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Enthalpy Relaxation near the Glass Transition of Polystyrenes with Controlled Interchain Proximity

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ABSTRACT: Interchain coupling of polymers was investigated by detecting the segmental proximity using ^{1}H solid-state NMR under fast magic angle spinning. The NMR experiment based on the dipole–dipole interaction provided information about intersegment distances on length scales of several angstroms, over which the van der Waals attraction force occurs. The NMR and DSC were combined to get insight into the dependence of the enthalpy relaxation by sub-T_g annealing on the local segmental motion. Parameters of the TNM model were used to quantitatively discuss the glassy-state structural relaxation behavior near the glass transition of the prepared samples. Our experimental results demonstrated that if the intersegment distance was controlled to be larger than 0.5 nm, the enthalpy relaxation time spectrum through the glass transition region became narrower and the stretch exponent β for the TNM model was larger. When the polystyrene (PS) sample was a cast film or powder prepared from a concentrated solution, the chains were detected to be in close proximity, and thus their β value became smaller. It is interesting that the PS sample from a 10 wt % solution in DOP exhibited nearly the same relaxation behavior as the sample prepared from a 0.1 wt % solution in benzene. ^{1}H solid-state NMR detection indicated that these two samples showed a similar level of intersegmental proximities, although they had different entanglement concentrations. On the basis of our experimental results, we argued that the segmental proximity restricted the local segmental motions on short length scales and thus influenced the glassy-state relaxation behavior.

Introduction

Polymer glasses usually exist in a nonequilibrium state, which have higher specific volume, enthalpy, and entropy than in their equilibrium state at the same temperature. The polymer glasses relax toward the thermodynamic equilibrium amorphous state by annealing at temperatures below the glass transition. This glassy-state structural relaxation below the glass transition can be distinguished from the cooperatively motion associated with glass transition; the latter is associated with the α-relaxation [i.e., relaxation of cooperatively rearranging regions of some tens to hundreds of repeat units], whereas the former is commonly associated with the local motion of segments. As for polymers, the glassy-state structural relaxation, often referred to as physical aging, can result in a time dependence of end-use properties of critical importance such as increased modulus, increased brittleness, and reduced permeability.[2] Hodge et al.[3–5] have demonstrated that the development of sub-T_g heat capacity peaks observed in the differential scanning calorimeter scans (DSC) with aging is a consequence of the glass transition kinetics and the relation between the glass transition phenomenon and aging effects. The effect of sub-T_g annealing on enthalpy relaxation was treated by the TNM (Tool–Narayanaswamy–Moynihan) model,[1,6] which has been widely accepted in consideration of the glass transition kinetics.[1,7]

As pointed by Ngai et al.,[1] the kinetic nature of the glass transition and its phenomenological understanding have been based on the structural relaxation above and below T_g. The role of intermolecular interaction or coupling in the dynamics of local segmental relaxation has remained incompletely understood. It was well-known that the forces involved in the interchain coupling are van der Waals forces between nonbonded neutral segments when they come into close contact with each other. The attraction forces provide constraints on segments and therefore limit their local mobility below T_g, which are the origin of the complex molecular motions and the dispersion of structural relaxation.[1,8]

Polymer glasses can be in different degrees of interpenetration of chains by special "manipulation" methods, such as solution freeze-drying[9–11] and controlled synthesis.[12] The conception of chain entanglement provides the basis of our current understanding of the flow behavior of polymer melts.[1] The critical entanglement molecular weight for polystyrene (PS) was reported to be about 33 000 g/mol. It means that there are tens to hundreds of segments between the entangled points along the polymer chains. A typical segment can in principle interact with each of these segments on the same chain and also with a number of neighboring chains, each of which contains another tens to hundreds of segments. It is difficult to calculate the segmental trajectory, which is truly a many-body problem that would be hard to address, even with the massive computing power that is available today. Here we simplified this complex question to the investigation of intersegment proximity on short length scales. We tried to relate the intersegment distance to van der Waals interaction which is effective on short length scales of several angstroms and dies off as R^{-6} at larger separations.

