

Glass transition of nano-sized single chain globules

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Abstract

Nano-sized polymer globules were prepared by atomization spraying and drying of a dilute polymer solution. Transmission electron microscope measurements indicated that the particle of the globules matched with that of polymer single chains. Thermal analysis showed that the nano-sized particles exhibit a significantly higher glass transition temperature (T_g) than does the corresponding bulk polymer. This discovery cannot be explained by kinetic theories. Entropy analysis does indicate that polymer chains in the globular state should have a higher T_g . © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The glass transition of polymers in confined geometries has been the focus of much recent research [1–25]. The glass transition temperature (T_g) in thin film geometry, as measured by spectroscopic ellipsometry, X-ray reflectivity, and Brillouin scattering, depends on the film thickness and the molecular weight of polymer [1–12]. In particular, the measurement of a free-standing polystyrene film has demonstrated a 70 °C decrease in the effective T_g when film thicknesses approached tens of nano-meters [8]. The physical origin of this discrepancy in T_g is thus far unclear and has been the subject of many investigations. Various explanations for this phenomenon have been proposed, including a decrease in the film density [13], a decrease in the entanglement [14], an enrichment of chain ends on the surface [15,16], the enhanced mobility of surface layers [6, 8], and the sliding-loop dynamics of De Gennes [17]. However, the effect of thin film geometry can also be interpreted in terms of a second-order transition, because, in Ising models [20,21], the critical temperature in two dimensions is lower than its corresponding value in three dimensions. Since the thin film puzzle could be simply a quasi-two-dimensional problem, a test on a nano-sized three-dimensional particle will shed light on the problem. In

this study, we present a case in which polymer chains are confined in three-dimensional nano-sized globules. We observed a significantly higher T_g in the globular state than in the bulk state. The results are clearly not in agreement with those reported for thin films [1–12] and proposed by kinetic theories [6–8,13–17]. We have therefore explained the results based on an entropy analysis.

2. Sample preparation

Polyacrylamide (PAL) with a molecular weight of $MW = 5,000,000$ – $6,000,000$, was purchased from Polysciences, Inc. (Warrington, PA, USA). The polymer was dissolved in deionized water and diluted to about 10^{-4} wt% concentration. Under such dilute conditions, polymer chain coils were well separated without entanglement. The dilute solution was then sprayed from an atomizer (Gladsaxevej 305, DK-2806 Soeborg, Denmark) and then passed through a drying channel to remove the water. The isolated polymer chain coils were thus preserved in a solid form. A transmission electron microscope (TEM) image of single-chain molecules is shown in Fig. 1. The details of the preparation of the PAL single chain particles were reported previously [26]. The differential scanning calorimetry (DSC) samples of the bulk PAL were prepared by solution casting of 1% aqueous solution on a Teflon substrate.

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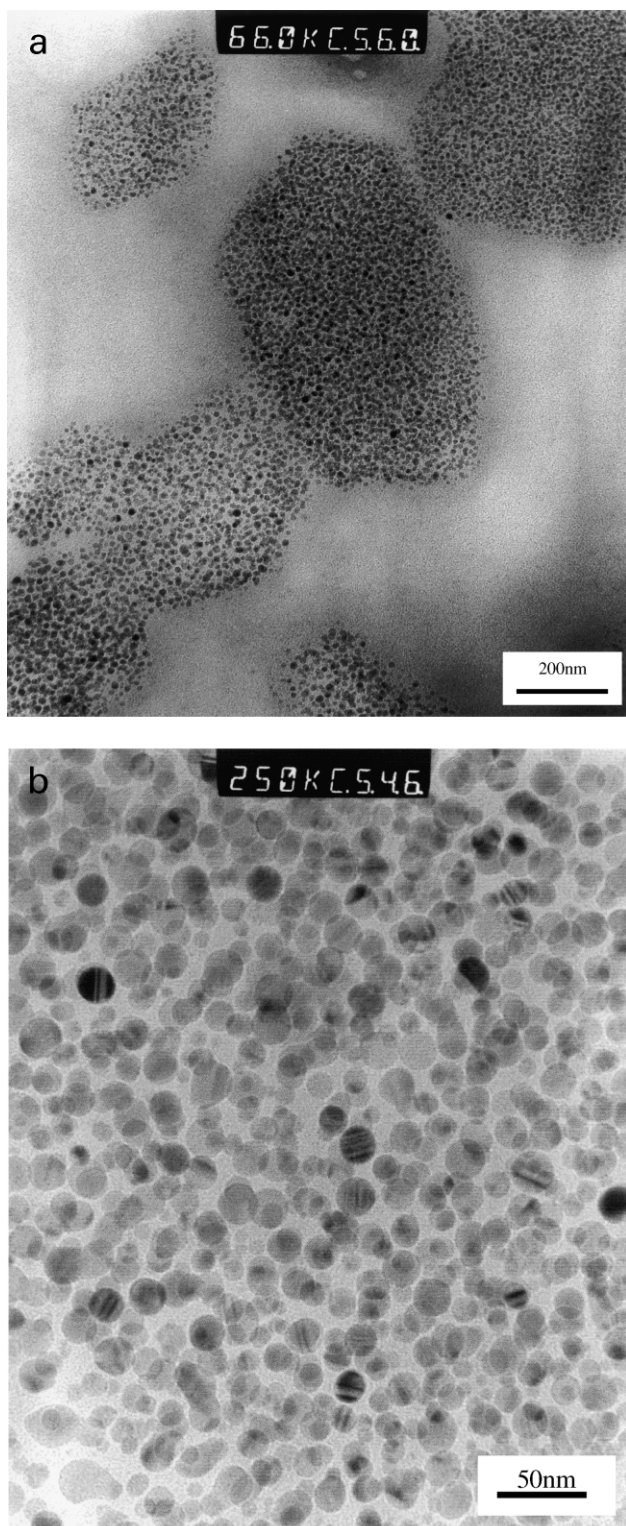


