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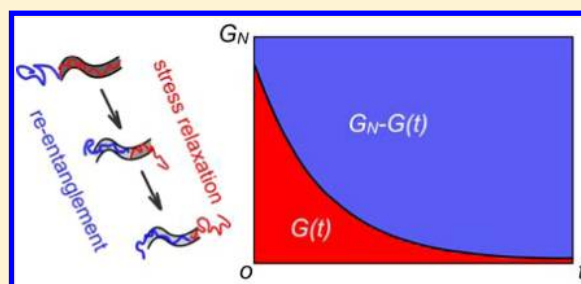
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Reentanglement Kinetics of Freeze-Dried Polymers above the Glass Transition Temperature

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ABSTRACT: Rheology experiments were performed to monitoring the kinetics of the entanglement recovery process of freeze-dried polystyrene. Complete reentanglement time requires unexpected long time, which does not monotonically reduce with the concentration of precursor solution. The entanglement recovery was treated as the complementary process of stress relaxation in Doi–Edwards model and was found to agree well with the exponential law. We clarified that freeze-drying is an effective way to achieve disentanglement for polymer chains. The correlation between recovery time and the concentration of precursor solution is in good agreement with previous results from molecular dynamics (MD) simulations.



INTRODUCTION

The tube model based on the original Doi–Edwards theory has been taken as the most successful molecular model for polymer entanglement dynamics.^{1,2} Even some nonlinear viscoelastic processes are supported by the tube model, such as the nonlinear relaxation after large step shear strain.³ However, previous works show that, after cessation of the shearing, the recovery of entanglement requires time 2 or 3 orders of magnitude longer than the time for stress relaxation, both in polymer solution and in melt.^{4–6} The fact that the reentanglement time is substantially longer than the linear viscoelastic relaxation time is not predicted by the tube model or any other models.^{4–6}

Nonlinear shear solution is frequently used to achieve the disentangled polymer samples. The kinetics of entanglement recovery in nonlinear shear modified polymer solution were particularly studied by Roland and Robertson.^{4,5} They found the time scale for entanglement recovery was 2 orders of magnitude longer than linear viscoelastic relaxation time and concluded that the process of reentanglement required larger length scale of cooperative chain motions than that associated with linear relaxation.

Besides the nonlinear shear solutions, freeze-drying from dilute polymer solution is also considered as a route to achieve disentangled polymer samples.^{7–10} The confined solid chains pretreated by freeze-drying are in highly nonequilibrium state, and the dynamics of polymer chains confined in nanoscale attract tremendous experimental attention.^{9,11–15} Liu and Morawetz⁸ employed fluorescence technique on the recovery of freeze-dried polymers and found that it took 16 h for a 100 000 molecular weight PS sample at $T_g + 50$ °C to achieve an intensity ratio halfway between the initial and equilibrium values. Nonetheless, the effect of freeze-drying solutions has not

been reached a consensus.^{16–18} Kotliar examined the viscosity of polystyrene freeze-dried from dilute solution at temperature well above T_g and found no significant differences on the viscoelastic melt properties between the bulk and polystyrene freeze-dried from dilute solutions.¹⁸

In this work, we prepared polystyrene samples by freeze-drying a series of benzene solutions with desired concentrations and studied the evolution of entanglement density and its dependence on the concentration of precursor solution. The results were compared with previous works^{16–18} and Doi–Edwards theory.^{1,2}

To monitor the reentanglement process, rheology experiments were performed. The elastic modulus in the rubbery plateau region, G_N^0 , is proportional to the entanglement density, according to

$$G_N^0 \sim \nu_e k_B T \quad (1)$$

where ν_e is the entanglement density, k_B the Boltzmann constant, and T the absolute temperature, which is constant in our experiments. Therefore, the measured plateau modulus $G'(t)$ here is proportional to the entanglement density, assuming that eq 1 will still hold in nonequilibrium situation. This basic concept reveals that the plateau modulus G_N^0 is an intrinsic property as it arises from the elastic response of the entangled polymer melt.

EXPERIMENTAL SECTION

Materials. A commercial monodisperse PS (Polymer Source Inc., $M_w/M_n = 1.08$) with molecular weight of 205 000 g/mol was used as

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the experimental sample, which shows a calorimetric T_g at 105 °C measured by DSC. Details of the freeze-drying procedure have been published previously.¹⁰

Rheology Experiments. PS samples freeze-dried from desired concentration of PS/benzene solutions were first compressed into round pellets, and the resulting dishes were heated fast (about 30 °C/min) to 150 °C. Master curve of bulk PS were characterized by small-amplitude oscillatory shear measurements using a HAAKE Rheo-Stress 600 rheometer over a wide temperature, 130 °C $\leq T \leq$ 180 °C. Measurements were performed using a set of 20 mm diameter parallel plates with a sample thickness of ca. 0.7 mm. Time-temperature superposition (TTS) was used to generate master curves at 150 °C spanning nearly 6 decades of frequency. Results for bulk PS are provided in Figure 1.

