

Flory Theorem for Structurally Asymmetric Mixtures

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The generalization of the Flory theorem for structurally asymmetric mixtures was derived and tested by direct visualization of conformational transformations of brushlike macromolecules embedded in a melt of linear chains. Swelling of a brush molecule was shown to be controlled not only by the degree of polymerization (DP) of the surrounding linear chains, N_B , but also by the DP of the brush's side chains, N , which determines the structural asymmetry of the mixed species. The boundaries of the swelling region were established by scaling analysis as $N^2 < N_B < N_A/N$, where N_A is the degree of polymerization of the brush backbone. Experiment and theory demonstrated good agreement.

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Polymer solutions are unique physical systems in which the interactions between macromolecules become screened as polymer concentration increases. In polymeric melts, where the interactions are completely screened, macromolecules behave as almost ideal chains obeying random walk statistics. The ideality of polymer chains in a melt was first established over 50 years ago by Flory [1] and became latter known as the Flory theorem [2,3]. There is a very interesting consequence of the Flory theorem related to the swelling behavior of polymer chains in a polydisperse melt. A "guest" molecule with the degree of polymerization N_A embedded into a melt of chemically identical polymer chains with the degree of polymerization N_B starts swelling when $N_A > N_B^{2/(4-d)}$, where d is the space dimensionality. For three-dimensional (3D) and two-dimensional (2D) mixtures, shorter macromolecules tend to penetrate and swell the guest macromolecule when $N_A > N_B^2$ and $N_A > N_B$, respectively. Experimental studies on both 3D and 2D binary mixtures confirmed swelling of longer chains in a melt of shorter chains [4–8].

The recent developments in nanocomposite materials pose new challenges in determining the controlling factors for the stability and conformation of polymeric mixtures that contain molecular species with different architectures [9–11]. Mixtures of linear polymers with dendrimers, branched polymers, nanoparticles, carbon nanotubes, and clay platelets are used to create novel nanocomposite materials. Since the structures of these molecules are significantly different from those of linear polymer chains, this makes applicability of the classical Flory theorem to these mixtures questionable. In this letter, we show that one can modify the Flory approach to describe mixtures of structurally different species. We use atomic force microscopy (AFM) to monitor conformations of well-defined brushlike macromolecules [12–14] with a degree of polymerization (DP) of the backbone N_A and DP of side chains N embedded into a monolayer of linear chains that have a degree

of polymerization N_B (Fig. 1). The experiments clearly show that molecular brushes swell as the DP of the surrounding linear chains, N_B , decreases. The intriguing finding of this study is that the swelling behavior not only depends on the length of the linear chains (N_B) but it is also affected by the length of the brush's side-chains (N) that define the structural asymmetry of the mixed species. To explain these findings, the Flory theorem of polymer melts was reformulated to account for the structural asymmetry and to establish the boundaries of the swelling regime.

The brushlike macromolecules used in this study consist of a long flexible backbone ($N_A = 1580$) with densely grafted poly(*n*-butylacrylate) (pBA) side chains ($N = 10$). These macromolecules were synthesized by atom transfer radical polymerization [15]. For the polymeric solvent/matrix to be chemically identical to the molecular brushes, we used melts of linear pBA chains. A series of well-defined linear pBA's with degree of polymerization ranging from 10 to 9000 and monomer molecular weight $M_0 = 128$ g/mole were purchased from Polymer Source Inc.

Monolayers of pBA brushes dispersed in linear pBA chains were prepared by the Langmuir-Blodgett technique.

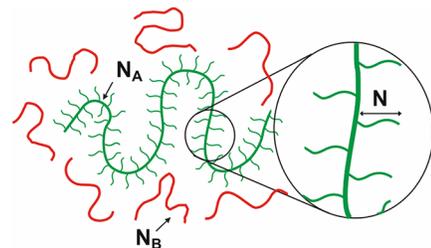


FIG. 1 (color online). Schematics of a brushlike macromolecule embedded in a melt of linear chains with a degree of polymerization, N_B . Brush's backbone and side chains have the degrees of polymerization N_A and N , respectively.

