperin[9] and by Marko[10] using a Flory–Huggins type theory. In the present study we have used the same type of approach and discuss more exhaustively the different aspects. This gives us the possibility of finding an association between brush collapse and the demixing effect in a polymer solution, of using an effective interaction parameter, and of showing the influence of the preferential solvation effect on brush characteristics. The results obtained are in good agreement with the experimental[8] and theoretical[9,10] data.

I. Model. We considered a standard model of a planar polymer brush[11] (Figure 1), i.e., a layer of flexible polymer chains with the great number N of spherical symmetric segments. The segment dimension is $a = 1$. The chains are grafted not very dense, $\sigma \gg a^2 = 1$ (σ is a grafting area per chain), but quite dense for fulfillment of the overlapping condition: $H > \sigma^{1/2}$ (H is the layer height). This condition is extremely critical in the case of the collapsed state with a limiting high density when $\sigma H = N$. It is valid when

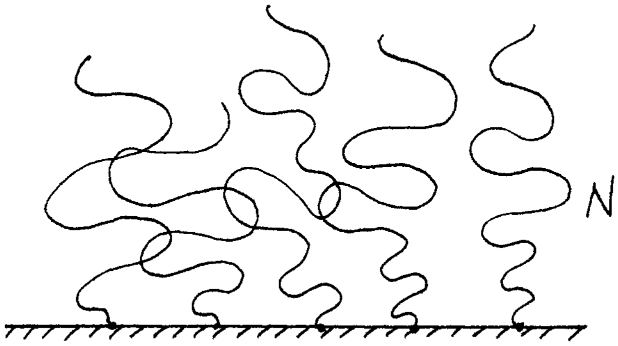

Figure 1. Polymer brush.

$$\sigma \ll N^{2/3} \tag{1}$$

The failure of the condition (1) results in the heterogeneity of the collapsed layer in the direction parallel to the grafting surface[12] that requires a special consideration. The chains are also assumed to be always stretched in the direction perpendicular to the grafting surface as compared to the Gaussian sizes. In the case of the brush immersed in a good or Θ solvent, it is always valid under the condition (1). For the collapsed brush a stronger condition, $\sigma < N^{1/2}$, is required, but the theory can be easily modified also in the case of the failure of this condition (cf. refs 11 and 13).

We have restricted ourselves by consideration of the layer as a whole, describing it only by average characteristics (height, volume fractions of the polymer, and solvent components) without going into the heterogeneity of the distribution of polymer and solvents along the height of the layer. This effect was considered in detail in the case of the brush in a one-component solvent[4,5,11] and recently also in a binary solvent.[10]

We have used the mean-field approximation and described the free energy of the brush by standard equations of the Flory–Huggins theory.[14]

II. Polymer Brush in a One-Component Solvent. Let us consider a polymer brush of height H. Free energy F^{in} of the brush can be written in the following way:

$$F^{\text{in}} = n \ln \Phi + \chi n \Phi_{\text{P}} + n_{\text{P}} \frac{3H^2}{2N} \tag{2}$$

where χ is the Flory–Huggins parameter of the polymer–solvent interactions and n and n_{P} are the numbers of

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⊗ Abstract published in *Advance ACS Abstracts,* January 1, 1994.

0024-9297/94/2227-1256$04.50/0

molecules of the solvent and the polymer (P) in the volume; the corresponding volume fractions are

$$\Phi = \frac{n}{n + n_P N}, \qquad \Phi_P = 1 - \Phi = \frac{n_P N}{n + n_P N} \qquad (3)$$

The volume of the solvent molecules is decided to be equal to that of polymer segments, $a^3 = 1$. All energetical parameters are expressed in kT units.

The first addend in eq 2 is the translational entropy of the solvent molecules. Note that grafted chains have no translational entropy. The second addend corresponds to the binary contacts polymer–solvent, and the last one is the elastic energy due to the chain stretching in the brush.

Taking into account an evident relationship

$$\Phi_P = N/H\sigma \qquad (3')$$

the expression (2) at given σ and χ is a function of one variable only. The following procedure can be made in different ways depending on the choice of the variable, the results being independent of the variable chosen.

In the works concerning the structure and properties of the brushes,[3-6,11] the height of the brush H is chosen usually as the variable and the procedure is used to find the minimum free energy of the brush:

$$\delta F^{in}/\delta H = 0 \qquad (4)$$

For generalization to the case of a many-component solution, it is more convenient to use another description of the system. Let us consider two systems in equilibrium: the layer (in) and the solvent (out). These systems are "divided" by a semipenetrable membrane that is not penetrated by the polymer but is so by the solvent molecules. Thus, the obvious variable in the system is the number of solvent molecules in the layer n, and the equilibrium between the two systems is obtained from the condition of equality of the chemical potentials of the solvent in two systems:

$$\mu^{in} = \mu^{out} \qquad (5)$$

where

$$\mu^x = (\delta F^x/\delta n)_{n_P = \text{constant}}, \qquad x = \text{in, out} \qquad (6)$$

is the excess of chemical potential of the solvent as compared to that in the bulk phase. In the case of a one-component solvent $\mu^{out} = 0$ and eqs 5 and 6 are equal to eq 4. The use of the expression (2) for F^{in} in eqs 5 and 6 gives

$$\mu^{in} = \ln(1 - \Phi_P) + \Phi_P + \chi{\Phi_P}^2 + \frac{3}{\Phi_P \sigma^2} = 0 \qquad (7)$$

Using virial expansion at $\Phi_P \ll 1$, we obtain well-known power dependences of $H = N/\Phi_P\sigma$ for the cases of a good solvent, a Θ point, and a collapsed state, respectively:[11]

$$H \sim N\sigma^{-1/3}(1/2 - \chi)^{1/3} \qquad \chi < {}^1/_2 \qquad (8)$$

$$H \sim N\sigma^{-1/2} \qquad \chi = {}^1/_2 \qquad (9)$$

$$H \sim N\sigma^{-1}(\chi - 1/2)^{-1} \qquad \chi > {}^1/_2 \qquad (10)$$

In this paper we were interested in both the cases $\Phi_P \ll 1$ and $\Phi_P \cong 1$; hence, we did not use the virial expansion and solved eq 7 numerically.

We started from the χ dependence of the height of the brush that is the value experimentally observed. This dependence is shown on Figure 2. It is seen that the height of the brush becomes greater when the solvent becomes stronger.

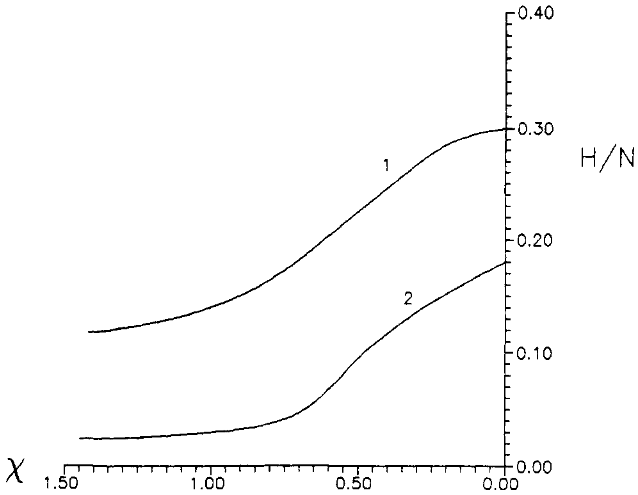


Figure 2. Relative brush height H/N vs interaction parameter χ for the brush in a one-component solvent: (1) $\sigma = 12$, (2) $\sigma = 60$. At $\chi = 0$, 0.5, and 1.5 H(1)/H(2) = 1.7, 2.2, and 5 correspondingly in agreement with eqs 8–10.

