# Single and Multichain Association of Polystyrene in Solvents with Various Molecular Sizes

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ABSTRACT: The association and aggregation of polymers in the semidilute solution regime during cooling from above to below the Θ temperature were investigated by the nonradiative energy transfer (NET) and rheological method. The molecular size of the solvent was found to affect the association and aggregation behaviors of the chains. When the normal small-sized solvent, for example decalin or cyclohexane is used, the polystyrene chains first associate among each other, and form aggregates of chains with strong interchain interpenetration at the end of cooling process. However, when the solvent with larger molecular size (also called middle-sized solvent), for example dioctyl phthalate (DOP) is used, polystyrene chains contract separately and form aggregates of collapsed globules at the end of cooling process. The interpenetration between chains for the polystyrene solid sample freeze-dried from different concentrations was detected by a new strategy using dipolar filter $^1$H solid-state NMR under fast magic angle spinning. We found that when the small-sized solvent was used, the extent of interpenetration in the polystyrene glasses basically kept constant with the concentration of the original solution and it increased suddenly near the critical overlapping concentration ($[\eta]c \sim 4$). However, in the case of middle-sized solvent, even up to $[\eta]c = 10$, the extent of the interpenetration kept in a very low level comparable to that from extremely dilute ($[\eta]c \sim 0.01$) small-sized solvent solution. Such results help us to understand the behaviors of fast crystallization and relaxation dynamics of serials of polymer samples freeze-dried from middle-sized solvent solutions discovered in this laboratory.

## Introduction

The collapse of macromolecular chains to globular state, chain association and phase demixing usually occur in polymer solutions with various concentrations below the Θ temperature if the solutions change from good to poor upon decreasing temperatures.[1−4] These phenomena are of great scientific importance, not only because of their fundamental role in the understanding of polymer segment-segment and segment-solvent interactions, but also because of their importance in the use of a simplified model for interpreting enzymatic activity, protein folding, or DNA packing.[5−7] By using dynamic light scattering, Chu et al. successfully measured the hydrodynamic radius, $R_h$, of ultrahigh molecular weight PS as a function of time after suddenly quenching the solution below the collapsed temperature and they observed two-stage kinetics of the coil-to-globule transition in the single chain.[8] Besides light scattering, fluorescence excimer had also been employed to characterize polymer coil-to-globule transition in extremely dilute solutions. Martinho et al. studied the transition of polystyrene chains randomly labeled with a pyrene derivative in dilute cyclohexane solution by fluorescence, which opened the opportunity for studying the coil−globule transition of low molecular-weight polymer chains in dilute polymer solutions.[9,10] While this dilute solution picture has been widely accepted,[8,11] the chain behavior as a function of solvent quality, especially the solvent molecular sizes, remains unresolved at concentrations in the near-overlap and semidilute regions.

Some experimental and simulation studies have been performed on the conformation changes of polymer chains in the semidilute regions.[4,12−14] In their molecular theory, Raos and Allegra demonstrated that conformation of a single chain in a "Gaussian cluster" below the Θ temperature remained unperturbed over the whole poor solvent regime, and the collapse to the globular state should occur only at $T < T_C$ ($T_C$ stands for phase demixing temperature).[4] Later on, Melnichenko et al. presented the first measurements of the radius of gyration ($R_g$) for polystyrene in deuterocyclohexane at the critical concentration over a temperature range $\Theta \geq T \geq T_C$ using small-angle neutron scattering. They did not observe a reduction of $R_g$ at the critical temperature of phase demixing $T_C$ as compared to $R_g$ in the Θ region, which indicates that the critical polymer solution cannot be considered as an ensemble of partially collapsed noninterpenetrating coils.[12−14]