Some modern technologies, such as atomic force microscopy, thermal analysis, and scattering methods (visible light, X-ray, neutron) were frequently used to investigate dimensions and structures of molecule chains.[13] Unfortunately, these methods failed to identify chain interactions in a homopolymer at a length scale of several angstroms. Solid-state NMR (SSNMR) is a unique method for relaxation studies of polymer glasses on a short length scales of 0.1–100 nm and at a range of time scales of 10^{-9}–10^{1} s. Among various nuclei, ^{13}C SSNMR has been most widely applied for its good resolution. However, the poor sensitivity of ^{13}C SSNMR has required a larger amount of sample and longer measuring time (several days or weeks) compared with other analysis because of the low abundance of ^{13}C. ^{1}H SSNMR is an attractive alternative to ^{13}C, particularly for unlabeled systems and samples in limited quantities because

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of its high sensitivity. Though the strong $^1H-^1H$ dipolar−dipolar interaction veils many important information and limits the use of ^1H SSNMR, a suitable pulse sequence has been required, together with magic angle spinning (MAS), to suppress line broadening. Recently, we reported a new method to probe the degree of interpenetration of chains in hydrogenous PS (PS-H)/deuterated PS (PS-D) isotopic blends by solid-state ^1H NMR (^1H SSNMR).[11,14] Chain interpenetration and the intimacy of segmental mixing in PS samples, which were recovered from solutions at different concentrations, were successfully and qualitatively characterized. Note that ^1H SSNMR experiment based on the dipole−dipole interaction reflects interchain coupling occurring over short distances about 0.5 nm.[11] In this paper, we aimed to investigate the effect of intersegment proximity on the local structural relaxation behavior of PS glasses by the combination of ^1H SSNMR and DSC.

Experimental Section

Materials. Benzene (Aldrich, spectrophotometric grade) was shaken with concentrated sulfuric acid and then with water, dilute NaOH, and again water. And then it was dried with anhydrous Na_2SO_4 and distilled. Dioctyl phthalate (DOP) was commercially available.

Polystyrene with a narrow molecular weight distribution ($M_w/M_n = 1.03$) and medium molecular weight ($M_n = 1.18 \times 10^5$) was purchased from Polymer Source Inc. The deuterated polystyrene (PS-D, Polymer Source Inc., sample P2404-dPS) has the number-average molecule weight of 1.04×10^5, with polydispersity index of 1.38. The residual level of protonation in the PS-D is about 3.5%, as determined by liquid-state ^1H NMR on a Varian UNITYplus-400 NMR spectrometer at a proton frequency of 400.2 MHz.

The freeze-dried samples were prepared by dissolving the desired amount of PS in benzene to obtain PS/benzene solutions with concentrations of 0.1 and 20 wt %, respectively. The solutions were then poured into liquid nitrogen to freeze the binary system in a fraction of second. The solvent was sublimated at −35 °C, which was below the melting point of the solution and was well below the glass transition temperature of PS, typically for 2 weeks.

The samples freeze-extracted from DOP were prepared by dissolving the desired amount of PS in DOP at 120 °C. The solutions were dropped into a large amount of liquid nitrogen with stirring and frozen in a fraction of a second; solvent was extracted by adding a large amount of cold ethanol into the frozen system at about −10 °C and was stirred for 24 h with a magnetic stirring bar. The powdered PS was then separated by ultracentrifugation and dried under vacuum at room temperature. The separated PS specimens were then repeatedly extracted with ethanol and dried under vacuum until reaching a constant weight.

Simon et al.[15] pointed out that the residual solvent could have an effect on the measurement of glass transition for the polymer glass prepared by freeze-drying. In order to ensure that there was no residual solvent in our samples, the initial freeze-dried or freeze-extracted polymer powders were further dried under vacuum for 2 weeks at room temperature until reaching a constant weight.[15] Before the samples were studied by DSC, they were held in the cell at 130 °C for 5 min. Our DSC measurements did not detect significant depression in the calorimeter glass transition for these dried samples. A 12-pulse dipolar filter sequence ^1H solid-state NMR technique under fast magic angle spinning has been using to detect semiquantitatively the residual solvent in polymers [see the Supporting Information (1)].