Fig. 1. The TEM image of single-chain globules. The scale bar is (a) 200 nm and (b) 50 nm.

3. Differential scanning calorimeter results

All samples were subjected to drying in a vacuum oven for 6 days at 60 °C. The DSC measurement was performed at a heating rate of 10 °C/min using a Perkin–Elmer-7 DSC.

We first examined the heat capacity (C_p) of the PAL samples both in the bulk state and in the globular single chain state. The procedures for C_p measurement were as reported in the literature using Al_2O_3 , sapphire, as the standard [30]. Fig. 2 shows the C_p change as a function of temperature. It is noted that the C_p change at the glass transition between the bulk state and the single-chain globular state is insignificant. However, the single-chain PAL sample has a T_g that is about 10 °C higher than that of the bulk-state PAL.

The samples were annealed at 220 °C for 30 min and then quenched to 30 °C. The DSC thermalgrams are shown in Fig. 3. Curve A shows that the bulk PAL sample has a T_g of 193 °C, whereas Curve C shows that the single-chain PAL has a T_g of 205 °C. Curve B shows that, when the single-chain nano particles were redissolved in water and a film was cast, the T_g of the resulting film was again 193 °C. Clearly, the polymer chains resume their original entangled state as in the bulk polymer.

4. Discussion

The discovery of an increase in T_g for the polymer single-chain globules cannot be interpreted in terms of proposed kinetic theories [6–8,13–17]. Explanations derived from the thin film geometry, i.e. a decrease in film density [13], a decrease in entanglement [14], the enrichment of chain ends on the surface [15,16], and an enhanced mobility of surface layers [6,8], predict a decrease in T_g . We realize that the surface of the single-chain globules is in contact with molecules of the surrounding media, i.e. nitrogen in the DSC cell. An increase in the contact with the surrounding media might lead to liquid-like behavior of the surface layer. However, the polymer chains used in this study possess strong hydrogen bonding. In this case, the sliding loop dynamics [17] will not be sufficient to provide penetration of the surface layers deep into the globule. One may argue that the observation might originate from an enthalpy-related issue, such as the surface energy [12], since Laplace pressure depends on both the interfacial tension and the amount of exposed surface area. However, a simple estimation based on water drops (where $\sigma_{\text{water},18^\circ\text{C}} = 73.05$ dyn/cm) shows that the Laplace pressure (σ/R) is about 36 bar for particles that are 20 nm in diameter, making it unlikely that this pressure is responsible for the 12 °C increase in T_g observed here. Considering the above-mentioned circumstances, we present a different theoretical explanation for the experimental results, based on a simple entropy argument [27–29]. First, we quantify the entropy loss from switching the polymer chain from the bulk state to its globular state. Second, we carry out an analysis of the finite size effect, in order to check how the entropy at the glass transition depends on the finite size. Finally, we combine the results with a theoretical explanation to assess