Our previous studies have focused the effect of solvent molecular size on the microscopic structures of polymer solids prepared from the solutions.[15−19] Li and An also explored how the solvent molecular sizes affected the critical overlap concentration $\phi^*$, which is a fundamental parameter to distinguish between isolated and overlapped states of polymer chains.[20] It was reported that the addition of a medium molecular weight DOP, also called middle-sized solvent,[17] into a concentrated solution can facilitate the crystallization of the polymer from solution and result in higher crystalline conformation. For example, the extent of interpenetration of PVC chain decreases even in concentrated solution in DOP.[16,18] And *i*PS particles prepared by freeze-extracting concentrated solutions in middle-sized solvent are in a highly ordered $3_1$ helix state and can crystallize much faster than the bulk polymer.[17,19,20] These metastable properties of the above samples can be attributed to less interchain interpenetration.[15,17−19] Recently, NET was used to study the interchain contraction and association of polystyrene in semidilute solution near the Θ temperature.[21] NET was first developed by Morawetz and co-workers to study the interpenetration of polymer chains. It is sensitive in charactering interchain approach and interpenetration on short-range scales of 2−3 nm.[23] Two portions of polystyrene labeled with donor

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(carbazole) or acceptor (anthracene), respectively, were dissolved in solutions with desired concentration. The interchain interpenetration of the freeze-dried sample was expected to increase with the increasing concentration of the original solution, so when the freeze-dried sample was irradiated in the carbazole's absorption band, the nonradiative energy transfer from carbazole to anthracene, $I_A/I_C$, increased according to the Forster mechanism. However, NET experiments performed directly in solution were complicated by the variation of the temperature, the solvent polarity and the viscosity. So $I_A/I_C$ obtained in different solvents and different temperature should be corrected before it can be used to reflect the "real" change of interchain proximity. We proposed the method of normalizing $I_A/I_C$ with $(I_A/I_C)_0$.[21] $(I_A/I_C)_0$ was measured in a solution by keeping exactly the same concentration of polymer and fluorescent molecules, and the same temperature with the above experiments. However, the fluorescent molecules are free, instead of bonded to the polymer chains. NET results revealed that when undergoing a gradient drop of temperature, polystyrene chains went through different states: a smooth change of conformation above the Θ temperature, and an accelerated contraction and association with decreasing temperature below the Θ temperature.[22]

The aim of this contribution is to follow the chains association and collapse behavior on a variety of solvent systems, which all have as a common feature an accessible Θ temperature, but differ in the molecular sizes. For this purpose we apply the NET, which allows us to follow the change of average interchain distance in both the Θ region and the critical region of phase demixing of semidilute polymer solutions.[21] Monodispersed polystyrene (PS) chains in normal small-sized solvent (cyclohexane, decalin) were found to follow the behavior of multichain association and collapse while in middle-sized solvent DOP with the same concentration following single chain association, when temperature decreasing well below the Θ point.

In a recent communication, we developed a new and general strategy to characterize the chain interpenetration in isotopic enriched polymer glasses within a length scale of 0.5 nm,[22] which was enlightened by the pioneer work of VanderHart.[23] This method combines the preparation of the isotopically enriched polymer blends with $^1$H dipolar filter solid-state NMR under fast magic angle spinning (MAS). The intimate segment mixing in polystyrene isotopic blends of hydrogenous and deuterated chains at different interpenetration degree was successfully characterized. Although one component should be deuterated in the blend, this method has the advantages of high sensitivity and simplicity of the experiment over the NMR cross polarization method. It is noteworthy that this method is successful even for blend like PS−D/PS−H having undistinguishable chemical shifts of the two components, which prevents traditional NMR methods to be effectively employed. Furthermore, since high resolution $^1$H NMR spectrum can be achieved due to the fast MAS this method also provides a simple and alternative way to probe intermolecular interactions in polymer blends on a short length scale of 0.5 nm through the observation of $^1$H NMR signals "isolated" by the deuterated PS.[22] Motivated by this work and to further verify the universality of our NMR method, here we employ this new technique to characterize the chain interpenetration in the glassy state of PS recovered from solvents with various molecular sizes. And the NMR results were also compared with NET measurements which allow us to identify single and multichain collapses around the phase demixing temperatures. These above results will help us to interpret why polymer powders freeze-extracted from middle-sized solvents have highly ordered $3_1$ helix structure and can easily crystallize.[18,19]