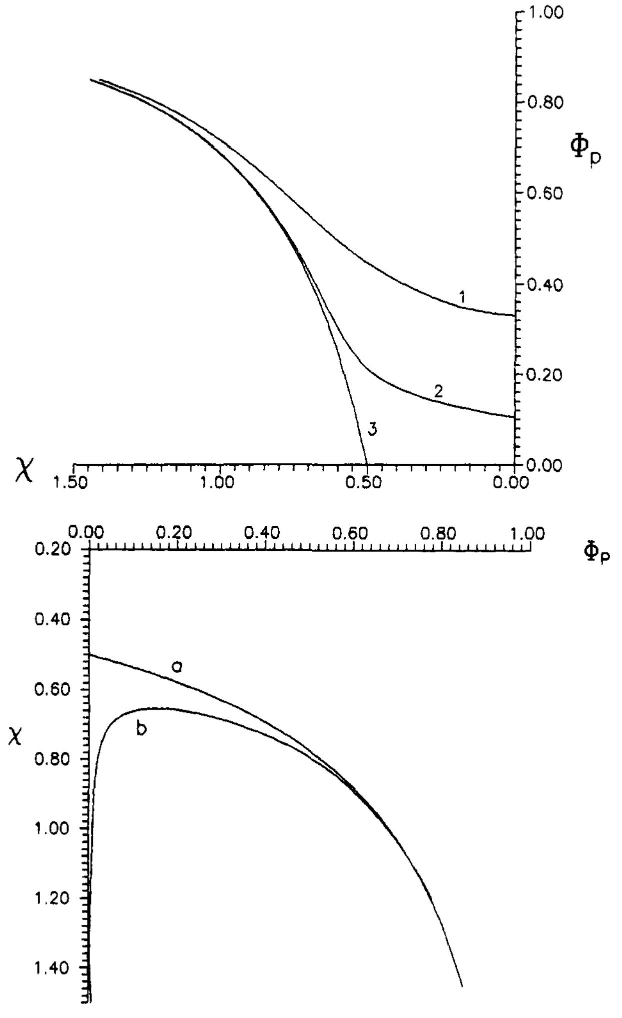


Figure 3. (a) Polymer concentration Φ_P vs interaction parameter χ for the brush in a one-component solvent: (1) $\sigma = 12$, (2) $\sigma = 60$, (3) $\sigma \to \infty$. (b) Phase separation in a solution of polymer with degree of polymerization $p \to \infty$ (a) and $p = 100$ (b).

Somewhat more essential from the theoretical point of view is the analysis of the behavior of the volume fraction of polymer in the brush Φ_P. Figure 3a illustrates the dependences of $\Phi_P = \Phi_P(\chi)$ according to eq 7 for the values of $\sigma = 12$ and 60 (curves 1 and 2) just as in Figure 2 and also for $\sigma \to \infty$ (curve 3).

Consider first the case of $\sigma \to \infty$. In this limit free energy F^{in} (eq 2) does not contain the last addend and, hence, it is equal to the free energy of the solution of polymer with a polymerization degree $p \to \infty$. Just at $p \to \infty$ the polymer chain in solution as well as the grafted chain in the brush does not contribute to translational entropy. The chemical potential of the solvent μ in the polymer solution is given by:

$$\mu = \ln(1 - \Phi_P) + (1 - 1/p)\Phi_P + \chi\Phi_P^2 \qquad (11)$$

$$\mu = \ln(1 - \Phi_P) + \Phi_P + \chi\Phi_P^2, \qquad p \to \infty \qquad (12)$$

The similarity between the brush (in the limit $\sigma \to \infty$) and the polymer solution (in the limit $p \to \infty$) gives us the possibility of connecting the characteristics of the brush in a poor solvent with some characteristics of a well-known demixing transition in a polymer solution (Figure 3b). Really, if $p \to \infty$, then at $\chi > {}^1/_2$ the concentrated polymer solution coexists with a free solvent, i.e.

$$\mu(p \to \infty) = 0 \qquad (13)$$

A brush is also in equilibrium with a free solvent. Hence, the χ dependence of the volume fraction Φ_P of the polymer in the brush in the poor solvent case ($\chi \geq {}^1/_2$, $\sigma \to \infty$) must coincide with the binodal branch for the polymer solution ($p \to \infty$, $\chi \geq {}^1/_2$). At finite σ the brush thermodynamics is not completely equivalent to that of the polymer solution. Nevertheless, the Φ_P value in a poor solvent is only slightly above the binodal (Figure 3a); there is no power-law dependence on σ for Φ_P (cf. eq 10). This "binodal-like" regime describes the collapsed state of the brush.

At the same time in good- and Θ-solvents Φ_P has a nonzero value and increases with an increase in $1/\sigma$ according to the power law (eqs 8 and 9; Figure 3a). As a result, the collapse of the brush is realized by a smooth increase in the polymer concentration Φ_P in the brush with an increase in χ, approaching the binodal of the polymer solution (at $p \to \infty$) and passing along and slightly above the binodal (Figure 3a).

As follows from the analysis of eq 7 there is no singularity in Φ_P or in the free energy of the brush (see also ref 11). Thus, in spite of the similarity of the brush collapse and phase separation in the polymer solution, collapse of the brush (at finite σ) is not a phase transition; i.e., it is not a real thermodynamic transition.[11]

One of the consequences of this known property of brush collapse is the dependence of the transition position, obtained in the experiment, on the studied characteristic. As is seen, for example, from the comparison of Figures 2 and 3a, a pronounced alteration of the brush height $H = H(\chi)$ is observed in the region of smaller values of χ (stronger solvent) than alteration of the polymer concentration Φ_P in the brush. We shall consider it below in more detail.

III. Collapse–Stretching Transition of the Brush in a Binary Solvent. A. General Formalism. Pass over now to the main object of our consideration. The polymer brush considered in the previous section is now assumed to be immersed in a binary mixture of low molecular weight components A and B with volume fractions Φ and $1 - \Phi$ correspondingly. The dimensions a of the molecules A and B and polymer units are assumed to be equal and $a = 1$ as previously.

Just as it was above, the balance of the two systems will be considered: (1) the polymeric brush contained the solvent components and (2) a binary solvent in the bulk. The volume interactions in the systems are described by Flory parameters χ_A and χ_B for polymer–solvent pairs and χ_{AB} for the A–B pair.[14]

Unknown fractions Φ_A and Φ_B of components A and B in the brush and $\Phi_P = 1 - \Phi_A - \Phi_B$ are determined by equality of the chemical potentials of the solvent components in the brush (in) and in the bulk (out):

$$\mu_x^{\text{in}} = \mu_x^{\text{out}} \qquad x = \text{A, B} \qquad (14)$$

Free energy F^{in} of the brush in the volume $\sigma H = n_A + n_B + N$ can be written in the form:

$$F^{\text{in}} = n_A \ln \Phi_A + n_B \ln \Phi_B + \Phi_P(\chi_A n_A + \chi_B n_B) + n_A\Phi_B\chi_{AB} + 3H^2/2N \qquad (15)$$

where the first two addends are the mixing entropies for the A and B components of the solvent, the three addends containing χ_A, χ_B, and χ_{AB} are related to binary interactions, and the last one is the elastic energy of the chains in the brush. Equation 15 without the last addend gives us the free energy of the solution of the free infinite-length polymer.

The free energy of the solvent contains an entropy of mixing addend and the free energy of binary interactions with χ_{AB} only:

$$F^{\text{out}} = n_A \ln \Phi + n_B \ln(1 - \Phi) + n_A(1 - \Phi)\chi_{AB} \qquad (16)$$

The chemical potentials then are given by:

$$\mu_x^{\text{in,out}} = \delta F^{\text{in,out}}/\delta n_x \qquad x = \text{A, B} \qquad (17)$$

$$\mu_A^{\text{in}} = \ln \Phi_A + \Phi_P + (\chi_{AB}\Phi_B + \chi_A\Phi_P)(\Phi_B + \Phi_P) - \chi_B\Phi_B\Phi_P + 3/(\phi_P\sigma^2)$$

$$\mu_B^{\text{in}} = \ln \Phi_B + \Phi_P + (\chi_{AB}\Phi_A + \chi_B\Phi_P)(\Phi_A + \Phi_P) - \chi_A\Phi_A\Phi_P + 3/(\phi_P\sigma^2) \qquad (18)$$

$$\mu_A^{\text{out}} = \ln \Phi + \chi_{AB}(1 - \Phi)^2$$

$$\mu_B^{\text{out}} = \ln(1 - \Phi) + \chi_{AB}\Phi^2 \qquad (19)$$

Equations 18 and 19 and the balance condition (14) give us the system of two equations for determining the equilibrium characteristics of the brush as a function of the solvent composition in the bulk Φ, Flory interaction parameters χ_A, χ_B, and χ_{AB}, and the density of surface coverage $1/\sigma$:

$$\ln(\Phi_A/\Phi) + \chi_{AB}[\Phi_B(1 - \Phi_A) - (1 - \Phi)^2] + \Phi_P + [\chi_A(1 - \Phi_A) - \chi_B\Phi_B]\Phi_P + 3/\Phi_P\sigma^2 = 0 \qquad (20)$$

$$\ln(\Phi_B/(1 - \Phi)) + \chi_{AB}[\Phi_A(1 - \Phi_B) - \Phi^2] + \Phi_P - [\chi_A\Phi_A - \chi_B(1 - \Phi_B)]\Phi_P + 3/\Phi_P\sigma^2 = 0 \qquad (21)$$

Equations 20 and 21 are totally equivalent to the equations obtained in ref 9 and give a full description of the system as a whole. We have investigated numerical solutions of equations 20 and 21 in the wide region of the parameter variation. Below typical dependences of brush characteristics on these parameters will be shown.