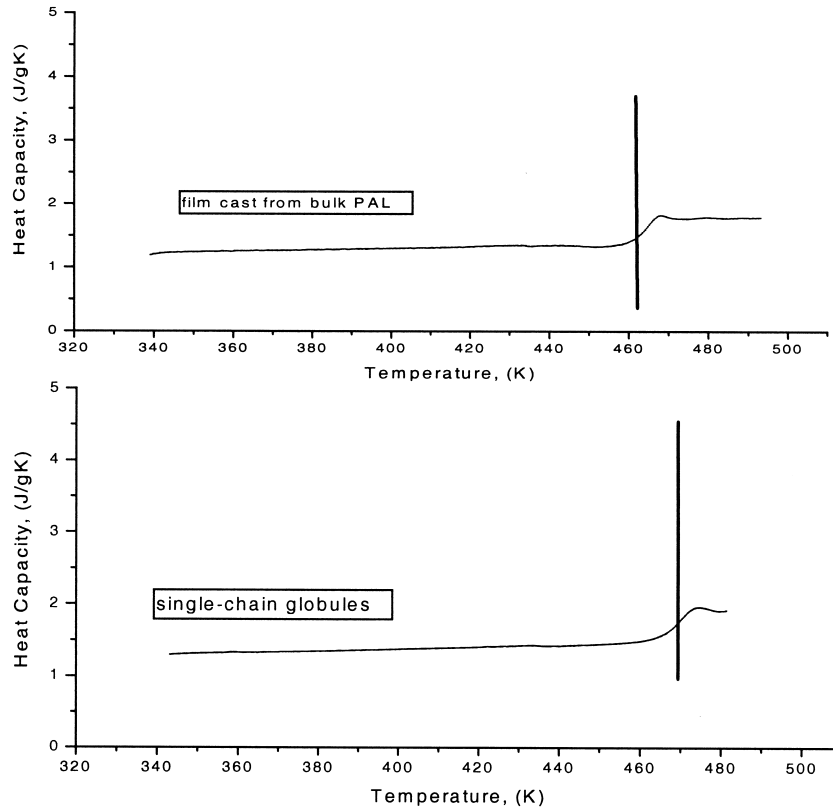


Fig. 2. Heat capacity measurements of single-chain globules and bulk PAL at the heating and cooling rate of 10 °C/min.

the conditions under which the enhancement of T_g is to be expected.

First, let us consider a flexible polymer chain with the degree of polymerization N and of monomer size a^3 . In the bulk state, the polymer chain adopts the random-walk configuration and the radius of the polymer chain is of $aN^{1/2}$ in size. In the single-chain globular state, however, the radius of the polymer chain should be close to $aN^{1/3}$. If the polymer chain behavior in those two states are compared, one may note that there is a change in the configuration entropy [29] between the bulk and the globular state:

$$\Delta S \cong kN \left(\frac{a}{R} \right)^x \quad (1)$$

where R denotes the radius of the polymer chain in the collapsed state ($R \cong aN^{1/3}$), k is the Boltzmann constant, and the exponent x equals 5/3 for a self-avoid chain and 2 for a random-walk chain. The criterion for glass formation, according to entropy theory [27], is that the temperature-dependent configuration entropy becomes zero. Accordingly, one can speculate that a single-chain globule will increase its T_g because it has a lower configuration entropy.

Now, if we view the problem from a different angle, we see that the molecular motion near the glass transition adopts a cooperative nature. The probability of a cooperative rearrangement is a function of its size, ξ , which increases as the temperature decreases. The relationship between the cooperative size and the configuration entropy

[28] is:

$$S \cong \frac{s^*}{\xi} \quad (2)$$

where s^* denotes the smallest entropy for a cooperative rearrangement and a first estimation gives $s^* \cong k \ln(2)$. Near the glass transition, the cooperative motion size, ξ , tends to diverge for the bulk state. The configuration entropy of the bulk state is, therefore,

$$S_{gb} = S|_{\xi \rightarrow \infty} = 0 \quad (3)$$

where the subscript gb stands for the glass state of the bulk.

However, the same deduction is not applicable to a single chain in its globular state, as the up-limit of the size, ξ , is restricted by the globule's size, i.e.

$$\xi \leq \left(\frac{R}{a} \right)^3 = N. \quad (4)$$

The existence of such a cooperative size will also lead naturally to the finite-size effect. In other words, the configuration entropy of a single chain in its globular state cannot decrease to zero upon approaching the glass transition. This leads to

$$S_{gs} \geq \frac{s^*}{N}, \quad (5)$$

where the subscript gs stands for the glass state of a single chain.