To obtain these dispersions, the brush molecules were first mixed with matrix polymers at a ratio of 10/90 wt/wt % in chloroform, a common solvent for both the brush and linear polymers. The solution was then deposited onto the water surface of a Langmuir trough. After allowing 30 minutes for system equilibration, the water-supported monolayers were transferred onto a solid substrate (mica) at a constant pressure of 0.5 mN/m and a transfer ratio of 0.98. The transfer pressure $\pi = 0.5$ mN/m corresponds to 10% compression of a dense pBA monolayer. This leads to desorption of 10% of the side chains, which in turns causes decrease in the persistence length of the brush. To ensure that all samples have the same fraction of desorbed side chains, all monolayers were transferred at the same 0.5 mN/m pressure and the same 10% compression ratio. The transferred samples were studied by AFM with the aim of visualization of individual brush molecules. The samples were imaged in Tapping-mode using a Multimode AFM (Veeco Metrology group) and silicon cantilevers from Mikromasch USA with a resonance frequency of about 160 kHz, spring constants of 5.0 N/m, and a tip radius being smaller than 10 nm.

Figure 2 depicts a sequence of conformations of brush-like macromolecules sparsely dispersed in a matrix of linear pBA chains. The height contrast results from the partial desorption of the side chains that segregate around the backbone of the brush and form a ridge of approximately 0.5 nm in height. The side chains that remain adsorbed to the substrate are not distinguishable from the surrounding melt of linear pBA chains. Upon increasing N_B , brush macromolecules undergo conformational transformations from swollen coils in a melt of short chains

[Figs. 2(a) and 2(b)] to a compact coil in a melt of longer chains [Figs. 2(g) and 2(h)]. Note that in 2D systems, the ideal coil conformation corresponds to a dense packing of the polymer chain. There is also a crossover region between the two pure regimes [Figs. 2(c)–2(f)].

Molecular conformations were analyzed using a custom-designed software program which allowed automatic detection of individual molecules and measurements of their contour length, radius of gyration, and curvature distribution. The determined molecular dimensions are accurate since the persistence length of brush macromolecules (~ 100 nm) is larger than the radius of an AFM tip (~ 10 nm). In addition, the molecular resolution is facilitated by adsorbed side chains that separate the neighboring backbones by a distance of 20 ± 2 nm. Clear resolution of the individual molecules enabled visual fractionation of isolated molecules and molecular clusters. The latter were manually excluded from a set of detected species prior to the conformational analysis. Figure 3(a) depicts the square root of the mean-square radius of gyration of the section of the brush backbone, R_S , as a function of the number of monomers in the section, N_S , measured in two different matrixes, i.e., $N_B = 11$ and $N_B = 1766$. Both plots display two conformational regimes. For the short chain sections ($N_S < 200$), their size R_S scales linearly with N_S , i.e., the short sections of the backbone adopt a rodlike conformation. At the larger length scales, the size of the chain section approaches the power law $R_S \cong bN_S^\alpha$ with $\alpha = 0.69 \pm 0.03$ for $N_B = 11$ and $\alpha = 0.48 \pm 0.04$ for $N_B = 1766$. The value of the former exponent is close to $\alpha = 0.75$, which is characteristic for a 2D swollen chain, while the value of the second exponent is close to $\alpha = 0.5$, which is typical for a 2D coil. The analysis of similar plots for the mixtures of the brush molecules with linear chains of different degree of polymerizations, N_B , shows that the apparent exponent α gradually decreases from 0.75 to 0.5 with increasing values of N_B . This is in agreement with the conformational transformations of the brush macromolecules shown in Fig. 2.

Figure 3(b) combines measurements of the root mean-square radius of gyration of the pBA brushes for different degrees of polymerization of the pBA linear chains. For every data point in Fig. 3(b), we recorded 30–40 height micrographs from four separately prepared samples with an average number of molecules per image of about 50 to collect in total about 300 images of single chains with a similar contour length. This ensures a standard error of the square root of the mean-square radius of gyration to be below 10%. The error was smaller for more populated ensembles of shorter chains ($\sim 5\%$) and larger for fewer longer chains ($\sim 10\%$). Note that the swelling stops at much longer chains ($N_B \gg 1$), unlike linear chains that are expected to continue swelling down to $N_B \cong 1$. Therefore, the location of the crossover region notably differs from those of structurally symmetric melts.