B. Collapse–Stretching Transition in the Brush. The numerical solution of Equations 20 and 21 will be used now in the analysis of the collapse–stretching transition of the brush immersed in the mixture of good solvent A ($\chi_A < {}^1/_2$) and precipitant B ($\chi_B > {}^1/_2$), with components A and B being compatible but without attraction to one another ($0 < \chi_{AB} < 2$). Figures 4 and 5 demonstrate dependences of the height of the brush and polymer volume fraction Φ_P on the binary solvent composition in the bulk. As an example of a good solvent it was chosen an athermal solvent ($\chi_A = 0$) and θ solvent ($\chi_A = {}^1/_2$). The influence of the precipitant strength is

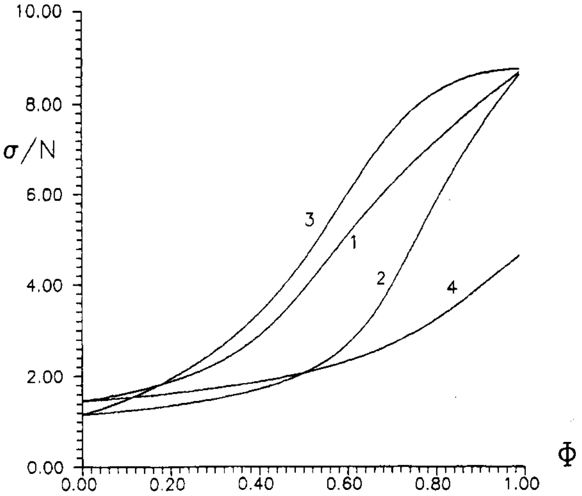


Figure 4. Relative brush height $H\sigma/N$ as a function of the fraction Φ of good solvent A in a binary solvent, $\sigma = 60$: (1) $\chi_A = 0$, $\chi_B = 1$, $\chi_{AB} = 0$; (2) $\chi_A = 0$, $\chi_B = 1.5$, $\chi_{AB} = 0$; (3) $\chi_A = 0$, $\chi_B = 1.5$, $\chi_{AB} = 1.5$; (4) $\chi_A = 0.5$, $\chi_B = 1$, $\chi_{AB} = 0$.

demonstrated ($\chi_B = 1$ and 1.5). Two cases are presented: the absence of interaction between A and B components ($\chi_{AB} = 0$) and their strong repulsion ($\chi_{AB} = 1.5$).

It is seen that there is more or less an S-shaped transition from the collapsed state at low values of Φ to the swollen state at a high fraction of good solvent A in the bulk. The position of the transition depends on the strengths of the solvent χ_A and precipitant χ_B and the value of χ_{AB}. The analysis of the solution of equations 20 and 21 shows that there is no singularity in Φ_P, H, or the free energy of the brush; hence, this brush collapse is not a phase transition. As a consequence, the regions of main alterations in the height of the brush H and in the polymer concentration of the brush Φ_P do not entirely coincide. Figure 5 shows derivatives $\delta H/\delta\Phi$ and $[\delta\Phi_P/\delta\Phi]$, with maxima defining the position of the transition point.

A more detailed analysis of the transition can be made on the basis of Figure 6 that shows volume fractions of polymer Φ_P, good solvent Φ_A, and precipitant Φ_B in the brush as functions of volume fraction Φ of good solvent A in the bulk.

It is seen from Figure 6a–c that there are two regimes of the brush composition variation. Let us start from the collapsed state that corresponds to the brush in precipitant, $\Phi = 0$. The value Φ_P in this case depends only slightly on σ (cf. Figure 3). With addition of a good solvent (from $\Phi = 0$ to $\Phi \cong 0.6$–0.7 in Figure 6), the regime of decollapse (or swelling) of the brush is realized; Φ_P decreases more or less sharply. This swelling is realized mainly due to penetration of the solvent molecules A in the brush: the value of Φ_A increases with increasing Φ. At the same time, precipitant is not forced out from the brush. On the contrary, additional though weak penetration of the precipitant in the brush appears to take place; i.e., Φ_B increases slightly with the increase in Φ.

The second regime of the brush behavior is realized in the swollen brush at a high fraction Φ of the solvent A in the bulk. In this regime the polymer concentration in the brush depends on σ (cf. eqs 8 and 9) and changes slightly with variation of the binary solvent composition. An increase in Φ results mainly in forcing the precipitant B out from the brush and exchanging it with solvent molecules A. It is seen from Figure 6 that Φ_B passes the maximum and then decreases with increasing Φ; Φ_A always increases.

C. Preferential Solvation. To study the effect of preferential solvation, consider also a hypothetical system (base system with a quasi-one-component solvent) where such an effect does not take place. In this case $\Phi_A/\Phi_B = \Phi/(1 - \Phi)$ and

$$\Phi_A = \Phi(1 - \Phi_P), \qquad \Phi_B = (1 - \Phi)(1 - \Phi_P) \qquad (22)$$

That means an assumption of virtual bonds between molecules A and B such that every Φ molecules A are accompanied by $1 - \Phi$ molecules B in the exchange bulk solvent–brush. Thus, the equilibrium condition (14) must be displaced by the condition:

$$\Phi\mu_A^{\text{in}} + (1 - \Phi)\mu_B^{\text{in}} = \Phi\mu_A^{\text{out}} + (1 - \Phi)\mu_B^{\text{out}} \qquad (23)$$

corresponding to summation of eqs 18 and 19 with coefficients Φ and $1 - \Phi$. Substitution of eqs 20 and 21 and the condition (22) in eq 23 gives

$$\ln(1 - \Phi_P) + \Phi_P + [\chi_A\Phi + \chi_B(1 - \Phi) - \chi_{AB}\Phi(1 - \Phi)]\Phi_P^2 + 3/\Phi_P\sigma^2 = 0 \qquad (24)$$

It can be easily seen that eq 24 is equivalent to eq 7 for the case of the brush immersed in a one-component solvent with effective polymer–solvent interaction parameter χ:

$$\chi = \chi_A\Phi + \chi_B(1 - \Phi) - \chi_{AB}\Phi(1 - \Phi) \qquad (25)$$

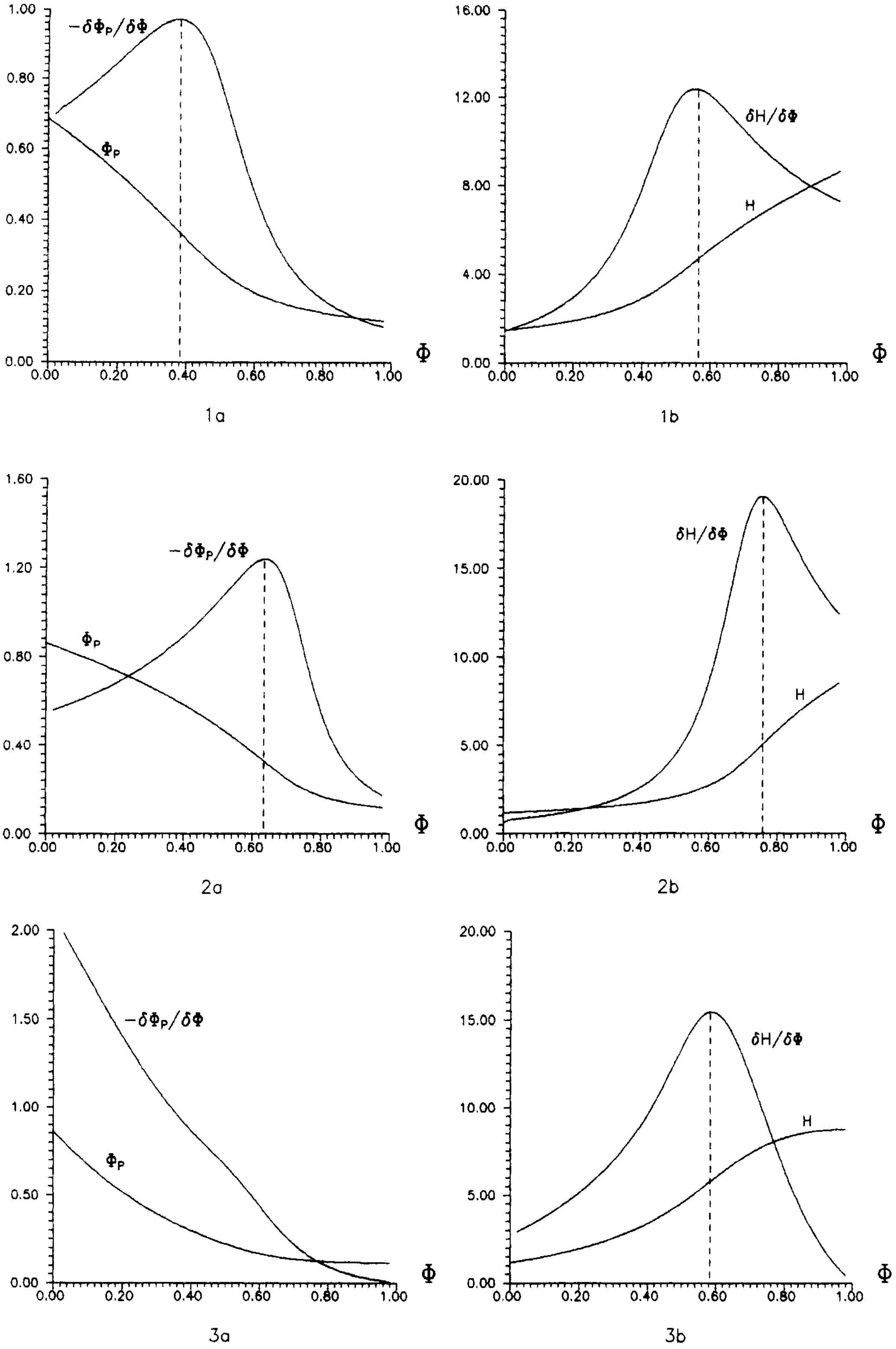
Thus, a binary solvent in a hypothetical base system appears to be totally equivalent to a one-component solvent with Flory parameter χ according to eq 25 that depends on χ_A, χ_B, χ_{AB}, and also on the fraction Φ of solvent A in the bulk and does not directly depend on brush characteristics Φ_A, Φ_B, and Φ_P.