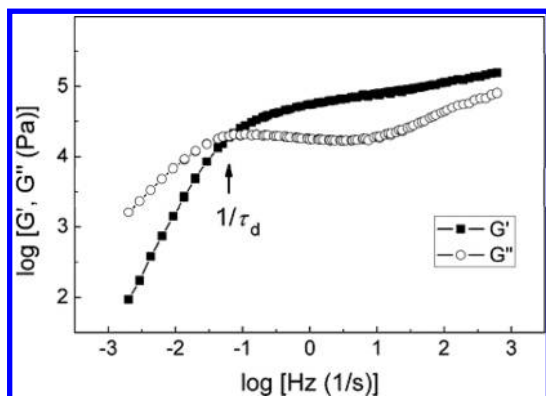


Figure 1. Storage modulus G' and loss modulus G'' as functions of frequency at 150 °C of the bulk PS sample.

For the entanglement recovery experiment, the applied strain (0.05%) and frequency (1 Hz) are chosen to be in the linear viscoelastic regime and on the rubber plateau region of the master curve. Elastic modulus was recorded as a function of time.

RESULTS AND DISCUSSION

Figure 2a summarizes a series of experiments, showing a buildup of measured plateau modulus ($G'(t)$) as a function of time for different concentrations of precursor solutions. The elastic modulus $G'(t)$ is normalized by the equilibrium plateau modulus (G_N^0) of each sample at the measurement frequency. Indeed, a lower $G'(t)$ is observed at first, which indicates the

low entanglement density according to eq 1. With time, entanglement formation takes place and is reflected by an increase in modulus. During the modulus buildup phase, the sample is in a thermodynamically unstable state. Ultimately, as $G'(t)$ reaches its asymptotic value, the equilibrium state of chains is obtained. The time required for modulus buildup changes with the concentration of precursor solution, as illustrated in Figure 2b. The recovery time does not decrease with concentration monotonically. As the concentration of original solution becomes denser, the recovery time drops off promptly during $[\eta]c < 1.7$, from 15.9 to 2.2 h, and then becomes longer with concentration.

Comparing to Kotliar's result,¹⁸ the recovery of entanglement density for freeze-dried polystyrene is quite clear in our experiment. Although both of us employed the rheology to investigate the entanglement environment, there are several major differences, which may lead to different conclusions. First of all, they performed a rotation mode experiment with a fixed shear rate, at 1–8 1/s. As previous works show, steady shear itself may cause a loss of entanglement, resulting from the flow-induced orientation of the chains.^{5,19,20} Therefore, the steady shear experiment with a relatively large shear rate would not capture the fully entanglement state. In our test, the oscillation mode with very small shear strain was set, so that we could measure the elastic modulus without perturbing the system structure. Second, the main index of entanglement extent we used was the plateau modulus, G_N^0 , which is proportional to the entanglement density, ν_e . In Kotliar's work, they used melt viscosity as an indicator of entanglement, which is less sensitive and indirect to entanglement. Furthermore, they did find about 10% increase in melt viscosity for freeze-dried polystyrene in their experiment during the first 90 min, but they compared it with the "initial-state" sample, which they thought was most likely precipitated from a 5–15% solution and was considered as the equilibrium state of an entangled polymer. Nevertheless, polystyrene precipitated from a 5–15% solution is far from the equilibrium entanglement state, as shown in Figure 2. Finally, they measured the elastic modulus as a function of frequency and compared it with other disentangled samples. To reduce parallel errors, it is more authentic to monitor G' normalized to the measured plateau modulus G_N^0 of each sample.