To understand the physical mechanism of the observed swelling behavior we have developed a scaling model of

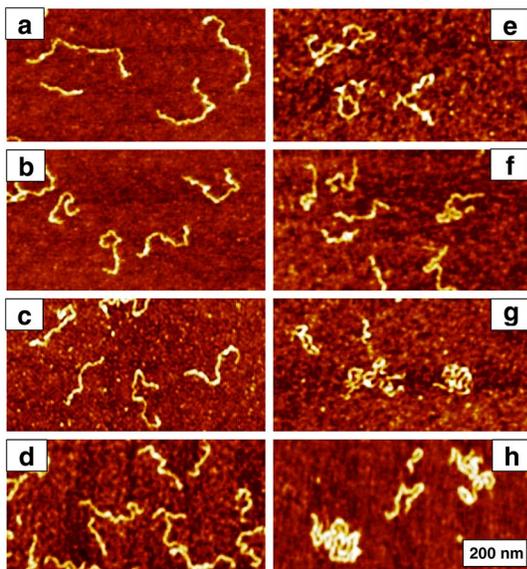


FIG. 2 (color online). Height AFM images of individual brush molecules embedded into monolayers of linear pBA chains having different degrees of polymerization: (a) $N_B = 11$, (b) $N_B = 24$, (c) $N_B = 102$, (d) $N_B = 214$, (e) $N_B = 322$, (f) $N_B = 602$, (g) $N_B = 1766$, and (h) $N_B = 8813$.

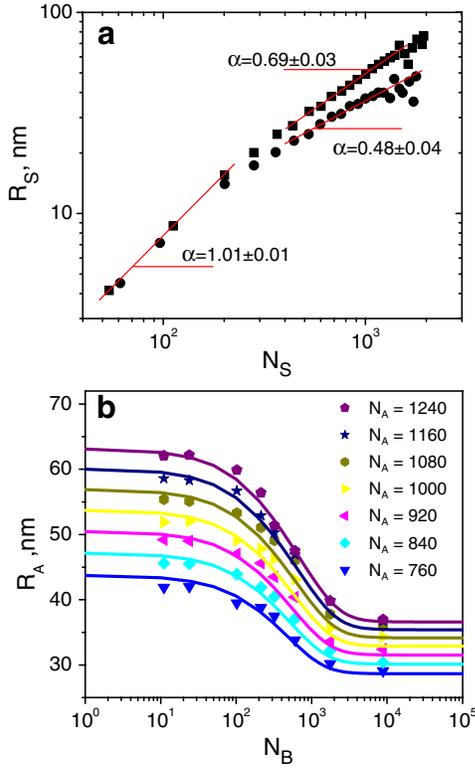


FIG. 3 (color online). (a) The square root of the mean-square radius of gyration of a section of the backbone of brush macromolecules $R_S = \sqrt{\langle R_S^2 \rangle}$ as a function of the polymerization degree of the section N_S was measured for two matrixes of linear chains with $N_B = 11$ (■) and $N_B = 1766$ (●). (b) Dependence of the square root of the mean-square radius of gyration of the pBA brush on the degree of polymerization of linear pBAs chains for different degrees of polymerization of the backbone (N_A). The corresponding solid lines are the best fit by the crossover Eq. (6) with a single set of three adjustable parameters $A_1 = 0.33 \pm 0.01$, $A_2 = 0.36 \pm 0.08$, $A_3 = 0.47 \pm 0.03$.

brushlike macromolecules in a melt of linear chains. An adsorbed brush molecule is considered as a ribbon with a width of $D \equiv bN$ and a contour length of $L_0 = bN_A$, where b is the monomer size (Fig. 1). Since we are dealing with an extremely dense brush, wherein every monomeric unit of the backbone contains one side chain, we assume that the linear chains do not interpenetrate the side chains. The penetration is sterically unfavorable because the tightly adsorbed side chains represent a dense 1D brush aligned perpendicular to the main chain backbone. Thus, the effect of the linear chains on the swelling behavior of molecular brushes is solely associated with the entropy of mixing of these chains with a brush. A test molecule occupies only the fraction of the area φR_A^2 , where $\varphi = L_0 D / R_A^2 = b^2 N_A N / R_A^2$ is the volume fraction of monomers belonging to a brush inside area R_A^2 , which leaves an area $(1 - \varphi) R_A^2$ accessible for the linear chains. The entropic contribution to the free energy due to placement of the linear chains with the degree of polymerization N_B over the area R_A^2 is equal to

$$\frac{F_{\text{mix}}}{k_B T} \approx \frac{R_A^2 (1 - \varphi)}{b^2 N_B} \ln(1 - \varphi) \underset{\varphi \ll 1}{\approx} -\frac{N_A N}{N_B} + \frac{b^2 (N_A N)^2}{2 N_B R_A^2}. \quad (1)$$