Figures 6 and 7 allow us to compare the characteristics of the real system with that of quasi-one-component systems. Figure 7 demonstrates the effect of preferential solvation in real systems. It is seen that the relative fraction of good solvent in the brush is bigger than that in the bulk. The effect of preferential solvation occurs mainly in the regime of brush collapse, and the magnitude of the effect in this region increases with an increase in distinction between solvent components, $\chi_B - \chi_A$ and χ_{AB} (see also Appendix 1). The effect can be quite great; for example, at $\chi_A = 0$, $\chi_B = \chi_{AB} = 1.5$ (curve 4 in Figure 7) and at 20% of good solvent A in the bulk, the solvent inside the brush contains more than 60% of good solvent. A detailed study of the effect of preferential solvation in brushes is also given in ref 9.

At the same time, the effect of disproportionality of a binary solvent does not change the main qualitative regularities of brush swelling in the mixed solvent (Figure 6). So, in the region of brush decollapse an increase in Φ_A as well as Φ_B with an increase in Φ is always observed. Comparison of solid and dashed curves in Figure 6 shows that preferential solvation in the decollapse regime results only in a more pronounced increase of Φ_A with Φ and a less pronounced increase of Φ_B with Φ than in the case of the restriction of disproportionality. Concerning Φ_P, preferential solvation can both increase and decrease the value of Φ_P, as can be seen from Figure 6a–c (and Appendix 1). As a result, the dependences $\Phi_P = \Phi_P(\Phi)$ are less abrupt than in the case of a quasi-one-component solvent. The effect is not very large.

In the regime of a swollen brush the effect of solvent disproportionality is small and has no primitive dependences on the parameters $\chi_B - \chi_A$ and χ_{AB}.

D. Ternary Diagrams. Considering a swelling–collapse transition of the polymer brush in a one-component solvent, we have shown that the dependence $\Phi_P = \Phi_P(\chi)$ partially goes along the binodal of the phase



1a 1b

2a 2b

3a 3b

Figure 5. Polymer concentration Φ_P (a) and brush height $H\sigma/N$ (b) and their derivatives vs the fraction Φ of good solvent A in a binary solvent, $\sigma = 60$: (1) $\chi_A = 0$, $\chi_B = 1$, $\chi_{AB} = 0$; (2) $\chi_A = 0$, $\chi_B = 1.5$, $\chi_{AB} = 0$; (3) $\chi_A = 0$, $\chi_B = 1.5$, $\chi_{AB} = 1.5$.

diagram of the polymer solution. An analogy between the ternary systems, i.e., a brush in a binary solvent and a polymer solution in a binary solvent, appears to be a generalization of this consequence.

The investigations of a ternary polymer solution have a long history starting from the 1940s.[14] The ternary diagram in Figure 8 shows a phase separation curve of the polymer solution[14] at $p \to \infty$ (curve 1) that corresponds also to mutual dependences between Φ_P, Φ_A, and Φ_B in the brush at $\sigma \to \infty$. Phase boundaries in the polymer solution at $p \to \infty$ as well as in the brush at $\sigma \to \infty$ are in equilibrium with the mixed solvent without polymer.

Curves 2–4 of Figure 8 correspond to brushes with decreasing areas σ of surface coverage. As is seen from Figure 8, the collapsed regime of the brush analyzed above is a "binodal" regime. The peculiarities of the collapsed regime observed in Figures 6 and 7 entirely correspond to the peculiarities of the phase separation of polymer ($p \to \infty$) in the mixture of a good solvent and a precipitant. In particular, just the path along the binodal corresponds to an increase in Φ_A and Φ_B with an increase in Φ and a decrease in Φ_P (see Figure 10 and Appendix 2).

E. Effective χ Value. The effective χ value (eq 25) was introduced in the section III.C for the hypothetical

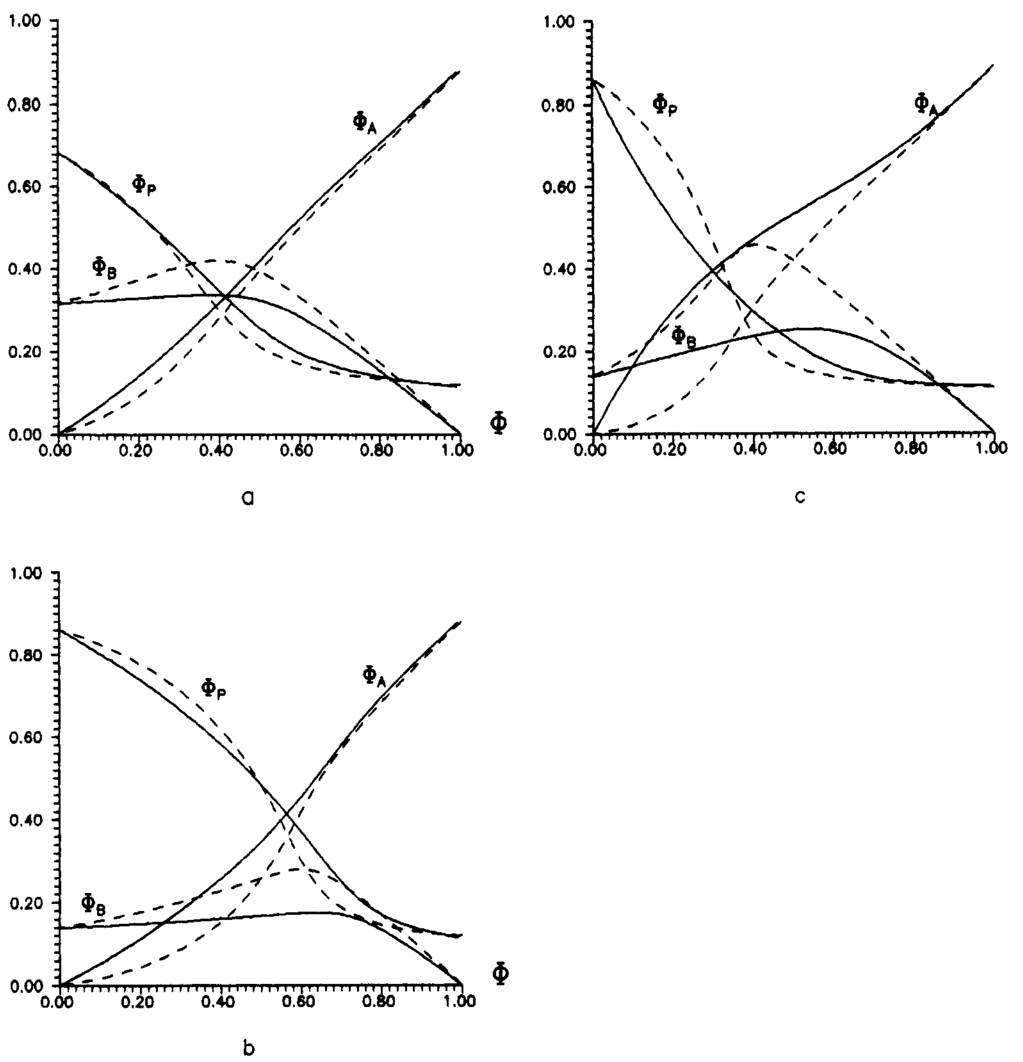


Figure 6. Concentration of polymer (Φ_P), good solvent A (Φ_A), and precipitant B (ϕ_B) in the brush vs the fraction Φ of good solvent A in a binary solvent. Solid curves correspond to the brush in a binary solvent with preferential solvation; dashed curves correspond to the brush in a quasi-one-component solvent without the effect of preferential solvation, $\sigma = 60$: (a) $\chi_A = 0$, $\chi_B = 1$, $\chi_{AB} = 0$; (b) $\chi_A = 0$, $\chi_B = 1.5$, $\chi_{AB} = 0$; (c) $\chi_A = 0$, $\chi_B = 1.5$, $\chi_{AB} = 1.5$.