## Experimental Section

**Materials.** The polystyrene (PS) sample (Polymer Source Inc.) has a number average molecule weight of $2.14 \times 10^5$, with polydispersity index of 1.03. The PS samples labeled with a carbazolyl probe (PS−Cz) or an anthryl probe (PS-An) were prepared. The details of the preparation could be found else where.[24] Absorption spectra were measured with a Perkin-Elmer Lambda 35 UV−vis spectrophotometer. The contents of carbazolyl or anthryl group in the polymers were determined from the molar extinction coefficient of the model compound. The content of monomer units in percents labeled with the emission probes were 0.425% (PS−Cz, mol %) and 0.272% (PS−An, mol %). Decalin (trans:cis = 4:6, wt %), cyclohexane, benzene, and DOP was prepurified.[17]

**NET Measurements.** Equal weights of PS-Cz and PS-An were dissolved in above solvents (3 g/dL) at room temperature respectively. The homogeneous solution was held at 40 °C for 24 h. The reflectance fluorescence was determined with a Jasco FP6500 fluorometer at excited wavelength of 294 nm. The solutions were also held at each centigrade for 1 min. As a comparison, the similar experiments were done to a solution containing the same quantity of polymer and fluorescent molecules as the above experiment without bonding the donor or acceptor to the polymer chains, and the details could be found elsewhere.[21]

**Rheological Measurement.** Polystyrene solutions in decalin and DOP with desired concentrations (3 g/dL) were also prepared. The unlabeled homogeneous solution was held at 40 °C for 24 h to achieve full equilibrium before rheological measurements, which were conducted on a HAAKE Rheo-Stress 600 instrument by using a set of 60 mm diameter parallel plates with a sample thickness of ca. 0.8 mm. The steady-shear experiments were carried on in the Newtonian fluid region at all testing temperature. The solutions were also held at each centigrade for 1 min. The viscosities of pure solvents at each centigrade were also measured.

**NMR Measurements.** $^1$H SSNMR spectra were recorded for samples of isotopic blends of PS (PS−H) 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 $^1$H chemical shifts were referenced to external TMS. More details of NMR experiments could be found elsewhere.[22]

## Results and Discussion

The relative intensity of fluorescent acceptor to donor $[(I_A/I_C)/(I_A/I_C)_0]$ versus temperature in a good solvent is shown in Figure 1a and those in solvents around the Θ temperature are shown in Figure 1, parts b and c. All the concentrations were kept the same, 3 g/dL, which lie in the range of semidilute solutions($1 < c[\eta] < 4$).[25]

The relative emission intensity of anthryl to carbazolyl probes was measured when the system was irradiated at 294 nm after equilibrating for 1 min at each centigrade. The rate of temperature change used was slow enough such that thermal equilibrium could be reached to avoid temperature gradients within the cell and solution.[8,21] Equilibrating for 1 min at each point was assumed sufficient to let the solution reach a homogeneous temperature at the desired state.[21] There are many other factors that affect the fluorescence measurements, such as temperature, viscosity, and so on. For example, the solvent itself affects the fluorescence quantum yield of both labels, and the quantum yield changes with temperature. The change in viscosity with decreasing temperature affects the movements of chains and the fluorescent moieties. As a result, a solution that contained the same quantity of polymer and fluorescent molecules as in the above experiment without bonding the donor or acceptor