Calorimetric Measurements. Differential scanning calorimeter (DSC) measurement was run on a Perkin-Elmer DSC-Pyris 1 system. Temperature calibration was performed using indium. Temperature scans were made as follows: All samples were first held for 5 min at 130 °C, then cooled from 130 to 50 °C at specified cooling rates, ranging from 1 to 20 K/min, and held for 1 min at 50 °C. Subsequently, they were heated from 50 to 130 °C at 10 K/min. The heating leg that followed the 10 K/min cooling leg was used as an internal reference.[16,17] Our NMR studies indicate that there is no change in segmental proximity after holding the sample at 130 °C.

NMR Measurements. ^1H SSNMR spectra were recorded for samples of isotopic blends of PS and deuterated PS (PS-D) prepared from various solutions on a Varian Infinityplus-400 wide-bore (89 mm) NMR spectrometer at a proton frequency of 399.7 MHz using a 2.5 mm T3 double-resonance CPMAS probe, and this probe can provide stable sample spinning up to 30 kHz using a zirconia PENCIL rotor. All the NMR data were processed with Varian Spinsight software, and all experiments were carried out at room temperature. The ^1H chemical shifts were referenced to external TMS. More details of NMR experiments could be found elsewhere.[11]

Results and Discussion

NMR and Interchain Proximity. Recently, our group demonstrated a new approach to characterize the interpenetration degree of bulk polymer glasses using fast MAS (spinning speed, $\upsilon_R > 20$ kHz) and a dipole filter pulse. The MAS at about 25 kHz induces crucial changes in spin dynamics for organic solids by eliminating the majority of $^1H-^1H$ and $^1H-^{13}C$ dipolar couplings. We used deuterated sample as a diluter to dilute the strong $^1H-^1H$ interaction when the deuterated chain was closely overlapped with the hydrogenated one in the isotropic blend. Faster spinning may eliminate the strong chemical anisotropy for the detected species. A dipolar filter pulse sequence together with fast magic angle spinning was used to suppress line broadening induced by the strong dipolar interaction to characterize the chain proximity on short-range scales of 0.2−1.0 nm in isotopic blends of PS glasses.[11]

The relationship between the distance and signal intensity of NMR can be expressed by the equation[18]

$$M_2 = \frac{3}{5}\hbar^2\gamma^4 I(I+1)\sum_j r_{ij}^{-6} \qquad (1)$$

When the protons are in close proximities less than 0.5 nm, the $^1H-^1H$ dipolar−dipolar interaction was very strong. When the length scale of the distances (r_{ij}) is larger than 0.5 nm, the dipolar interaction signals were dramatically reduced in intensity. If the deuterated PS (PS-D) chains were blended with PS-H, the so-called “deuterium-induced ^1H dipolar interaction dilution effect” could selectively isolate the signal of the PS-H, which is in a close proximity of 0.5 nm with PS-D. The plot of NMR intensities vs the intersegmental distances (*d*) is shown in Figure 1A. Figure 1B is the plot of van der Waals interaction forces (*f*) vs distance (*d*) between two particles.[22] The correlation between van der Waals attraction forces and the NMR data is significant. The detection of the spatial proximity between segments could provide information about interchain attraction for nonpolar segments. In the following sections, we shall further correlate the segmental proximity to the glass-state structural relaxation.

The ^1H SSNMR spectra of isotopic blends of PS freeze-dried from solutions in benzene and dioctyl phthalate (DOP) are shown in Figure 2. Figures 1A and 2 show that a unique ^1H signal was selectively isolated when the deuterated PS (PS-D) chain was in a close proximity to the hydrogenous PS (PS-H) within 0.5 nm; therefore, the isolated signal is a clear evidence of segmental mixing within a distance of 0.5 nm. When the length scale for the distances between PS-D and PS-H chains are larger than 1 nm, the NMR signal was dramatically reduced in intensity. Here, the cast film is regarded as the sample in which the segments are closely compacted. In Figure 2, one can see that the signal from isolated aromatic protons (7 ppm) is very strong for the cast film and for PS recovered from a 20 wt % solution in benzene, indicating that the chains are in closer proximity (less than 0.5 nm) in these PS glasses. The aromatic peak is very weak for the PS freeze-dried from 0.1 wt % solution

