Size Separation of Macromolecules during Spreading

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Spreading of homogeneous mixtures of bottle-brush and linear macromolecules of poly(n-butylacrylate) on a solid substrate has been monitored on the molecular scale by atomic force microscopy. Despite the nearly identical chemical composition and similar molecular weight, brush-like macromolecules move markedly slower than linear chains. Moreover, smaller bottle-brushes have been shown to flow faster than the larger bottle-brushes, resulting in fractionation of the macromolecules along the spreading direction. This behavior was explained by the difference in sliding friction coefficient between the bottle-brush macromolecules and linear chains with the substrate. A theoretical model of molecular size separation is in a good agreement with experimental data.

Introduction

Understanding the spreading behavior of thin polymeric films is vital for the advancement of lithography, microfluidics, lubrication, and printing. Thermodynamic and kinetic properties of a spreading process are determined by the interactions between macromolecules and the substrate. The interfacial interactions could change molecular conformations, ordering, and even chemical structure of the adsorbed macromolecules. The short-range molecular interactions also have an effect on sliding friction and thus control motion of individual molecules on a substrate. On heterogeneous substrates, the local variations in the friction coefficient may enhance molecular diffusion in the frame of the flowing film. However, on homogeneous substrates, spreading usually demonstrates a plug-flow behavior; that is, all molecules, regardless of their size, move with the same velocity. The size dependence of the spreading rate may, however, emerge in polymer blends, that is, homogeneous fluids composed of two different polymers. Particularly interesting are structurally asymmetric mixtures, that is, molecular mixtures composed of chemically identical polymers with different architectures.

Does molecular architecture influence the spreading rate? This question becomes increasingly relevant when mixing macromolecules with different architectures to prepare formulations for oil recovery, nutrition, and health care applications. To investigate this problem, we have studied spreading of a mixture of bottle-brush macromolecules and linear polymer chains, both having the same chemical structure of poly(n-butylacrylate) (PBA). By considering mixtures of chemically similar species, we have suppressed phase separation and thus dealt with homogeneous fluids.

Unlike the plug-flow behavior of single-component melts, the mixtures revealed the difference in spreading velocities between brushes of different sizes, resulting in spreading-induced molecular fractionation. The origin of the fractionation was ascribed to the difference in friction coefficient between the PBA bottle-brushes and PBA linear chains.

Experimental Section

Materials. Bottle-brush macromolecules with PBA side chains that are densely grafted to a polymethacrylate (PMA) backbone have been synthesized by atom transfer radical polymerization. Two different architectures of brushes have been prepared: (i) a backbone degree of polymerization, \( N_n = 560 \pm 20 \), and a side chain degree of polymerization, \( n = 36 \pm 2 \), called short bottle-brushes (for the short average length of their backbone), and (ii) \( N_n = 3600 \pm 280 \) and \( n = 58 \pm 5 \), dubbed long bottle-brushes. For this study, we have chosen macromolecules with short side chains to prevent rupture of the bottle-brush backbone upon spreading on a substrate. The number-average

molecular weights ($M_n$) of the two brush polymers are $2.7 \times 10^6$ and $2.6 \times 10^7$ g/mol, respectively. Their polydispersity indexes (PDI = $M_w/M_n$) are 1.2 and 1.7, respectively. We have also synthesized a linear PBA with degree of polymerization $n = 214$ and with PDI 1.1. Four homogeneous molecular systems have been prepared by mixing solutions of each type of polymer in the appropriate ratio and subsequently evaporating the solvent in a vacuum oven (Figure 1). The compositions of the studied mixtures are summarized in Table 1.

**Table 1. System Parameters**

<table>
<thead>
<tr>
<th>System</th>
<th>Brush 1 Weight Fraction</th>
<th>Brush 2 Weight Fraction</th>
<th>Linear PBA Weight Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.00</td>
<td>0.05</td>
<td>0.95</td>
</tr>
<tr>
<td>2a</td>
<td>0.05</td>
<td>0.05</td>
<td>0.95</td>
</tr>
<tr>
<td>2b</td>
<td>0.05</td>
<td>0.95</td>
<td>0.05</td>
</tr>
<tr>
<td>3</td>
<td>0.95</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>4</td>
<td>0.05</td>
<td>0.05</td>
<td>0.95</td>
</tr>
</tbody>
</table>

*Brush 1: $N_n = 560, n = 36, \text{PDI} = 1.2$. *Brush 2: $N_n = 3600, n = 58, \text{PDI} = 1.7$. *Linear PBA: $N_n = 214, \text{PDI} = 1.1$.