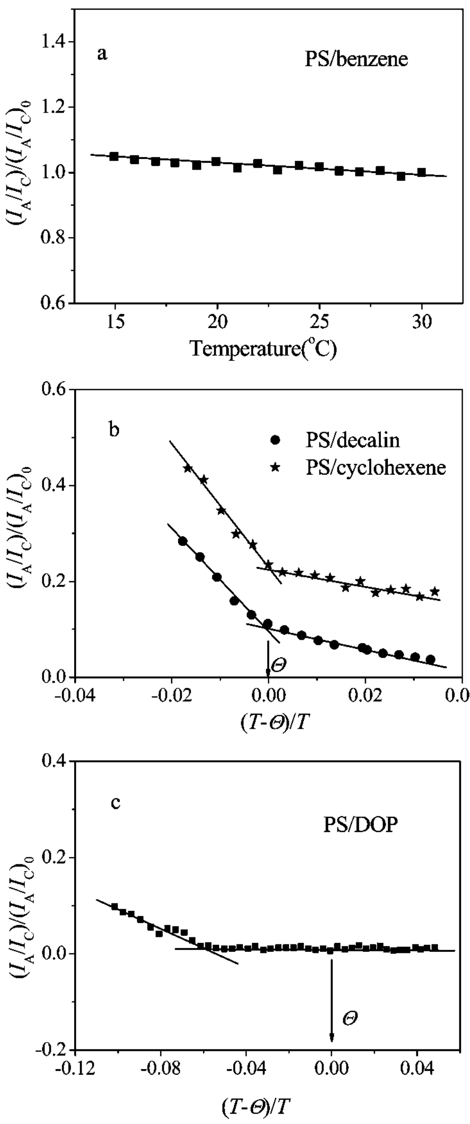

**Figure 1.** Plot of $(I_A/I_C)/(I_A/I_C)_0$ versus temperature ($T$) in (a) benzene, (b) decalin and cyclohexene, and (c) DOP. The cooling rate is 1 K/min. The same experiments were done to a solution containing the same quality of polymer without bonding the donor or acceptor. The results were marked as $(I_A/I_C)_0$. Each point in the curves was the ratio of the relative emission intensity of acceptor to donor $(I_A/I_C)/(I_A/I_C)_0$ at the corresponding temperature.

was used. The same experiments were performed and the results were marked as $(I_A/I_C)_0$. The interference of solvent could be eliminated and the values of $(I_A/I_C)/(I_A/I_C)_0$ reflect the real changes of interchain distance in solution.

Benzene was known as a good solvent of polystyrene under the measured temperatures. There is a slight change of NET relative intensity with decreasing temperatures in Figure 1a, indicating that the expanded chains change their conformations slightly when the solution was cooled.

The reported Θ temperatures for polystyrene in cyclohexane, decalin, and DOP are 35, 15, and 22 °C, respectively.[26] The values of the critical temperatures (cloudy point measured by the visual observation) of the above solutions are 27 , 6, and 5 °C, respectively. The homogeneous solution was first held for 30 min at Θ + 10 °C for homogeneity and then cooled step by step from Θ + 10 °C to Θ − 20 °C at a cooling rates of 1 K/min, and held for 1 min at each centidegree followed by a fluorescence spectrum scan. Figure 1b shows that PS chains went through different states when subjected a gradient drop of temperature in decalin: a smooth change of conformation

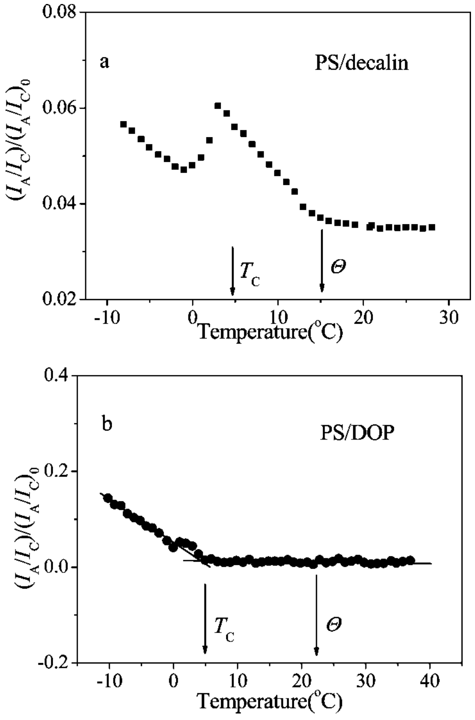

**Figure 2.** Plot of $(I_A/I_C)/(I_A/I_C)_0$ versus $T$ in (a) decalin and (b) DOP. The experiment details are the same as in Figure 1.