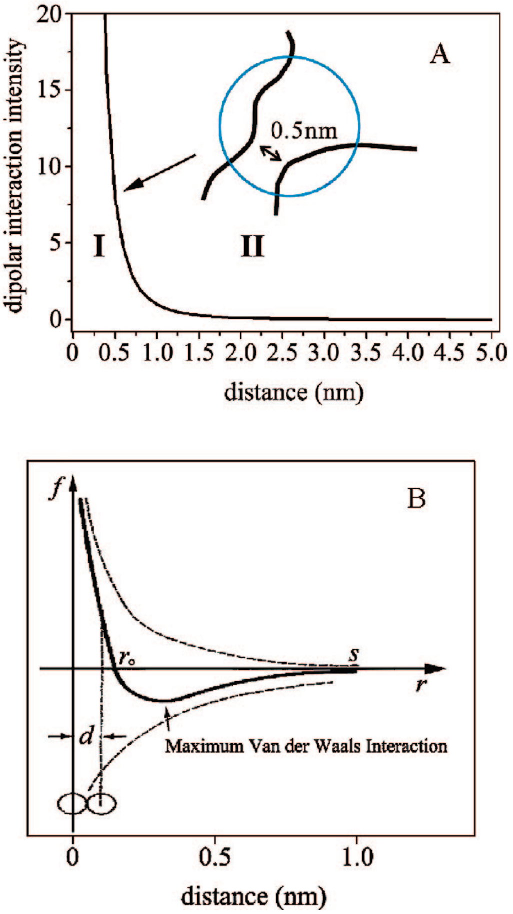

Figure 1. (A) NMR signal intensity vs the distances based on the equation $M_2 = {}^3/_5\hbar^2\gamma^4 I(I + 1)\sum_j r_{ij}^{-6}$). When the PS chains were in a close proximity within 0.5 nm, the aromatic proton signal was very high. When the length scale of the distances between PS segments is larger than 0.5 nm, the NMR signals were dramatically reduced in intensity. (B) Plot of van der Waals attractive interaction forces (*f*) vs distance between two nonpolar particles, which reaches the maximum at the distances of 0.4 nm and dies off at 1 nm.[23] Regions I and II illustrate conformations with different intersegment proximities of polymer glasses.

in benzene. It is widely accepted that the polymer chains are less interpenetrated in the solid state prepared by freeze-drying dilute solutions. Surprisingly, the aromatic peaks in NMR spectra for the samples recovered from DOP in Figure 2 are weak and held almost constant for the samples prepared from solutions with concentrations up to 20 wt %. These results suggest that the intersegment distances for PS glasses recovered from solutions in DOP are larger than 0.5 nm. Here, it should be noted that the conception of intersegment proximity for polymer glasses is distinguished from the commonly used conception of chain entanglements. The former is associated with the local segmental motion of the glassy-state chains on short-range scales. The NMR data in Figure 2 indicate that PS glass prepared by freeze-drying dilute solution shows the same level of intersegment proximity as that prepared from a concentrated solution in DOP. However, these two samples have different concentrations of chain entanglements which were detected by the nonradiative energy transfer (NET) method developed by Morawetz et al.[10] The experimental details are described in the Supporting Information (2).

On the basis of the experimental data for polystyrene samples, we found that the conformation of PS prepared from various solutions could be located in one of the two regions shown in Figure 1A. Region I is a closely packed region for molecule chains, in which the intersegment distances *R* are smaller than 0.5 nm. The samples of solution-cast film and the powders freeze-dried from concentrated PS/benzene solution (20 wt %) are ranked in this region. In region II, the chains are controlled with the proximity larger than 0.5 nm. The samples of PS prepared by freeze-extracting PS/DOP, and the freeze-dried sample from dilute solutions can be ranked in this region. Our NMR experiments showed that this segmental proximity is stable below the melting temperature.