**Samples.** Drops of the polymer melts with a radius of $R = 100 \mu m$ were deposited on a mica substrate using a needle with a diameter of 100 $\mu m$. The polymer melts were then allowed to spread at 25°C under a relative humidity (RH) of 97% for times between 30 and 45 min.

**Molecular Imaging.** Atomic force microscopy was used to image individual molecules within the precursor layer at different distances from the drop after a defined spreading time. The AFM measurements were conducted with a multimode AFM (Nanoscope IIIa, Veeco Metrology Group) using Si probes with a cantilever spring constant of 6 mN/m and a resonance frequency of 160 kHz. We characterized the imaged molecules for length distribution by using home-built software for analysis of digital images.

**Results and Discussion**

**Experiments.** We first measured the spreading rate of the bottle-brushes and linear chains alone. Respectively, two 100 $\mu m$ drops of linear ($m = 214$) and brush-like ($N = 560, n = 36$) PBAs have spread for 45 min under the identical environmental conditions (mica substrate, $T = 25^\circ C$, and RH = 97%). Because of the favorable wetting conditions (spreading parameter $S > 0$), molecular interactions with the substrate drive a monolayer of liquid, called the precursor film, to spread ahead of the drop (Figure 2). The precursor films of the brush-like and linear polymer melts spread to radii of $R = 235$ and 1195 $\mu m$, respectively. Because the interfacial energies of the chemically similar polymers are almost identical, the significant difference in the spreading rates is ascribed to the differences in the friction coefficients of the linear and brush-like PBA with the substrate. The kinetics of the spreading process is controlled by the gradient of the film pressure driving the flow and by the sliding friction responsible for the film-substrate interactions as follows

$$\frac{-d\Pi}{dr} = \xi \cdot V(r)$$

where $\Pi(r)$ is the local film pressure, $\xi$ is the friction coefficient per unit area, and $V(r)$ is the local film velocity. Integration of eq 1, first over distance $r$ and then over time $t$, gives the time dependence of the precursor film radius as a function of the spreading rate $D = S/\xi$ and the drop radius $R_0$.

$$\left( \ln \frac{R}{R_0} - \frac{1}{2} \right) + \frac{R_0^2}{2} = D t$$

One can use eq 2 to determine the corresponding friction coefficients to be $\xi = 2.1 \times 10^6$ N-s/m$^2$ for the brush-like PBA and $\xi_0 = 2.5 \times 10^6$ N-s/m$^2$ for the linear PBA; that is, the bottle-brush macromolecule has ca. two orders of magnitude higher friction coefficient than its linear counterpart.

The observed difference in friction coefficients had a dramatic effect on the spreading behavior of the polymeric mixtures (Table 1). A 96 $\mu m$ drop of System 2b, that is, mixture of linear chains ($m = 214$) and long bottle-brushes ($N = 3600, n = 58$), was deposited on a mica substrate. After 45 min spreading, the precursor film had a total length of $R = 2800 \mu m$. However, when the film was examined using AFM, the brush-like macromolecules within the film were found to have propagated a smaller distance of 920 $\mu m$ from the drop, a significantly shorter distance than the matrix of linear chain. AFM images of the flowing macromolecules were captured every 40 $\mu m$ along the precursor film. Figure 3a shows a few selected AFM images at various distances from the drop. Three conclusive observations can be made. First, PBA brushes are finely dispersed with the matrix of linear PBA. This is consistent with the prediction of the Flory theorem for structurally asymmetric mixtures, that is, mixtures of the molecular bottle-brushes and linear chains. Second, in agreement with the broad molecular weight distribution of the long bottle-brushes, the contour length of the imaged molecules ranges from 100 to 2000 $\mu m$. Because the contour length is on the order of or larger than the brush persistence length (~100 nm), the dispersed brushes behave as semiflexible chains. Third, the contour length of the brush molecules decreases as one looks farther away from the drop edge. As shown in Figure 3b, the number-average length remains constant close to the drop edge and begins to decrease at distance $r = 300 \mu m$. We confirmed the fractionation by analyzing the length distributions at different distances from the drop edge (Figure 3c).


**Figure 2.** Schematic representation of the precursor film that spreads ahead of a drop deposited on a substrate. $R_0$ and $R$ are the time-dependent radii of the drop and the precursor film relative to the drop center.
Barrett et al. Article

One may suggest that fractionation occurs at the drop edge \((r = R_0)\) during translation of macromolecules from the drop to the precursor film. To rule out this possibility, we have compiled a cumulative distribution of the entire film. As shown in Figure 3d, the cumulative distribution fully matches the distribution of the bulk melt yielding the same PDI \(= L_w/L_n = 1.7\). This indicates that the translation rate of brush molecules from the drop to precursor film does not depend on the molecular weight and hence is not the cause of the observed fractionation.