with temperatures above the Θ temperature, an accelerated arising of NET efficiency below Θ. We also found that similar slope arising of $(I_A/I_C)/(I_A/I_C)_0$ happened in cyclohexene at Θ temperature, with decreasing temperature. These results confirmed that NET is very sensitive in characterizing chains approach around Θ.[22] According to the work by Melnichenko et al.,[14] there is no reduction of $R_g$ at the critical temperature of phase demixing $T_C$ as compared to $R_g$ in the Θ region, which indicates that the deterioration of the solvent quality leads to the formation of distinct microdomains, representing undisturbed, strongly interpenetrating polymer coils. So the increasing of $(I_A/I_C)/(I_A/I_C)_0$ in cyclohexane and decalin (Figure 1b) at the temperature range of $T_C < T < \Theta$ did not mean contraction and collapse of polymer chains but indicated association of multichains and the interpenetration of polymer coils[14,21]

In the PS/DOP solution, some different phenomena in chains association can be observed with decreasing temperature, as shown in Figure 1c. First, the relative fluorescent intensity keeps unchanged, as the temperature decreasing from above to below Θ (22 °C), indicating little increase in interchain approaching, consequently no formation of distinct microdomains and overlapping of polymer coils. As the temperature decreased to about 5 °C, the relative fluorescent intensities turned to increase quickly. This turning point is 17 °C below the reported Θ temperature for PS/DOP.[26] At this temperature, the solution became cloudy due to aggregation of the separated coils. We assumed that separated chains started to contact and aggregate at the temperature well below the Θ point in the middle-sized solvent, while interchain association was observed at the points immediately after Θ in the small-sized solvents. This argument will be confirmed by the reheating measurement described in later sections.

From Figure 2a, four different regimes can be found which are in good agreement with the prediction of the blob model proposed by de Gennes et al.[1,2,27] Above the Θ temperature, values of $(I_A/I_C)/(I_A/I_C)_0$ rise slightly with decreasing temperature as a result of the small contraction of expanded blobs in a good solvent. Below the Θ temperature, values of $(I_A/I_C)/(I_A/I_C)_0$

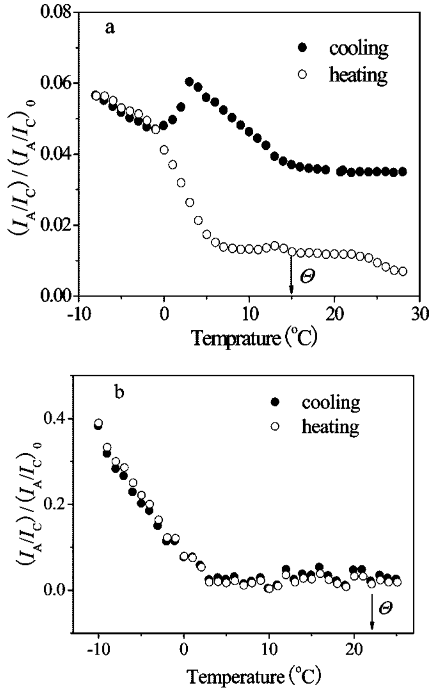

**Figure 3.** Plot of $(I_A/I_C)/(I_A/I_C)_0$ versus temperature: (a)PS in decalin; (b) PS in DOP. The cooling began immediately after holding for 30 min at 30 °C with a cooling rate of 1 K/min. After cooling, the sample was immediately heated with a heating rate of 1 K/min. The same experiments were performed with a solution that contained the same quantity of polymer and fluorescent molecules as in the above experiment without their being bonded together. The results are marked as $(I_A/I_C)_0$. Each point in the curve is the ratio of the relative emission intensity of acceptor to donor $(I_A/I_C)/(I_A/I_C)_0$ at the corresponding temperature.

increase continuously with decreasing temperature, which suggests association and contact of blobs in different chains. An abrupt reduction of the relative emission intensity can be observed at the further cooling, which indicates the onset of phase separation. The sharp decrease of viscosity at a similar temperature is also observed by rheological measurements, which are detailed below. However, phase separation in semidilute solutions are complicated and affected by association of the collapsed globules, compared with chains in dilute solutions. A continuous increase of the relative emission intensity after phase separation is shown in Figure 2a, owing to the further contraction of the entangled globules in the poor solvent. The Figure 2b shows the changes of $(I_A/I_C)/(I_A/I_C)_0$ with temperatures in a PS/DOP solution. One can see the differences between PS/DOP and PS/decalin in chain conformations changes with decreasing temperature: little contact of the coils until a cloud point at the temperature well below the reported Θ. And further cooling resulted in the increase in $(I_A/I_C)/(I_A/I_C)_0$. We argued that these chain associations are due to aggregation of single chains with less coil interpenetration. A proton solid state NMR study confirmed that little interpenetration existed between the individual chains recovered from the collapsed chains in PS/DOP, will be shown in Figure 5 later.