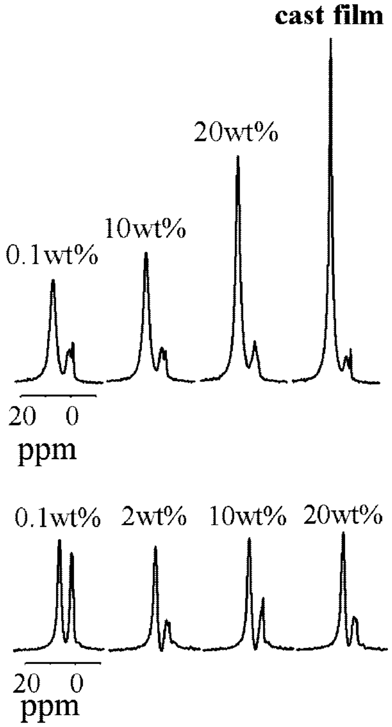

Figure 2. Solid-state ^{1}H NMR spectra of isotopic blends of PS-H and PS-D. Upper: recorded from a cast film and freeze-dried from PS/Benzene. Lower: freeze-extracted from PS/DOP. The concentration of the original solution is indicated near each spectrum. The sample weight in each experiment was used for normalizing the signal intensity.

TNM Model for DSC Results. In TNM model, the structural relaxation of glasses is mathematically described based on the plot of the heat capacity C_p vs temperature during cooling and reheating through the glass transition.[3] The physical parameters, characterizing the enthalpy relaxation of PS samples quantitatively, were obtained by best fitting the C_p–T plot to our experimental DSC data. Modeling was performed on the DSC results that are provided in Figure 3. We stressed the following important parameters in TNM model:

(a) T_f is defined as the temperature at which a glassy material would possess the equilibrium thermodynamic state if heated to that temperature. Here T_f is found by integrating the heat flow curve and then extrapolating the liquid line to the glassy line. (b) Δh^* is the corresponding enthalpy activation energy, defined by $\Delta h^* = -R \text{ d} \ln Qc/\text{d}(1/T_f)$. R is the gas constant. The values of $\Delta h^*/R$ for different PS samples are supposed to be the same, indicated as the same slope in Figure 4. (c) $0 < x < 1$ is the nonlinearity parameter ($x = 1$ in the linear case). (d) $0 < \beta < 1$ is the phenomenological measure of the width of the relaxation time spectrum ($\beta = 1$ for a single relaxation time). Here, we adopted $x = 0.426$ and $\ln A = 261.2$ widely used in published papers to obtain β in the fittings. More details regarding calculation of TNM parameters can be found elsewhere.[3,4,19] All the results are shown in Table 1.

As shown in Table 1, T_f's for all the samples are obtained at a heating rate of 10 K/min after cooling at the reference cooling

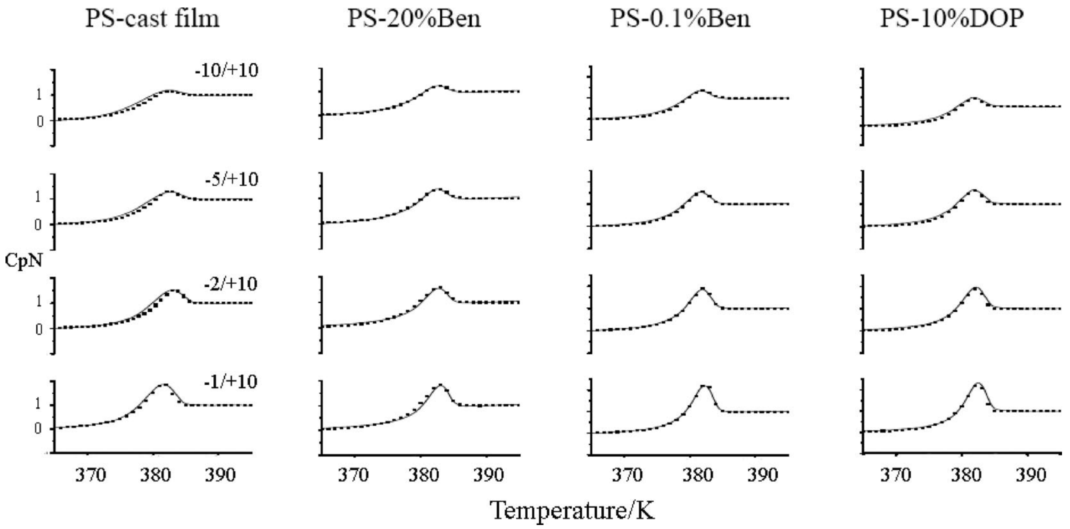

Figure 3. DSC glass transition responses during heating at 10 K/min after cooling from the temperature above T_g at the indicated cooling rates. Experimental (full lines) and theoretical (points) dependences of C_p^N on temperature for PS-cast film, PS freeze-dried from 20 wt % in benzene, PS freeze-dried from 0.1 wt % in benzene, and PS freeze-extracted from 10 wt % in DOP. Note: PS-20%Ben indicates the PS powder freeze-dried from a 20 wt % solution in benzene.