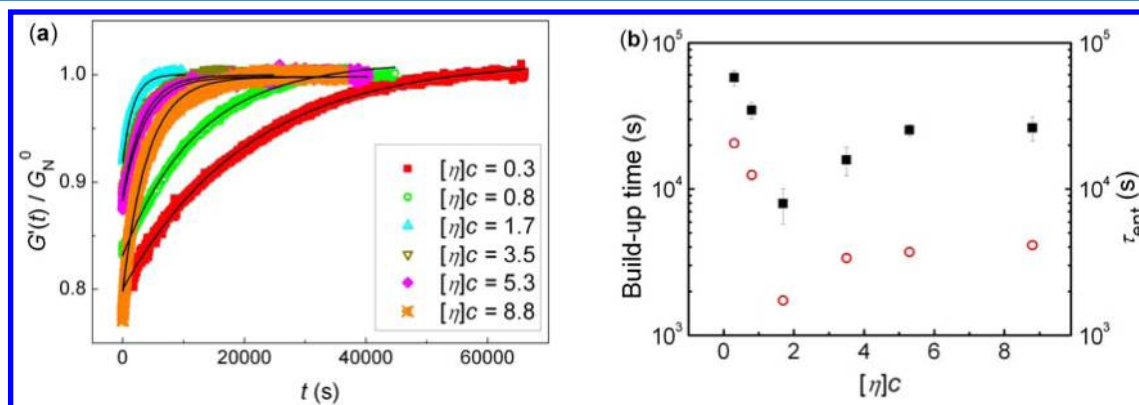


Figure 2. (a) Buildup of modulus in polystyrene samples with time. The red, green, cyan, gray, magenta, and orange lines are due to PS samples freeze-dried from PS/benzene solutions with $[\eta]c$ of 0.3, 0.8, 1.7, 3.5, 5.3, and 8.8. In the figure, the measured plateau modulus ($G'(t)$) is normalized by the equilibrium plateau modulus (G_N^0) of each sample. Thermal equilibrium is reached after ~ 300 s. (b) Equilibrium entanglement time of samples freeze-dried from solutions with different original concentrations. The solid black squares refer to the buildup time where $G'(t)/G_N^0 = 0.98$ of each data line in (a), and the open red circles correspond to the fitted parameters τ_{ent} according to eq 3.

Figure 2b shows that, for all the six samples, the entanglement recovery times τ_{ent} are 2–4 orders of magnitude longer than linear viscoelastic relaxation time of bulk sample, which is $\sim 10^1$ s, shown as τ_d in Figure 1. This results reveal that the entanglement recovery process requires cooperative chain motion over a length scale exceeding that associated with linear relaxation.⁵ Similar prolonged recovery time was also found in the recovery of stress overshoot and entanglement recovery in shear-modified polymer solutions.⁵

Present studies mostly focus on the solution and melt systems in which the initial local environment is homogeneous. However, the freeze-dried polymers are more complex systems with many features deviated from bulk state, such as the segmental mobility, entanglement density, interchain coupling, and chain packing density.^{7–10}

Despite the complex initial environment in freeze-dried polymers, their destination of reentanglement is identical. The inverse of entanglement recovery process, which is a disengagement process of the primitive chain escaping from the tube, is widely studied. In Doi and Edwards' work,^{1,2} they represented the topological constraints of mutually overlapping chains as a spatially fixed tube and considered the motion of a linear chain within the tube, depicted as the red coil in Figure 3. With time,

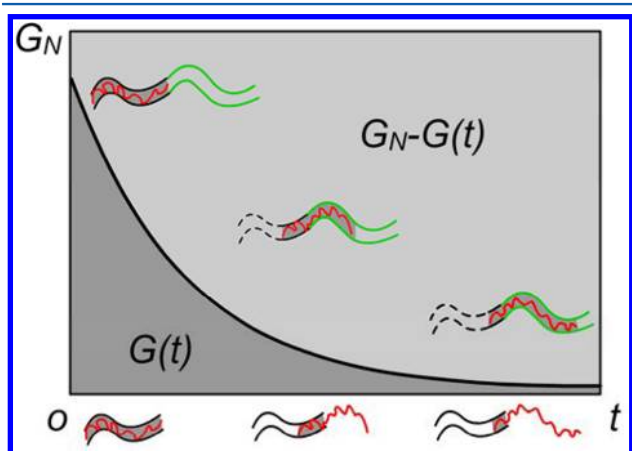


Figure 3. Schematic diagram of the relationship between stress relaxation modulus and entanglement recovery modulus. The red chain is slipping out of the tube during stress relaxation and reptating into the new tube simultaneously.

some segments of this chain escaped from the initial tube to relax. This reptative motion is equivalent to one-dimensional diffusion. When under deformation, the relaxation modulus, $G(t)$ is obtained as

$$\frac{G(t)}{G_N} = \sum_{p=\text{odd}} \frac{8}{p^2 \pi^2} \exp\left(-\frac{tp^2}{\tau_{\text{rep}}}\right) \quad (2)$$

where G_N is the entanglement plateau modulus and τ_{rep} is the reptation time required for the chain to escape from the tube.

Considering a chain slipping out of a tube, as the red coil shown in Figure 3, the relaxation modulus decreases with the segments outside the tube. $G(t)$ could be treated as the contribution of the remaining part of the chain in the original tube, shown as dark gray area in Figure 3. Since G_N is the effect of the whole chain, we suggest that $G_N - G(t)$ is the contribution of the segments outside the original tube at time t .

In a polymer solution or melt, after step deformation, when the chain end slips out of the original tube, it reptates into a

new tube (or create a new tube around it) at the same time, shown as the green tube in Figure 3. Therefore, the stress relaxation process includes both the chain slipping out of the deformed tube and reptating into a new tube simultaneously. The newly created tube is not under deformation as the original tube, so it does not contribute to the relaxation modulus.