In Figure 3, after the step cooling process, the solution was immediately heated with a heating rate of 1 K/min, held at each centidegree for 1 min followed by a fluorescence spectrum scan. As shown in Figure 3a, after undergoing a gradient drop of temperature in PS/decalin, an obvious hysterisis is observed in the heating back, which suggests chains do not recover to the original chain states during measurement time. According to the work by Lee et al., swelling of globules in normal solvent is a two-step process: fast swelling and slow disentanglement.[28] Chu et al.[29] reported that when compared with the coil-to-globule transition time of $10^2$ s, the recovery time from the collapsed globule ($R_h \sim 20$ nm) to the coil ($R_h \sim 63$ nm) take a somewhat longer time ($\sim 10^3$ s) to reach the final 10% of the Θ coil value. However, Figure 3b shows that the relative intensity of acceptor to donor in the heating back has a superposition with cooling process in a solution of PS/DOP, which indicates aggregated and collapsed chains in DOP recovered to the original state easily with the increasing temperature. We argued that the quick recovery of the aggregated chains upon heating is due to the lack of entanglement between collapsed chains in PS/DOP semidilute solution around its Θ temperature.

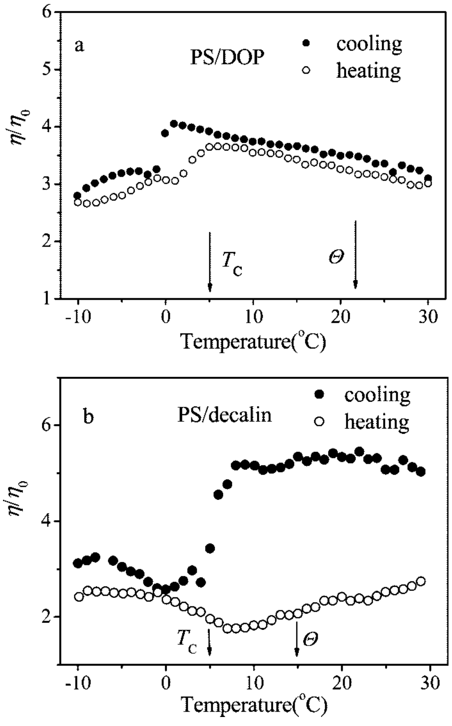

**Figure 4.** Plot of relative viscosity $\eta/\eta_0$ versus $T$. The temperature program is similar to Figure 3.

To compare with the NET results, rheology was used to characterize the viscosity change of the same homogeneous solutions mentioned above without attaching fluorescent labels. The viscosity of a polymer solution represents the mutual impact of solvent and polymer chains on a macroscopic scale.[30] The temperature program is similar to Figure 3. The solution was held at each centidegree for 1 min followed by a viscosity measurement. Figure 4 shows plots of relative viscosity versus temperature in PS/DOP (a) and in PS/decalin (b), respectively. Each point in the curve is the relative viscosity of the solution to the pure solvent versus temperature. In Figure 4, the curves all have a sudden fall of relative viscosity in the cooling process, suggesting phase separation.[21] And these phase demixing temperature consistent with the NET results, both in decalin and DOP. It is well-known that flow may induce phase separation during the measurement. Rangel-Nafaile et al. reported shifts in the cloud points of high-molecular weight polystyrene solutions in DOP of the order of 20 °C as a function of flow rate.[31] However, for low shear rate, the effect seems to be strongly reduced.[32] In Figure 4, a sharp break down during cooling also suggests that the flow induced phase separation could be eliminated.[32] Only small changes near the Θ temperature were observed, due to rheology is not as sensitive as NET in characterizing the contraction and association of chain blobs near Θ, but an abrupt reduction of relative viscosity near $T_C$ (well below the Θ temperature) was observed. This change in the viscosity/temperature diagram is in fairly good agreement with the NET results, and correlate to the phase separation. In