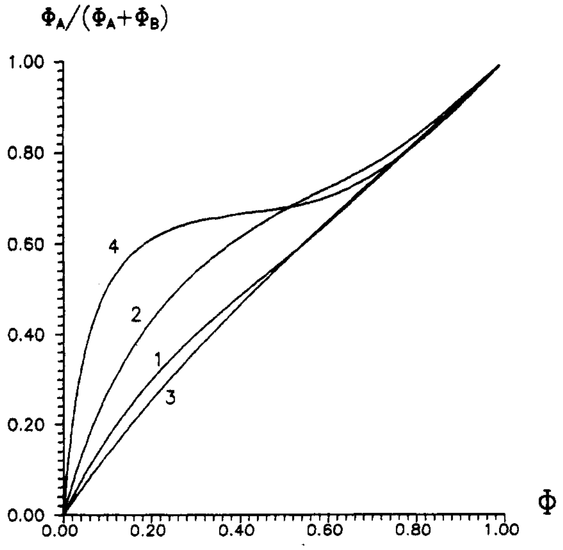


Figure 7. Composition of solvent inside the brush vs composition Φ of the bulk, $\sigma = 60$: (1) $\chi_A = 0$, $\chi_B = 1$, $\chi_{AB} = 0$; (2) $\chi_A = 0$, $\chi_B = 1.5$, $\chi_{AB} = 0$; (3) $\chi_A = 0.5$, $\chi_B = 1$, $\chi_{AB} = 0$; (4) $\chi_A = 0$, $\chi_B = 1.5$, $\chi_{AB} = 1.5$.

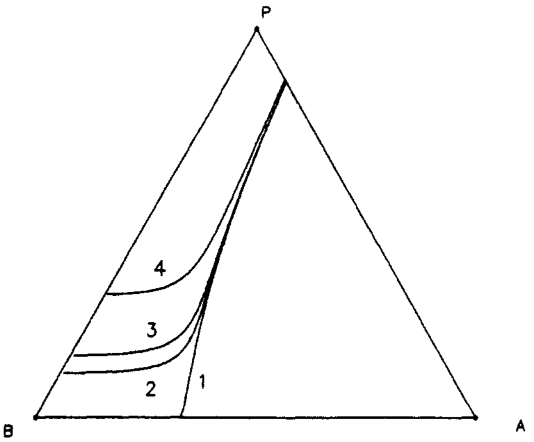


Figure 8. Ternary diagram of the polymer ($p \to \infty$) solution (1) and the brush in a binary solvent: $\sigma = 60$ (2), $\sigma = 36$ (3), $\sigma = 12$ (4), $\chi_A = 0$, $\chi_B = 1.5$, $\chi_{AB} = 1.5$.

base system. The analysis shows that this parameter gives us also a rough description of polymeric characteristics H and Φ_P of real brushes being in a binary solvent with the possibility of preferential solvation of its components. Really, as can be seen from Figure 9a,b, the use of χ allows us to shift the curves $H = H(\Phi)$ and $\Phi_P = \Phi_P(\Phi)$ (Figures 4 and 5) in such a way as to form a set of dependences located near the transition curve corresponding to the base system (quasi-one-component solvent). It should be emphasized that it is not mentioned in full coincidence with the base curve. The distinctions being the result of disproportionality of solvent components always remain; they increase with an increase in $\chi_B - \chi_A$ and $|\chi_{AB}|$. This distinction changes a sign with a decrease in χ. In the left part of Figure 9a curves $H = H(\chi)$ for the collapsed brush lie above the base one, and in the right part of Figure 9a

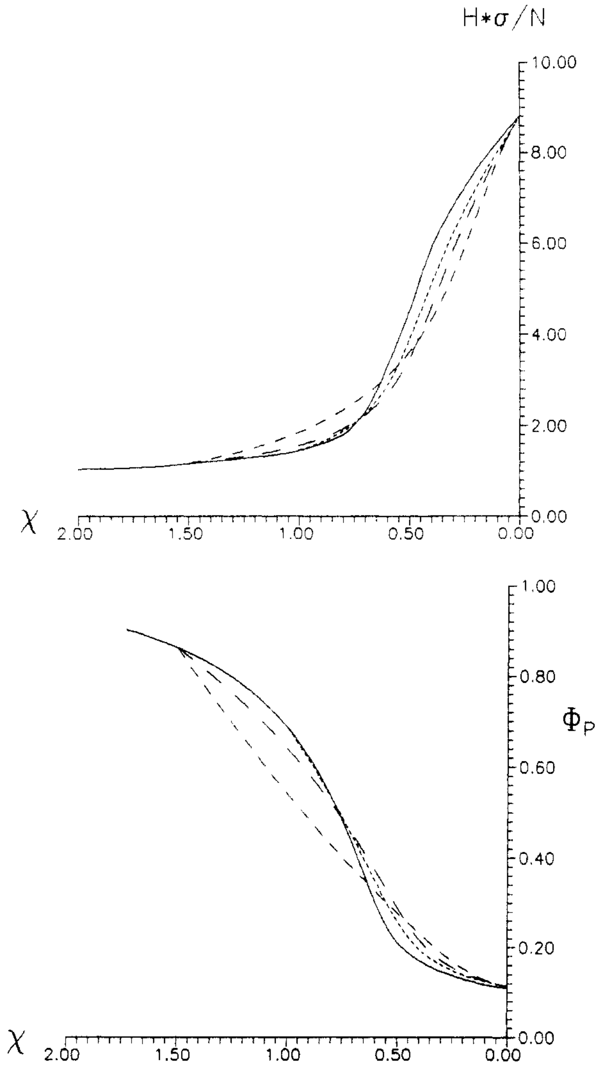


Figure 9. Relative brush height $H\sigma/N$ (a) and polymer concentration Φ_P (b) as a function of interaction parameter χ, $\sigma = 60$: in a one-component solvent (—) and binary solvents: (· · ·) $\chi_A = 0$, $\chi_B = 1$, $\chi_{AB} = 0$; (— —) $\chi_A = 0$, $\chi_B = 1.5$, $\chi_{AB} = 0$; (- - -) $\chi_A = 0$, $\chi_B = 1.5$, $\chi_{AB} = 1.5$.

the height of the brush swelled in a binary solvent appears to be less than that in the base system.

Obviously, just the opposite situation takes place for the variation of polymer concentration in the brush in a binary solvent (Figure 9b). In the collapsed state Φ_P is below base value; in the swollen state Φ_P is above it.

There are also some distinctions in the forms of the transition curves depending on the concrete values of interaction parameters χ_A, χ_B, and χ_{AB}. For example, at $\chi_{AB} = 0$ the curve $\Phi_P = \Phi_P(\Phi)$ appears to be convex in the decollapse regime, but at $\chi_{AB} > 0$ it is concave, (Figure 9b; see also Figure 6). In the last case the increase in Φ_A and Φ_B with increasing Φ in the decollapse regime appears to be more pronounced.

Parameter χ defined by eq 25 also gives one a rough description of the phase separation in the polymer solution. This is illustrated by Figure 10 where the binodal of Figure 8 is transformed in dependences of Φ_P, Φ_A, and Φ_B on χ.

As in the case of the polymer brush, the dependence Φ_P vs χ is deflected from the base curve and the sign of the deflection changes with a decrease in χ (at parameters considered).

A different sign of $\Phi_P(\Phi)$ deflection from the base curve can be accounted for by the influence of different factors in different regions of the binodal. In the region of great values of Φ_P the binodal for a binary solvent is deflected in the region of smaller Φ_P due to preferential solvation and an effective increase in the solvent strength of a swollen polymer. Approaching a critical point whose position is defined by equation:[14]

$$1 - 2\chi_B(1 - \phi_A) - 2\chi_A\phi_A + [2(\chi_{AB}\chi_B + \chi_{AB}\chi_A + \chi_A\chi_B) - \chi_{AB}^2 - \chi_B^2 - \chi_A^2]\phi_A(1 - \phi_A) = 0 \quad (26)$$

the main factor becomes displacement of this point in the region of a smaller value of effective parameter χ. As a result the binodal is deflected above the base.