Considering the chain reptating into the new tube, which is entanglement recovery, as the complementary process of stress relaxation, we have that the measured plateau modulus $G'(t)$ is also a measure of entanglement, we could fit our data with an analogue of eq 3 as

$$\frac{G'(t)}{G_N^0} = 1 - \frac{G(t)}{G_N} = 1 - A \exp\left(-\frac{t}{\tau_{\text{ent}}}\right) \quad (3)$$

where τ_{ent} measures the time for recovery of G' and A is a constant. Equation 3 fits well for all the data, shown as solid lines in Figure 2.

One of the major differences between stress relaxation and reentanglement is the time scale. The time scale for entanglement recovery is 2–4 orders of magnitude larger than that for stress relaxation. We believe that is due to the probability for the motion direction of the primitive chain. In stress relaxation process, the probability for a certain segment of the primitive chain reptates to the end of the tube is considered as the first-passage problem of one-dimensional Brownian motion, as proposed by Doi and Edwards.² Considering the difference of the geometrical constrain between the equilibrium state and the disentangled state, the probability is much lower for the primitive chain reptates from the less geometrical constrained tube (disentangled state) to the more constrained tube (equilibrium state). Therefore, it takes longer for the reentanglement process. A more detailed explanation will be shown later.

It is well documented that the entanglement density of polymer solution becomes higher with increasing concentration.^{21–25} Thus, higher entanglement density should be preserved in the sample freeze-dried from concentrated solution, and it needs shorter time to recovery its complete entanglement state. However, our results show conflict with this presumption.

The detailed information about chain motions in the reentanglement process is difficult to be observed, but suitable to be simulated. The process of interpenetration of polymer globules was simulated by means of molecular dynamics.²⁶ Two stages were found during the process of globules merging: the wetting stage and the interpenetration stage. The globules entering the first stage will take a while, because the globules would collide many hundreds of times before merging and before aggregation starts, even the chains were in the molten stage.^{26,27} In the second stage, one coil envelops the other and then the one being encircled counterattacks.

Freeze-drying the dilute PS solution leads to a collapse of the individual molecular chains into compact globules with no significant chain entanglement.⁸ It takes much longer in the first stage for so many individual chain globules to collide with each other before interpenetration starts. While for the sample freeze-dried from more concentrated solution, the interpenetration between chains has already formed in a certain degree before recovery experiment starts. Thus, the total entanglement recovery time for the samples freeze-dried from dilute solutions is much longer than those from concentrated solutions.

For $l/l_c > 1$, the entanglements between chains in the original solution are noticeable. With more concentrated solution, the entanglement density is higher and the chain coils become smaller.^{21–23} Therefore, after freeze-drying the solution, the globules become more compact with increasing original concentration of solution.²⁶ Therefore, it takes more time for the coils to envelop the neighbors in the second stage.

Besides the freeze-dried polymers, chain conformations in as-cast thin polymer film are also in nonequilibrium and partially disentangled state.^{11,14,15} Both freeze-drying and spin-coating introduce rapid drying of the solvent and partially preserve the chain conformations in the original solution, leading to a lower entanglement density in thin films and freeze-dried polymers. The loss of entanglement density was proved to have a strong influence on the residual stress and thus on the deviations relative to bulk values.^{14,15} It was found that the entanglement recovery time for thin film was longer than the reptation time of bulk polymer,¹⁵ which is analogous to that in freeze-dried polymers and nonlinear shear solutions. The reentanglement time for thin polymer film is affected by the coil size: poorer solvent leads to more compact chains and longer time to recovery its equilibrium state.¹⁵ This finding in thin film is consistent with what we found in freeze-dried polymer when $l/l_c > 1$: more concentrated solution results in smaller coil size^{21–23} and more compact globule, thus longer recovery time.

CONCLUSION

In this work, freeze-drying solutions were used to reduce the entanglements in polystyrene samples. We studied the entanglement recovery process by measuring the recovery of the plateau modulus. During recovery, the development of entanglements for freeze-dried polystyrene is quite clear. These results clarify that freeze-drying solution is effective method to achieve the disentangled polymers. The reentanglement process in freeze-dried polystyrene was found to be much longer than the linear viscoelastic relaxation time. The kinetics were studied as the complementary process of Doi–Edwards relaxation model and proved to agree well with the exponential law. The time scale for recovery of the entanglements is much longer (by 2–4 orders of magnitude) than the linear relaxation time. The concentration dependence of recovery time was explained by the previous results from MD simulations. This work will help us understand better about the process of entanglement recovery in bulk polymers as well as in thin polymer films.

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Notes

The authors declare no competing financial interest.

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