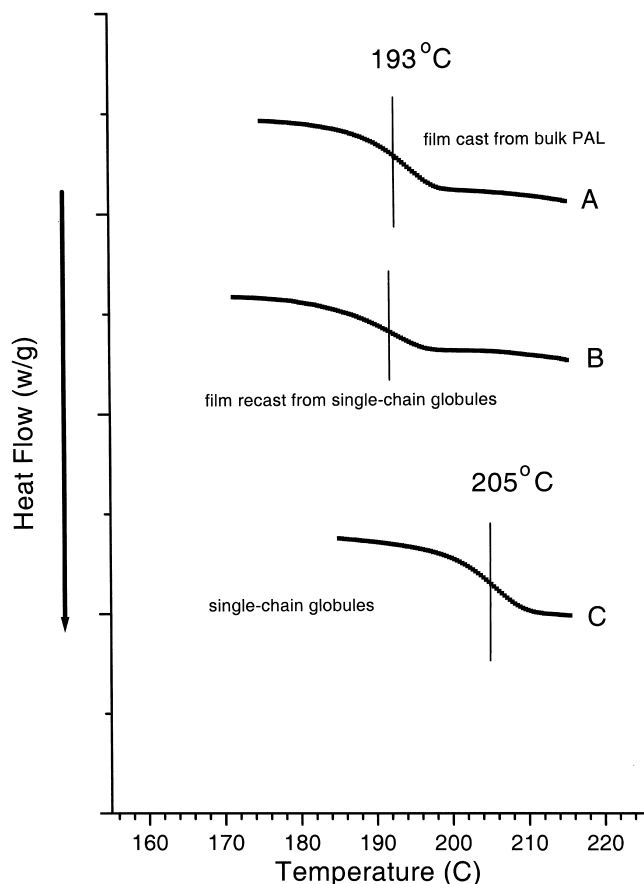


Fig. 3. The DSC thermograms of (A) film cast from bulk PAL, (B) film recast from single-chain globules, (C) single-chain globules.

Experimentally, it has been revealed that the value of T_g for single-chain globule can vary substantially from that of the bulk material. The magnitude of the change can be evaluated from the temperature dependence of the configuration entropy

$$S - S_g = \int_{T_g}^T \frac{\Delta C_p}{T} dT. \quad (6)$$

Considering that the specific heat, ΔC_p , of glass-forming liquids is approximately independent of temperature, we then obtain

$$S = \Delta C_p \ln \frac{T}{T_g} + S_g \quad (7)$$

where the subscript g stands for the glass state. Accordingly, the difference in the configuration entropy between a polymer chain in the bulk state and that in the globular state is given by

$$\Delta S = \Delta C_p \ln \frac{T_{gs}}{T_{gb}} + (S_{gb} - S_{gs}) \quad (8)$$

Introducing Eqs. (1), (3), and (5) into Eq. (8) leads to the

following equation:

$$\ln \frac{T_{gs}}{T_{gb}} \cong \frac{kN}{\Delta C_p} (N^{-x/3} + N^{-2} \ln 2). \quad (9)$$

Eq. (9) predicts that the T_g of a single-chain globule will be higher than that in the bulk state ($T_{gs} \geq T_{gb}$), since the right side of the equation is always positive. As the equality occurs only when $N \rightarrow \infty$, this is physically a finite-sized effect.

For further comparison of the theoretical prediction with the experimental data, we first observe that the quantity $Nk/\Delta C_p \sim O(1)$ for most polymers. When using $N \sim O(10^3)$, we find that

$$\frac{T_{gs} - T_{gb}}{T_{gb}} \cong CN^{-x/3} \sim C\% \quad (10)$$

where C is a numerical constant with a magnitude of order one. Theoretically, it is thus predicted that the T_g of a single-chain globule can vary by a few percent from that of the bulk material. This theoretical conclusion agrees well with our experimental data.

5. Conclusion

Nano-sized single-chain globules of PAL were prepared by spray drying of a dilute polymer solution. Thermal analysis showed that the particles exhibit a T_g that was significantly higher than the values of the corresponding bulk material. Entropy analysis supports that T_g of polymer single chains in the globular state should be higher than that in the bulk state.

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