The total distribution was used to calculate the instantaneous velocity of the bottle-brush macromolecules with different degrees of polymerization (DP) of the backbone. The calculation was based on the assertion that faster moving short bottle-brushes have lower relative concentrations on the surface than in the bulk compared with the larger macromolecules that move more slowly. This behavior can be rationalized by the following scaling argument: \(V_N \approx R_N \approx 1/\phi_N\), that is, instantaneous velocity of bottle-brushes with the degree of polymerization of the brush backbone DP = \(N\) is proportional to the maximum travel distance \(r = R_N\) and inversely proportional to their local number fraction \(\phi_N\) in the plateau region. It was tempting to use this scaling relation to calculate the bottle-brush velocity relative to that of linear chains directly, \(V_N/V_0 = \phi_0/\phi_N\), where \(\phi_0\) is the number fraction of linear PBA chains in the plateau region. However, this calculation would be inaccurate because AFM did not resolve the linear chains and thus forbade their counting for determination of \(\phi_0\). Therefore, we have calculated the relative velocity from the fraction of the shortest bottle-brushes by applying the scaling relation as

\[
\frac{V_N}{V_0} = \frac{R_1}{R_N} \frac{\phi_1}{\phi_N} \quad (3)
\]

where \(V_0\) is the spreading velocity of the linear PBA, \(R_0 = 2800 \mu m\) is the total length of the precursor film (after spreading during \(t = 45\) min), \(R_N = 920 \mu m\) is the maximum distance traveled by the shortest \((L_n = 50\) nm\) bottle-brush molecules during the time interval \(t = 45\) min, and \(\phi_1\) is the fraction of the shortest brushes within the cumulative film. Figure 4 shows that the relative velocity of bottle-brushes decreases with their size. Because we have studied bottle-brushes with different length of the side chains, the data are plotted as a function of the molecular area \(A = Ld\), which determines the magnitude of the friction force between the macromolecule and substrate.

Harnessing the phenomena described above, we have conducted experiments to study separation in a mixture of two types of PBA bottle-brushes with different degrees of polymerization of the bottle-brush backbone (System 3). This mixture consisted of long \((N_n = 3600, L_n = 640\) nm\) and short \((N_n = 560, L_n = 95\) nm\) bottle-brush macromolecules. Figure 5a shows selected images captured at three different locations from the drop edge. As expected for the chemically identical molecules, the long and short brushes are fully miscible. Note that the molecules exhibit different height contrasts due to difference in the degree of polymerization of the side chains. The short bottle-brushes are clearly visible in higher-resolution images. (See inset in Figure 5a.) The difference in contrast allowed us to monitor and separate two types of bottle-brushes by analyzing their length distributions. As before, the longer bottle-brushes of both types moved more slowly than the shorter macromolecules. At shorter distances from the drop edge (e.g., \(R = 130\) \(\mu m\)), one clearly see the
Figure 5. (a) Height images of a mixture of molecular bottle-brushes within a matrix of linear chains (System 3) along the precursor film. (b) Length distributions of the bottle-brush macromolecules from System 3 taken at various distances from the drop edge: $R = 150$ (dashed line), $140$ (dotted line), and $130 \mu m$ (solid line). The inset shows different types of the bottle-brush macromolecules. The arrows correlate AFM images and length fraction of the long and short bottle-brush macromolecules.

Figure 6. (a) Images from various positions in the precursor film spread from a melt of System 4. The total length of the film is $405 \mu m$. (b) Average length of the long brushes from system 4 throughout the precursor film.

bimodal distribution of the mixture. At longer distances (e.g., $R = 150 \mu m$) away from the drop edge, only the short bottle-brushes of both types are present in the image. This corroborates successful separation of the binary mixture.

**Model.** The observed fractionation is a transient phenomenon occurring in flow during spreading of a monolayer on an infinite substrate. We rule out molecular diffusion as a cause of the fractionation26 because diffusive and directed motions of spreading macromolecules occur on different time scales. The diffusion coefficient of large macromolecules within fluid monolayers is on the order of $10^{-10} \text{m}^2/\text{s}$, which is significantly slower than the spreading rate $D \approx 10^{-7} \text{m}^2/\text{s}$.19 The fractionation of the bottle-brush macromolecules within spreading monolayers is ascribed to the significant difference in sliding friction of the linear and bottle-brush PBA with the substrate that may result even from minute variations of the corresponding interaction energies. This difference in friction creates a drag force between the faster moving matrix of linear PBA and the slower moving PBA bottle-brushes. Assuming a no-slip boundary condition between a bottle-brush macromolecule and the matrix of linear chains,27 a model was developed to predict the following relation for the relative velocity $V/V_0$ (the ratio of the velocity of bottle-brushes to the velocity of the matrix of linear chains) as a function of the molecular area $A \approx Ld$. (See the Appendix for details.)