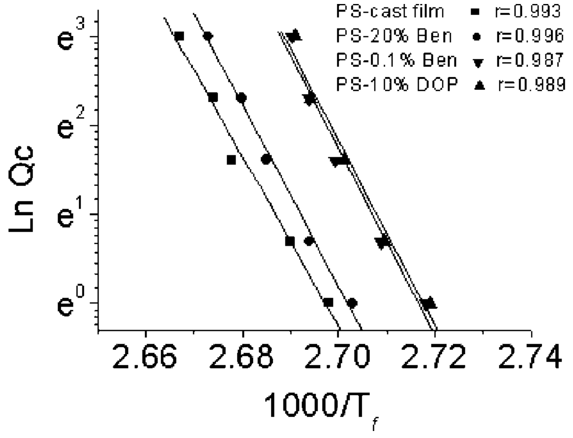

Figure 4. Logarithm of the cooling rate *Qc* as a function of the 1000/T_f for PS samples. Line is linear best fit and give values for $\Delta h^*/R$, listed in Table 1.

Table 1. Calorimetric Property for Bulk and Freeze-Dried Polystyrenes

PS samples designation	PS-cast film	PS-20%Ben	PS-0.1%Ben	PS-10%DOP
$T_{fQ_{\mathrm{ref}}}$ (K)	374.0 ± 0.2	373.1 ± 0.3	371.2 ± 0.2	371.1 ± 0.3
$\Delta h^*/R$ (kK)	98.1 ± 5.7	103.4 ± 5.9	104.8 ± 9.8	104.7 ± 8.6
β	0.47 ± 0.02	0.50 ± 0.02	0.60 ± 0.02	0.60 ± 0.02

rate (Q_{ref}) of 10 K/min. Our observation that T_f for PS recovered from a 0.1 wt % solution in benzene is 2 °C lower than that of the cast film is in agreement with Simon et al.[16] It was argued that the observed lower T_f could not be interpreted as a result of reduction of the chain entanglements. In this work, the PS chains were separated in the dilute solution, immobilized in the frozen benzene matrix, and maintain so after sublimation because of the slow relaxation rate at temperature well below T_g. As a result, the entanglement concentration of the freeze-dried powder is greatly reduced. NET experiment[10] revealed that PS glass recovered from a 0.1 wt % solution in benzene is in a state with a relatively larger interchain separation (>2.7 nm), testifying the assumption that the extent of chain interpenetration existing in original solutions would be somehow preserved during rapid freezing. In the solution-cast film, the PS chains are supposed to be fully entangled, and the segments are compacted closely. ^{1}H SSNMR results did show interchain distance less than 0.5 nm in PS-cast film. The depression of T_f for PS freeze-dried from a 0.1 wt % solution in benzene can be attributed to the larger interchain distance in the freeze-dried sample. Interchain proximity in PS recovered from 20 wt % solution in benzene is of the same level as that in PS-cast film, as shown in Figure 2. So their T_f's are believed to be equal, as indicated in Table 1. Obviously, our speculation that T_f correlates with interchain proximity in PS glasses is in agreement with the argument in ref 16.