Note that only the last term in the right-hand side of Eq. (1) depends on the size of the brush molecule R_A . Here and below we use a scaling analysis and neglect all numerical prefactors on the order of unity. The Flory free energy of a guest molecule mixed with the linear chains can be written as a sum of the free energy of mixing [Eq. (1)] and of the test molecule's elastic free energy [3]. The elastic free energy term accounts for the change of the conformational entropy as the guest macromolecule swells from the ideal size

$$R_A^0 \approx (L_p L_0)^{1/2} \approx b N_A^{1/2} N^{3/2}, \quad (2)$$

where $L_p \equiv bN^3$ is the persistence length of an adsorbed brush macromolecule, which is a ribbon with a width of $D \equiv bN$ [16]. Thus, the total free energy of the molecular brush dispersed in a melt of linear chains is

$$\frac{F}{k_B T} \approx \left(\frac{R_A}{R_A^0} \right)^2 + \frac{b^2 (N_A N)^2}{N_B R_A^2}. \quad (3)$$

The equilibrium size of the probe molecule is obtained by minimizing Eq. (2) with respect to the size R_A as

$$R_A \approx b N_A^{3/4} N^{5/4} N_B^{-1/4}, \quad (4)$$

which is valid for intermediate values of the matrix chain's degrees of polymerization, N_B . For very long linear chains, the intrabrush interactions are almost completely screened. In this case, the test macromolecule contracts and its size eventually approaches the ideal size $R_A \approx R_A^0$. This takes place at $N_B \approx N_A/N$. This upper boundary for the swelling regime is a surprising result because it points out that linear chains sense a brush macromolecule as a linear chain composed of N_A/N effective monomeric units. In other words, the ribbonlike brush with a width of bN and contour length bN_A can be viewed as a chain of N_A/N monomeric units each with linear size bN and having N^2 original monomers.

As the degree of polymerization of the linear chains, N_B , decreases the brush molecule swells. The brush becomes completely swollen with size

$$R_A^{\text{sw}} \approx L_p \left(\frac{bN_A}{L_p} \right)^{3/4} \approx b(NN_A)^{3/4}, \quad (5)$$

at $N_B \approx N^2$ for which $R_A \approx R_A^{\text{sw}}$. For $N_B < N^2$, the equilibrium size does not depend on the length of the surrounding linear chains. In Fig. 4, we summarize different swelling regimes as a function of the degree of polymerization of the solvent, N_B . It is important to point out that the interval of the intermediate N_B values, $N^2 < N_B < N_A/N$, only exists when the number of monomers forming the brush backbone N_A is larger than N^3 . The latter corre-

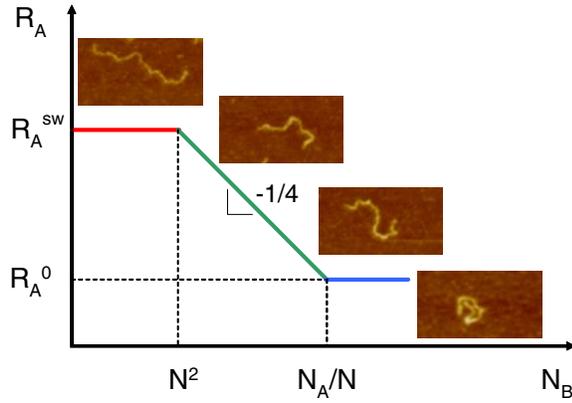


FIG. 4 (color online). Three conformational regimes of a brushlike macromolecule embedded in a melt of linear chains with a degree of polymerization, N_B . The upper boundary of the swollen chain regime, $N_B = N^2$, is determined by the degree of polymerization of the side chains (N), while the lower boundary of the ideal chain regime, $N_B = N_A/N$, also depends on the degree of polymerization of the brush's backbone (N_A).

sponds to the persistence length of brushlike macromolecules under conditions of strong adsorption [16].