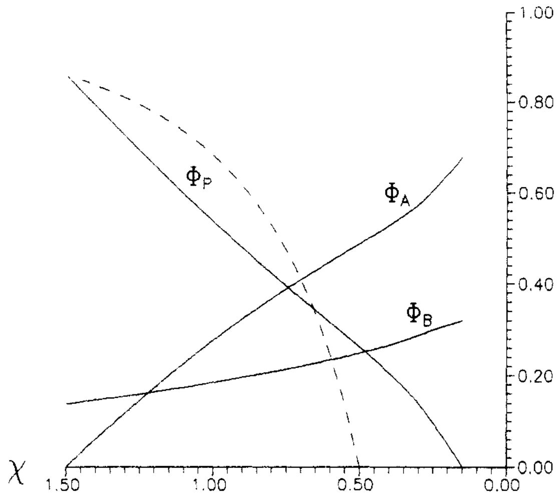


Figure 10. Concentration of the polymer (ϕ_P), good solvent A (ϕ_A), and precipitant B (ϕ_B) along the binodal of Figure 8 vs interaction parameter χ. The dotted line indicates the binodal in the case of the polymer ($p \to \infty$) in a one-component solvent.

Note that the effective χ parameter which gives the average interaction of the polymer with the solvent components provides us an approximate description of polymer concentration Φ_P in the system (brush or polymer solution). It evidently does not give us an effect of preferential solvation, providing nevertheless two main features of the collapse–decollapse transition: (1) nonlinear dependences $\Phi_P(\Phi)$ and $H(\Phi)$ that were considered in ref 9 as a result of preferential solvation and (2) approximately the true position of the transition point. This fact has a simple explanation. As is seen from Figure 6, dependences $\Phi_A(\Phi)$ and $\Phi_B(\Phi)$ obtained under the condition of preferential solvation (solid curves) have opposite signs of deflections from corresponding dashed curves obtained without preferential solvation. The greater the effect of preferential solvation, the greater are the deflections. Nevertheless, approximately equal Φ_A and Φ_B deflections compensate each other, providing a small deviation of the dependence $\Phi_P(\Phi)$ correctly obtained from that obtained in the absence of preferential solvation.

F. Nonmonotonous χ vs Φ Dependence. All systems so far considered were related to the mixtures solvent/precipitant, the parameter χ (eq 25) being a monotonous function on the solvent content. As is seen from eq 25, it is valid at $0 < \chi_{AB} \leq \chi_B - \chi_A$ (Figure 11). At $\chi_{AB} > \chi_B - \chi_A$ the dependence of χ on Φ passes through the minimum, and therefore one can expect a nonmonotonous dependence of the characteristics on the solvent composition. Such effects are known for polymer solutions. Thus, it is known[14] that in some cases the mixture of two precipitants (χ_A, $\chi_B > {}^1/_2$) appears to be a good solvent. It is possible at the condition of strong repulsion between A and B components. Really, it can be easily seen from eq 25 that, for example, at $\chi_A = \chi_B$ and $\chi_{AB} > 4(\chi_A - {}^1/_2)$ in a 50/50 mixture χ is less than ${}^1/_2$ than satisfies the solubility condition. Figure 12a shows the calculated curves of the phase separation of the polymer solution ($p \to \infty$), curves

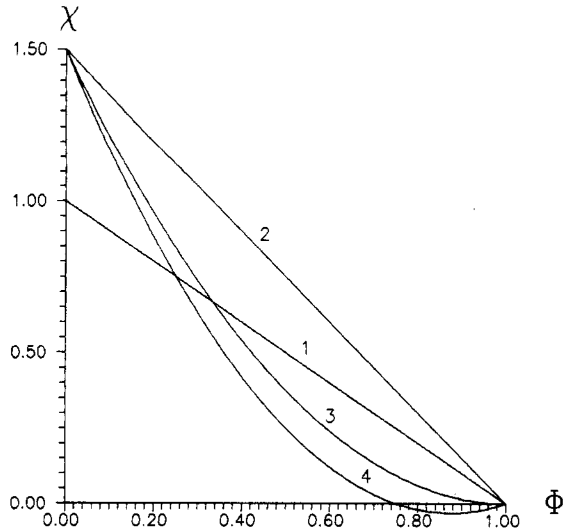


Figure 11. Dependence of the effective interaction parameter χ on the fraction Φ of good solvent A in the bulk: (1) $\chi_A = 0$, $\chi_B = 1$, $\chi_{AB} = 0$; (2) $\chi_A = 0$, $\chi_B = 1.5$, $\chi_{AB} = 0$; (3) $\chi_A = 0$, $\chi_B = 1.5$, $\chi_{AB} = 1.5$; (4) $\chi_A = 0$, $\chi_B = 1.5$, $\chi_{AB} = 2$.

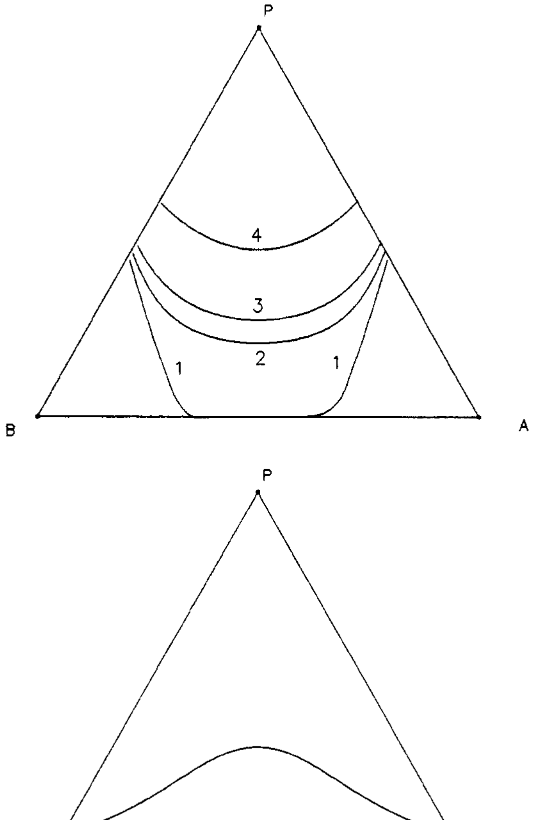


Figure 12. (a) Ternary diagram of the polymer solution (1) and the brush in a binary solvent: $\sigma = 60$ (2), $\sigma = 36$ (3), $\sigma = 12$ (4), $\chi_A = 0.7$, $\chi_B = 0.7$, $\chi_{AB} = 1$. (b) Ternary diagram of the brush in a binary solvent: $\sigma = 60$, $\chi_A = 0$, $\chi_B = 0$, $\chi_{AB} = -2.5$.

1, and calculated characteristics of the polymer brush at different surface coverage $1/\sigma$ in the mixture of two precipitants. At $\chi_{AB} < 0$, when solvent components are attracted to one another, an opposite situation is also possible (cf. ref 10). At $\chi_A = \chi_B = 0$ and $\chi_{AB} < -2$ in the 50/50 mixture $\chi > {}^1/_2$; hence, the mixture of two solvents appears to be precipitant. This case is illustrated by Figure 12b. Figure 12 shows additionally the connection between the brush behavior and the phase diagram of the polymer solution and can be a good background for further experiments.

Discussion

A. Main Results. Considered above was the collapse–stretching transition of a polymer brush immersed in a binary solvent composed of a good solvent (A) and a precipitant (B): $\chi_A < {}^1/_2$, $\chi_B > {}^1/_2$. Some conclusions can be drawn for the systems with $0 < \chi_{AB} < \chi_B - \chi_A$ when $\chi(\Phi)$ is a monotonous decreasing function:

1. There are two regimes of brush behavior successively realized in the system with increasing fraction Φ of good solvent A in the mixture: decollapse regime and regime of a swollen brush.

2. In the decollapse regime polymer concentration Φ_P in the brush depends slightly on surface coverage $1/\sigma$ and decreases along the binodal branch for an infinite-length ($p \rightarrow \infty$) polymer in solution. It is accompanied by an increase in both components of the solvent in the brush, Φ_A and Φ_B; Φ_A increases to a further extent than Φ_B.

3. In the decollapse regime a preferential solvation is observed: $\Phi_A > \Phi(1 - \Phi_P)$; $\Phi_B < (1 - \Phi)(1 - \Phi_P)$, the effect of disproportionality of the solvent, increases with an increase in $\chi_B - \chi_A$ and χ_{AB}.