As stated above, the stretch exponent β is an important parameter characterizing the structural relaxation near the glass transition. The larger β, the broader the DSC curve near the glass transition is. Stretch exponents for different samples are listed in Table 1. It is evident that the stretch exponent β for PS freeze-dried from a dilute solution in benzene is greater than the cast film. Privalko et al.[19] found that β decreases with increasing molecular weight of PS. As the molecular weight increases, the effect of end groups having relatively high segmental mobility becomes less significant. More cooperative motions of surrounding segments need to be involved in enthalpy relaxation. Consequently, the enthalpy relaxation time spectrum in the glass transition region becomes broader, and thus a smaller value of β is observed. In this work, ^{1}H SSNMR results demonstrated that intersegment distance in the freeze-dried PS from dilute solutions is larger than that in the cast film. It is believed that PS chains in the former sample feel fewer constraints, which are mostly imposed by interchain coupling. So a narrower relaxation time distribution is expected for the freeze-dried PS from a 0.1 wt % solution in benzene in contrast with the cast film, as is the case shown in Figure 3.

Counterintuitively, it is evident in Figure 2 that intersegment distances for PS chains freeze-extracted from DOP solutions are always larger than 0.5 nm even from a concentrated solution of 20 wt %. Scaling consideration of solvent size effect could date back to the particular case in ref 20, where one long chain was placed in the melt of shorter chains having degree of polymerization *Ns*. The size of the long chain is given as *R* $\sim Ns^{1-2v}$ ($v = 0.588$ for good solvent). The critical overlap concentration c^* scales as $c^* \sim Ns^{6v-3}$. So, the slightly increase in c^* in solution could not make chain disentangled in PS glasses which had been freeze-extracted from 10–20 wt % solutions in DOP. Whatever c^* is, we found that interchain proximities in PS freeze-dried from 0.1 wt % benzene and that in PS freeze extracted from 10 wt % solution in DOP are of the same level, i.e., >0.5 nm, and therefore similar DSC curves can be expected and were examined experimentally (see in Figure 3 and the values of β in Table 1). However, the NET results (in the Supporting Information) show that the two samples are different in concentration of entanglements. Our studies clearly indicate that the glassy-state structural relaxation corresponds to the local segmental motions, which are mainly restricted by intersegment coupling instead of the topological chain entanglements.

Additionally, much of our work has been devoted to the exploration of promoting crystallizability of polymer chains extracted from solvents with large molecular volumes, such as poly(ethylene glycol) oligomers or DOP.[21] The above interpretation of reduced constraints and enhanced segmental mobility due to large intersegment distance does agree favorably with previous experimental findings. Nevertheless, it is our further question whether solvent size effect[22] in polymer solutions includes physical meaning beyond deterioration in solvent quality induced by increasing solvent size. We hope computer simulations can help find the answer.

In polymers, there are several kinds of molecular motions corresponding to various length scales. The molecular motions involving more repeat units of each chain are possible, and they contribute viscoelastic properties over broad ranges. The molecular motions of longer range have characteristic times longer than the cooperative motions, which mean that the temperature has to be higher than the glass transition temperature. It is generally agreed that the primary or the α-relaxation involves reorientation of larger angles and transition of sizable distances. The length scales of glass transition, associated with the α-relaxation, associated with the cooperative rearrangement of some tens of repeated units, have been detected to be 2−4 nm.[18] Another kind of motion, which is referred as the secondary or β-relaxation, involves some local motions of side groups. Examples include the trivial rotating motion of the CH_3 group or motion confined to only a part of the molecule such as side groups of some polymer. When people show great interest in describing the motions of α- and β-relaxations, lesser attention is paid to the classification of the motions related to the enthalpy relaxation. This attitude limits the understanding of the structural relaxations in the glassy state. On the basis of NMR and DSC measurements, we argue that the spatial interchain proximity correlated to the local segmental motion on short-range scales and thus to the glassy-state structural relaxation.

Conclusion

We concluded that the depression of T_f in PS samples that freeze-dried from a very dilute solution may be distributed to the larger intersegment distance. Sharper DSC peaks and the corresponding larger β values were observed for both PS recovered from 0.1 wt % solution in benzene and PS recovered from a 10 wt % solution in DOP, indicative of the local segmental motions on short-range scales involved in enthalpy relaxation. Enhanced segmental mobility due to weaker constraints in PS glasses, where intersegment distance is larger than 0.5 nm, are responsible for the above larger β. It is believed that larger intersegment distance (>0.5 nm) in PS recovered from 10 wt % solution in DOP detected by ^{1}H SSNMR is related to solvent molecular size. Under way is our computer simulation toward understanding solvent size effect in polymer solutions.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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