$$\frac{V}{V_0} = \frac{2\beta Ld + \gamma}{(1 + \beta)Ld + \gamma}$$

In this equation, $\beta = \xi_0/\xi$ and $\gamma = 0.16\eta h/\pi \xi^2$ are two model parameters related to the following properties: $\eta$, viscosity of the matrix; $\xi$, coefficient of friction between the bottle-brush and the substrate; and $\xi_0$, coefficient of friction between the matrix and the substrate. As shown in the Appendix, parameters $\beta$ and $\gamma$ determine the position and the width of the fractionation region, respectively. Equation 4 was used to fit the measured velocity ratio as a function of the molecular area with two fitting parameters, $\beta = 0.005$ and $\gamma = 0.0002 \mu m^2$ (solid line in Figure 4).

To validate the model, we compared the obtained values with parameters $\beta$ and $\gamma$ determined experimentally. From the measured friction coefficients $\xi = 2.1 \times 10^6 \text{N} \cdot \text{s/m}^2$ and $\xi_0 = 2.5 \times 10^6 \text{N} \cdot \text{s/m}^2$, bulk viscosity $\eta = 290 \text{Pa} \cdot \text{s}$ of the matrix of linear chains (linear PBA, $m = 214$), and the thickness of the spreading film $h = 8 \text{Å}$, one calculates $\beta = 0.012$ and $\gamma = 0.00018 \mu m^2$. These values are in a good agreement with the corresponding model parameters. Here we assume that the film thickness ($h$) does not depend on drop radius and the distance from the drop. The second assumption is valid for bottle-brush molecules that maintain the constant height of the contact area between the matrix and side chains through adsorption of additional side chains during spreading. It follows from our data analysis that: (i) the friction coefficient between the bottle-brush PBA and the substrate is $\sim 100$ times higher than the friction coefficient between the linear PBA and the same substrate and (ii) the viscosity of monomolecular layers of linear PBA is close to the viscosity of bulk PBA.

According to the model, the fractionation occurs only when molecular brushes and matrix of linear chains have a different friction coefficient from that of the substrate ($\beta < 1$). When both materials have the same friction coefficients with the substrate, one should observe a plug flow; that is, all species move with the same velocity (Figure A2 in the Appendix). To test this prediction, we have studied a mixture of two different brush molecules (System 4). Figure 6a shows the images at various distances over the spreading precursor film. As shown in Figure 6b,
the average lengths of the bottle-brushes do not change throughout the precursor film; that is, all molecules in System 4 move with the same velocity regardless of their dimensions. This observation is consistent with the model because the friction coefficients of both short and long bottle-brushes with substrate are identical.

Conclusions

We have shown that bottle-brush macromolecules undergo size separation during the drop spreading when they are mixed with the linear polymer chains. A theoretical model of bottle-brush motion in the mixture of linear chains has confirmed that the degree of fractionation is related to the difference in the friction coefficient of the brush-like and linear macromolecules with the substrate. The fractionation window depends on the difference in the molecular friction coefficients, the viscosity of the spreading film, and the area of the bottle-brush macromolecules. The observed size separation opens the possibility of fractionating macromolecules according to their architecture and molecular weight.

The main factor that controls fractionation is the difference in friction coefficients. This difference could have chemical and physical origins. In both cases, minute alterations of the interaction with the underlying substrate may cause significant changes in the sliding friction coefficient, which magnitude depends exponentially on the strength of the interaction potential. The chemical origin of the difference in friction coefficients could be attributed to the difference in chemical composition of PMA backbone and PBA side chains. However, the contribution of the backbone to bottle-brush–substrate interactions is negligible because backbone’s molar fraction is <2% and it is encapsulated into a shell of the PBA side chains. A physical origin of the difference in friction coefficients could be explained by slightly stronger interactions of the aligned and tightly packed PBA side chains in bottle-brushes in comparison with those for randomly orientated and less constrained linear chains. Because of the particularly high grafting density, butyl tails in the extended side chains are forced to align perpendicular to the substrate, allowing stronger interaction between the more hydrophobic acrylic groups and the hydrophilic substrate. Further studies are needed to confirm our hypothesis.