4. In the regime of a swollen brush polymer concentration Φ_P has a power dependence on surface coverage $1/\sigma$ and changes relatively slightly with an increase in the fraction Φ of solvent A in the bulk. Inside the brush the exchange of component B to component A is realized. Preferential solvation in this regime is small.

5. In the case of a hypothetical quasi-one-component solvent (binary solvent with the preferential solvation effect excluded), three parameters χ_A, χ_B, and χ_{AB} combine a single parameter χ (eq 25), defined by the composition Φ of the bulk.

6. Qualitative behavior of the brush in all regions of solvent composition does not depend on preferential solvation. The parameter χ defined by solvent composition and interaction parameters gives also a rough description of the collapse–stretching transition in the brush immersed in a binary solvent. In such a description the value of Φ_A is always smaller than the real one, the value of Φ_B is always greater than the real one, and for the value Φ_P a sign of the error changes with an increase in Φ.

7. As the collapse–stretching transition is a continuous nonphase transition, the position of the transition observed depends on the studied characteristic.

Some of these conclusions are discussed above. We shall discuss below the transition position only and compare the theory with experiment and with the results of previous theories.

B. Collapse–Stretching Transition of a Polymer Brush. The transition of a polymer brush is not a phase one. Therefore, from the formal point of view, one can discuss only crossover between two regimes and, from the experimental point of view, one should characterize the transition position by the region of sharp alteration of the studied parameter.

Theoretical investigations of collapse in polymer systems are based usually on virial expansion that gives in particular

$$\chi - 1/2 \sim \sigma^{-1/2} \qquad (27)$$

for crossover between the Θ-regime and the collapsed state regime (eqs 9 and 10).

From the other side, analysis of the calculated smooth dependences $H = H(\phi)$ and $\Phi_P = \Phi_P(\Phi)$ (Figure 5) shows that the positions of maxima of these dependence derivatives differ noticeable. Actually, the dependences $\Phi_P = \Phi_P(\Phi)$ have the main alteration in the binodal regime, whereas dependences $H = H(\Phi)$ have it in the regime of the swollen brush. For $\delta H(\Phi)/\delta\Phi$ in all cases, the one-

Table 1. Position of the Transition Point ($\sigma = 60$)

	component A content Φ in free solvent			values of χ according to eq 25		
system	max $\mathrm{d}H/\mathrm{d}\Phi$	max $\mathrm{d}\Phi_P/\mathrm{d}\Phi$	max Φ_B	max $\mathrm{d}H/\mathrm{d}\Phi$	max $\mathrm{d}\Phi_P/\mathrm{d}\Phi$	max Φ_B
$\chi_A = \chi_{AB} = 0$ $\chi_B = 1$	0.56	0.38	0.50	0.44	0.62	0.50
$\chi_A = \chi_{AB} = 0$ $\chi_B = 1.5$	0.76	0.64	0.72	0.36	0.54	0.42
$\chi_A = 0$ $\chi_B = \chi_{AB} = 1.5$	0.58	(0.34)	0.60	0.27	(0.66)	0.24
Quasi-One-Component Solvent						
$\chi_A = \chi_{AB} = 0$ $\chi_B = 1$	0.58	0.70	0.44	0.58	0.70	0.56
$\chi_A = \chi_{AB} = 0$ $\chi_B = 1.5$	0.61	0.53	0.62	0.58	0.70	0.56
$\chi_A = 0$ $\chi_B = \chi_{AB} = 1.5$	0.38	0.32	0.40	0.58	0.70	0.56

component solvent included, the value of the parameter χ in a maximum is less than $^1/_2$, whereas maxima $|\delta\Phi_P(\Phi)/\delta\Phi|$ are located at $\chi > {}^1/_2$ (see Table 1). Note that, in the case of $\chi_A = 0$ and $\chi_B = \chi_{AB} = 1.5$, the dependence $\Phi_P = \Phi_P(\phi)$ is not S-shaped; the position of the middle of the transition is introduced in Table 1. All data in Table 1 are obtained at $\sigma = 60$; the dependence on σ was not analyzed.

The difference in the position of maxima $|\delta\Phi_P/\delta\Phi|$ and $\delta H/\delta\Phi$ is a direct consequence of the relationship (3′) and therefore is not surprising.

The results of this paper show that one more characteristic sensitive to the transition of the brush is the fraction of precipitant Φ_B in the brush. This characteristic has nonmonotonic dependence on Φ (and Φ_P), increasing with Φ in the binodal regime, decreasing in the swelling regime, and passing the maximum in the region of crossover between regimes. As is seen from Table 1, the maximum in Φ_B lies close to the maximum of $|\delta\Phi_P/\delta\Phi|$ and $\delta H/\delta\Phi$, closer to the second one. It corresponds to $\chi \leqslant {}^1/_2$, the value of χ depending on concrete values of χ_A, χ_B, and χ_{AB}.

It is interesting to note that in the case of the quasi-one-component solvent the position of maxima Φ_B lies at $\chi > 0.5$.

C. Comparison with Experiment and Previous Theories. Concerning the comparison with theoretical results, our investigation is performed in the same approximation as it was in ref 9. However, ref 9 was mainly devoted to the effect of preferential solvation. Our results are related to a wider set of problems. We have shown, in particular, what features of the system do not correspond to the effect of preferential solvation. Reference 10 was mainly devoted to the inhomogeneity of Φ_P along the height of the brush that was not considered in our work. In ref 10 it was also considered one of the cases of nonmonotonous dependence of brush characteristics on the solvent composition. This case was also studied experimentally[15] after this paper was submitted for publication.

In ref 8 the transition in the poly(dimethylsiloxane) brush in the mixture methanol (B)/dichloromethane (A) was studied by the SANS method. The results are presented in the form of dependences of the measured height of the brush H on the fraction Φ of dichloromethane in the bulk. As is shown in Appendix 3, the quantitative interpretation of the experiment in a good solvent needs an account of the nonuniform distribution of the polymer concentration in the brush. We did not take into account a decrease in the inhomogeneity of the brush in the collapsed state, whereas in the case of the precipitant (methanol) the inhomogeneity of the brush is not as great as that in the good solvent (dichloromethane) case. Experimental results (sample 1) show a high polymer concentration in the collapsed brush, $\Phi_P \cong 0.9$. It shows that the value of χ_B is sufficiently great.

Comparison of the form of the transition curve (Figure 5 from ref 8) with the curves of Figure 4 shows that H alteration is realized mainly in the region of $\Phi \cong 0.8$. A good coincidence of curve 2 of Figure 4 is seen at $\sigma/a^2 = 60$, $\chi_A = 0$, $\chi_B = 1.5$, and $\chi_{AB} = 0$ with the experimental data. In this case theoretical dependences have all peculiarities of experimental curves: a slight alteration of H in the region of $\Phi \cong 0.5$–0.6, a sharp transition in the region of Φ about $\Phi = 0.7$, and noticeable preferential solvation. The authors of ref 8 note that the chain remain collapsed in spite of a great value of $\Phi_A/(1 - \Phi_P)$. This also coincides entirely with the theoretical results as is seen from the calculated dependence $\Phi_A/(1 - \Phi_P)$ in Figure 7.

D. Concluding Remarks. The analogy obtained between the collapse–stretching transition of the polymer brush in a binary solvent and the phase separation of the polymer solution in a binary solvent is interesting in a number of aspects. From one side, there appears an opportunity to use additional experimental methods, for example, scattering methods, for measuring the height of the brush for problems of phase-separation study. From the other side, the problem of transition of the brush can enrich a long-standing experience in the study of phase separation in polymer solutions.

In this connection it should be noted that (1) in this paper all considerations were based on the scheme of Flory–Huggins theory with the assumption of constant values of χ parameters independent of polymer concentration and solvent composition. It is well-known that such simple assumptions in the case of a polymer solution in a binary solvent do not give entirely quantitative coincidence with the experiment. It should be the case also for the transitions in brushes. In principle, the theory can be easily generalized in terms of dependences of parameters χ on concentration. (2) The process of preferential solvation studied in this paper was guided only by the values of the parameters χ in the mean-field theory. The magnitude of disproportionality can depend also on specific interactions. (3) We did not take into account an inhomogeneity of the polymer concentration in the brush and change in an inhomogeneity after transition. Nevertheless, all these effects cannot influence the general picture of the transition.

Acknowledgment. We thank Dr. O. V. Borisov for helpful discussions of this problem. The work was partially supported by the Russian Foundation of Fundamental Investigations (Grant No. 93-03-5797).

Appendix 1. Preferential Solvation in a Polymer System

In this paper preferential solvation in the brush was studied numerically. This appendix concerns some simple evaluations that demonstrate the character of the dependence of the effect on parameters.