The dependence of a chain size on the system parameters in three conformational regimes depicted in Fig. 4 can be approximated by a simple crossover formula

$$R_A = A_1 L_p \left(\frac{N_A}{N^3} \right)^{3/4} \left[\left(\frac{1}{1 + A_2 N_B / N^2} \right)^\beta + A_3 \left(\frac{N^3}{N_A} \right)^\beta \right]^{1/4\beta} \quad (6)$$

with the fixed exponent $\beta = 3$ and three adjustable numerical constants A_1 , A_2 , and A_3 . The constants are introduced to adjust the molecular size and the location of the crossover region, respectively. For long linear chains ($N_B > N_A/N$), the formula approaches the ideal size of a polymer brush $R_A^0 = A_1 A_3^{1/4\beta} b N_A^{1/2} N^{3/2}$ [Eq. (2)]. For a melt of short linear chains ($N_B < N^2$), this expression reduces to the size of a completely swollen molecule $R_A^{sw} = A_1 b (N N_A)^{3/4}$. For different sizes of brushlike macromolecules, Eq. (6) accurately describes all three conformational regimes with a single set of three adjustable parameters $A_1 = 0.33 \pm 0.01$, $A_2 = 0.36 \pm 0.08$, and $A_3 = 0.47 \pm 0.03$ [Fig. 3(b)].

One can easily generalize the analysis presented above to the case of a test macromolecule with thickness D , contour length L_0 and having a persistence length L_p immersed into a melt of the linear chains with the degree of polymerization N_B by rewriting Eqs. (1)–(3) in terms of chain parameters D , L_0 , L_p and space dimensionality d . Such test chains begin to shrink when the volume occupied by the host chains $b^d N_B$ becomes larger than the volume occupied by an effective monomer D^d of the guest molecule, $b^d N_B > D^d$. Above this crossover value, the matrix

chains screen intrachain repulsive interactions between the monomers of the test macromolecule, which is manifested by the decrease of the size of the test molecule with increasing degree of the linear chains N_B as $R_A \approx \left(\frac{L_0^3 L_p D^{2d-2}}{N_B b^d} \right)^{1/d+2} \sim N_B^{-1/(d+2)}$. The shrinking continues until the size of the test molecule becomes comparable with its ideal size, $R_A^0 \approx (L_p L_0)^{1/2}$. This occurs when the degree of polymerization of the linear chains N_B is on the order of $L_0^{(4-d)/2} D^{2d-2} / (L_p^{d/2} b^d)$.

The generalized Flory theorem for mixtures of structurally asymmetric macromolecules can be formulated as follows: “Test macromolecules with thickness D , contour length L_0 and a persistence length L_p dispersed in a melt of linear chains with the degree of polymerization N_B will remain in their ideal (Gaussian) conformations until the degree of polymerization of the linear chains N_B exceeds $L_0^{(4-d)/2} D^{2d-2} / (L_p^{d/2} b^d)$. Shorter linear chains cause swelling of the test molecules. This swelling continues until the excluded volume occupied by the linear chain $b^d N_B$ becomes comparable with the volume of the effective monomer D^d of the test macromolecule.”

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- [1] P. J. Flory, *J. Chem. Phys.* **17**, 303 (1949).
- [2] P. G. J. de Gennes, *Polym. Sci. Polym. Symp.* **61**, 313 (1977).
- [3] M. Rubinstein and R. H. Colby, *Polymer Physics* (Oxford University, New York, 2003).
- [4] R. G. Kirste and B. R. Lehnen, *Macromol. Chem. Phys.* **177**, 1137 (1976).
- [5] M. R. Laudry, *Macromolecules* **30**, 7500 (1997).
- [6] C. Tangari, R. Ullman, J. S. King, and G. D. Wignall, *Macromolecules* **23**, 5266 (1990).
- [7] N. Torikai, N. Takabayashi, I. Noda, J. Suzuki, and Y. Matsushita, *J. Phys. Chem. Solids* **60**, 1325 (1999).
- [8] B. Maier and J. O. Rädler, *Phys. Rev. Lett.* **82**, 1911 (1999).
- [9] A. C. Balazs, T. Emrick, and T. P. Russell, *Science* **314**, 1107 (2006).
- [10] M. E. Mackay *et al.*, *Science* **311**, 1740 (2006).
- [11] S. W. Sides, B. J. Kim, E. J. Kramer, and G. H. Fredrickson, *Phys. Rev. Lett.* **96**, 250601 (2006).
- [12] H. Xu *et al.*, *Phys. Rev. Lett.* **93**, 206103 (2004).
- [13] H. Xu *et al.*, *Phys. Rev. Lett.* **94**, 237801 (2005).
- [14] S. S. Sheiko *et al.*, *Nature (London)* **440**, 191 (2006).
- [15] K. Matyjaszewski and J. Xia, *Chem. Rev.* **101**, 2921 (2001).
- [16] I. I. Potemkin, *Macromolecules* **39**, 7178 (2006).