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Appendix

Model of the Flow-Induced Fractionation. Bottle-brush macromolecules are assumed to have an elongated shape with length L, width d, and thickness h. The model assumes that the cause of the fractionation is the difference in friction coefficient with the substrate between the matrix of linear PBA and the bottle-brushes with PBA side chains. In addition, we have assumed a no-slip boundary between the matrix and bottle-brush macromolecules, which can be extended to the case of a finite slip length.

Figure A1 depicts four major forces acting on a bottle-brush macromolecule. The driving force \( F_D \) is generated by the pressure gradient \( \partial \Pi / \partial x \) along the film

\[
\vec{F}_D = -\frac{\partial \Pi}{\partial x} L d
\]

where \( \Pi(x) = h p(x) \) is a 2D film pressure. In a dilute solution of molecular brushes in a matrix of linear chain, the matrix velocity \( V_0 \) satisfies the local force balance

\[
\xi_0 \vec{V}_0 = -\frac{\partial \Pi}{\partial x}
\]

where \( \xi_0 \) is the friction coefficient between the matrix of linear chains and the surface. Using eqs A.1 and A.2, we obtain

\[
\vec{F}_D = \xi_0 \vec{V}_0 L d
\]

The friction force between the bottle-brush and the surface is proportional to the brush velocity, \( \vec{V} \), with the proportionality coefficient being equal to the brush friction, \( \xi \), times the area of a brush, \( L d \)

\[
\vec{F}_{fd} = -\xi \vec{V} L d
\]

The model considers two types of drag forces: (i) a substrate-induced drag

\[
\vec{F}_{sd} = \xi_0 L d (\vec{V}_0 - \vec{V})
\]

and (ii) a viscous drag

\[
\vec{F}_{vd} \approx \frac{4 \pi \eta h (\vec{V}_0 - \vec{V})}{2 - \ln \text{Re}} = \frac{4 \pi \eta h (\vec{V}_0 - \vec{V})}{2 - \ln \left( \frac{\rho (V_0 - V)}{\eta} \right)} - \ln L
\]

where \( \eta \) is the viscosity of the matrix, \( \text{Re} \) is the bottle-brush Reynolds number, and \( \rho \) is the film density. For our experimental parameters, eq A.6 can be approximated by

\[
\vec{F}_{vd} \approx 0.16 \pi h (\vec{V}_0 - \vec{V})
\]

The viscous drag component is similar to the drag that occurs when a thick liquid flows around a fixed rod oriented perpendicular to the flow direction. The surface-induced drag is a more complicated phenomenon that arises from the difference between friction coefficients of the bottle-brush and matrix with the substrate. For the steady-state regime, the projection of the forces on the direction of spreading should be equal to zero. From the force balance, one obtains the following relationship

(29) \text{Kim, C.; Esker, A. R.; Runge, F. E.; Yu, H. Macromolecules 2006, 39, 4889–4893.} \\
(30) \text{Richards, S. Fluid Mechanics; CRC Press: Boca Raton, FL, 1998.} \]
Figure A2. (a) Dependence of the velocity ratio on the value of the parameter $\beta$. (b) Dependence of the velocity ratio on the value of the parameter $\gamma$.

for the velocity of the bottle-brush relative to the velocity of the matrix

$$\frac{V}{V_0} = \frac{2\beta Ld + \gamma}{(1 + \beta)Ld + \gamma} \quad (A.8)$$

where $\gamma = 0.16 h/\pi \xi$ and $\beta = \xi_0/\xi$ can be used as fitting parameters for the experimental data.

Figure A2 demonstrates how strongly the velocity ratio depends on parameters $\beta$ and $\gamma$. As seen in Figure A2a, parameter $\beta$ (the ratio of the friction coefficients) controls the velocity of the bottle-brush macromolecules compared with that of the matrix of linear chains. In other words, it determines the location of the fractionation region within a spreading film. As the value of the parameter $\beta$ approaches unity (equal friction coefficients), the velocity of the molecular bottle-brushes becomes equal to the velocity of the matrix of linear chains, resulting in a plug flow. The value of the parameter $\gamma$ (matrix viscosity) determines the width of the fractionation region. As seen in Figure A2b, for the low viscosities of the matrix (e.g., $\gamma < 10^{-4}$), there is no fractionation within the studied range of the bottle-brush sizes ($0.1 < L < 1.5 \mu m$). For small values of the viscous drag force, all molecular brushes, regardless of their sizes, move with the same velocity determined by the ratio of the friction coefficients. However, when the value of the parameter $\gamma$ increases, the difference in velocities (and hence the spreading distances) between bottle-brushes of different lengths increases as well, resulting in a significant fractionation zone within the spreading film.