Consider for simplicity a mixed solvent of content $\Phi/(1 - \Phi) = 50/50$. In this case the difference of eqs 20 and 21 has quite a simple form:

$$\ln\left[\frac{1 - \Phi_P + \Delta\Phi}{1 - \Phi_P - \Delta\Phi}\right] - \chi_{AB}\Delta\Phi - \Phi_P(\chi_B - \chi_A) = 0 \qquad \text{(A1-1)}$$

where $1 - \Phi_P = \Phi_A + \Phi_B$ and $\Delta\Phi = \Phi_A - \Phi_B$. The value $(\Phi_A - \Phi_B)/(\Phi_A + \Phi_B) = \Delta\Phi/(1 - \Phi_P)$ characterizes the magnitude of disproportionality. Assuming $\Delta\Phi/(1 - \Phi_P)$

< 1, we have after expansion of the logarithm:

$$\frac{\Delta\Phi}{1-\Phi_P} \cong \frac{\Phi_P(\chi_B - \chi_A)}{2-(1-\Phi_P)\chi_{AB}} \qquad \text{(A1-2)}$$

It is seen that disproportionality increases with an increase in ϕ_P, $\chi_B - \chi_A$, and χ_{AB}. Thus, disproportionality, or preferential solvation, is guided by an unsimilarity of the solvent components in their interactions with the polymer and repulsion between the components. At the same time the polymer concentration in the system defines an opportunity for some interactions to occur. Solvent–polymer interactions are guided by polymer concentration Φ_P, whereas solvent–solvent interactions are guided by solvent concentration $1 - \Phi_P$. It is interesting to note that eqs A1-1 and A1-2 are valid both for polymer brushes and the swelling polymer in a mixed solvent; in both cases the polymerization degree plays no role. Concrete characteristics of the polymer system define only the magnitude Φ_P contained in eqs A1-1 and A1-2.

In order to define Φ_P, let us consider the sum of eqs 20 and 21 at the same condition $\Phi/(1 - \Phi) = 50/50$. It can be presented in the form:

$$\ln(1-\Phi_P) + \Phi_P + \frac{1}{2}\left(\chi_A + \chi_B - \frac{1}{2}\chi_{AB}\right){\Phi_P}^2 + \frac{3}{\Phi_P\sigma^2} + (\chi_B - \chi_A)\Phi_P\Delta\phi + \frac{\chi_{AB}}{2}\Delta\Phi^2 + \ln\left(1 - \left(\frac{\Delta\Phi}{1-\Phi_P}\right)^2\right) = 0 \qquad \text{(A1-3)}$$

With preferential solvation being not taken into account, $\Delta\Phi = 0$, it was shown that the value of Φ_P is defined by the single parameter χ (eq 25) only. Linear in $\Delta\Phi$ correction assuming slight preferential solvation leads to an increase of the effective χ value on the magnitude $(\chi_B - \chi_A)\Delta\Phi/\Phi_P$, i.e., to an increase in polymer concentration Φ_P. It is interesting to note that two effects that seem contradictory are associated in this case: preferential solvation leads to strengthening of the solvent in the brush, from one side, and to deswelling of the brush, from the other side.

Appendix 2. Polymer Swelling in a Quasi-One-Component Solvent

Consider the relative fractions of solvent components Φ_A and Φ_B in the polymer system ($p \to \infty$) along the boundary of the two-phase region in the case of a quasi-one-component solvent. In this case the conditions (22) are valid and hence:

$$\frac{d\Phi_A}{d\Phi} = \frac{d}{d\Phi}\Phi(1-\Phi_P) = (1-\Phi_P) - \Phi\frac{d\Phi_P}{d\chi}\frac{d\chi}{d\Phi} \qquad \text{(A2-1)}$$

$$\frac{d\Phi_B}{d\Phi} = \frac{d}{d\Phi}(1-\Phi)(1-\Phi_P) = -(1-\Phi_P) - (1-\Phi)\frac{d\Phi_P}{d\chi}\frac{d\chi}{d\Phi} \qquad \text{(A2-2)}$$

According to eqs 12 and 13, we have

$$\frac{d\Phi_P}{d\chi} = \frac{\Phi_P(1-\Phi_P)}{1-2\chi(1-\Phi_P)} \qquad \text{(A2-3)}$$

and according to eq 25:

$$d\chi/d\Phi = \chi_A - \chi_B - \chi_{AB}(1-2\Phi) \qquad \text{(A2-4)}$$

Since $d\Phi_P/d\chi > 0$ and $d\chi/d\Phi < 0$ (at $\chi_B \geqslant \chi_{AB}$, i.e., when the dependence of χ on Φ is monotonous), $d\Phi_A/d\Phi$ contains two positive addends, and, as would be expected, it is always positive, whereas the signs of the addends $d\Phi_B/d\Phi$ are different.

Substituting eqs A3 and A4 in eq A2, one can see that a sufficient condition for $d\Phi_B/d\Phi > 0$ is

$$\frac{\Phi_P\chi}{1-2\chi(1-\Phi_P)} > 1 \qquad \text{(A2-5)}$$

that is valid at

$$\chi > \frac{1}{2-\Phi_P} \qquad \text{(A2-6)}$$

Solving eqs 12 and 13 with respect to χ and taking into account positive-sign expansion of $(-\ln x)$ at $x < 1$:

$$-\ln x = 2\sum_{k=1}^{\infty}\left(\frac{1-x}{1+x}\right)^{2k-1}\frac{1}{(2k-1)} \qquad \text{(A2-7)}$$

we have at $x = 1 - \Phi_P$

$$\chi = -\frac{1}{\Phi_P} - \frac{\ln(1-\Phi_P)}{{\Phi_P}^2} > -\frac{1}{\Phi_P} + \frac{2}{\Phi_P(2-\Phi_P)} = \frac{1}{2-\Phi_P} \qquad \text{(A2-8)}$$

in correlation with eq A6. Thus, actually, at equilibrium swelling of the polymer in a quasi-one-component mixture precipitant/good solvent the content of both components in the polymer system should increase with an increase in the good solvent content in the mixture. An increase in Φ_B means that the swelling of the polymer $(1 - \Phi_P)$ increases greatly as compared to a decrease of the precipitant content $(1 - \Phi)$ in the bulk.

Appendix 3. Comparison with Experiment

In ref 8 the transition of the poly(dimethylsiloxane) brush in the mixture methanol (B)/dichloromethane (A) was studied by the SANS method. From the data obtained[8] on quantity γ mg/m^2 of a grafted polymer and experimental data on the height of the brush H one can obtain surface coverage $1/\sigma$ and mean polymer concentration in brush Φ_P. It should be taken into account that in the case of a good solvent there is a decrease in the polymer concentration along the height of the brush;[8] therefore, the value of H measured corresponds not to limiting H_{max} but to a somewhat smaller value.

Really, let us show that the use of a measured value of H_{max} leads to a contradiction.

The experimental value $\gamma = 19.7$ mg/m^2 (sample 1) and $H = 815$ Å measured in dichloromethane give $\Phi_P = 0.24$. According to more detailed theory, taking into account the inhomogeneity of the concentration in the brush[4] $\Phi_P = Na^3/(H_{max}\sigma) = (\pi^2/8)^{1/3}(\sigma/a^2)^{-2/3}$. Therefore, assuming $H = H_{max}$, we have $\sigma/a^2 = 10$. Comparison of this value with the experimental value of the grafting surface per molecule $\sigma = 1.37 \times 10^3$ Å^2 gives the segment dimension $a = 11.7$ Å. Comparison of the experimental value H and the theoretical dependence of H_{max} on the segment number in molecule N and the molecular weight of grafting chains $M = 166 \times 10^3$ gives the number of segments $N = 160$ and, hence, the molecular weight of the segment $M_{segm} = 10^4$; i.e., the segment contains about 13 monomer units.

Obviously, the value of M_{segm} is too high and cannot agree with segment length $a \cong 12$ Å from the same data obtained.

At the same time, this contradiction is entirely canceled when the measured height of the brush is assumed to be less than the maximum one, for example, in q times. As a result, all values obtained from the experiment differ. Thus, Φ_P decreases in q times, σ/a^2 increases in $q^{3/2}$ times, a decreases in $q^{3/4}$ times, H/a increases in $q^{7/4}$ times, N increases, and M_{segm} decreases in $q^{9/4}$ times. For example, at $q = 1.5$ we have $\sigma/a^2 \cong 30$, $a = 8.6$ Å, $M_{segm} \cong 400$; i.e., the segment contains about 5 monomer units. It is seen that values of a and M_{segm} in this case are in good coincidence.

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