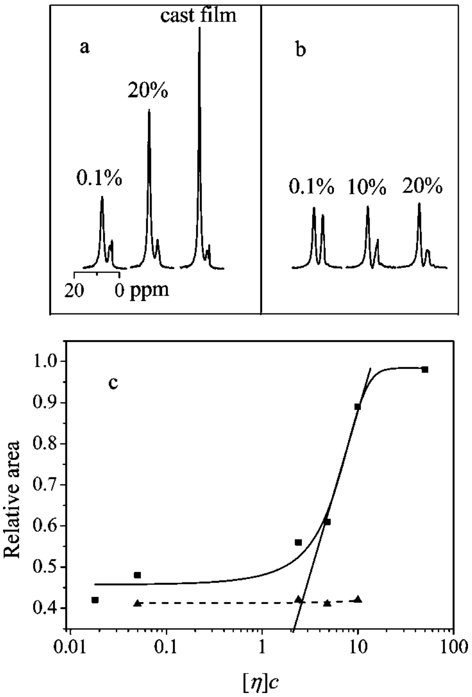

**Figure 5.** Solid state $^1$H NMR spectra of isotopic blends of PS-H and PS-D: (a) recorded from a cast film and freeze-dried from PS/benzene; (b) freeze-extracted from PS/DOP. The concentration of the original solution is indicated near each spectrum. The sample weight in each experiment was used to normalize the signal intensity. (c) Integration of the peak of aromatic ring at 7 ppm verse intrinsic viscosity multipled concentration. The intensity has been renormalized by sample weight. Key: (■) for PS-H/PS-D freeze-dried from benzene; (▲) for PS-H/PS-D freeze-extracted from DOP.

the reheating process, the changes in relative viscosity below the Θ temperature are different for PS in DOP and in decalin. Upon heating, the aggregated single chains could dissociate easily, so that the value of the relative viscosity have superpositions with those in cooling process in PS/DOP. However, in the time scale of this experiment the relative viscosity values in PS/decalin did not recovered when the aggregated coils were heated back due to the longer process of disentanglement. These phenomena shown in Figure 4 are in good agreement with the NET results shown in Figure 3.

At the phenomenological level, liquid solvents for polymers are divided into three classes, namely poor, theta (Θ) and good solvents.[33] The pairwise attractive and repulsive interactions compensate at the Θ temperature, which is defined as the upper critical solution temperature (UCST) for a polymer with infinite molecular weight, $M_w = \infty$. At $T = \Theta$, the radius of gyration $R_g$ of polymer chains is unperturbed by excluded volume effects and is also independent of the long-range critical concentration fluctuations. In the good solvent domain, $T > \Theta$, repulsive forces between the segments (excluded volume effects) work to expand $R_g$ above the unperturbed dimensions exhibited at $T = \Theta$. As $\phi$ increases beyond the overlap concentration $\phi^*$, where the chains start to interpenetrate, excluded effects gradually diminish with concentration at sufficiently high values of $\phi$ (i.e., in the "concentrated regime") and the unperturbed dimensions should be restored even in good solvent domain. In the poor solvent region, $T < \Theta$, the chains aggregate and collapse to globular state.[1] On the basis of our NET and rheological measurement, we proposed that the molecular size is important when chains associate below Θ. Now, let us discuss why the polymer in DOP form aggregated single chains with low level of interpenetration below Θ. Picarra and Martinho showed that in the phase separation of a thin-layer dilute polymer solution on surface, the collision would not be effective as long as the collision (or contact) time ($\tau_c$) is shorter than the time ($\tau_e$) needed to establish a permanent chain entanglement between two approaching aggregates.[34,35] Wu et al. inserted more hydrophobic comonomers into a thermally sensitive chain backbone and took the viscoelastic consideration to successfully explain the formation of mesoglobule which behaves like a tiny nonadhesive "glass" ball.[36] In the present case, DOP is a fairly large molecule compared with a repeat unit of PS. As compared to PS/decalin, the larger solvent molecular size and higher viscosity of the PS/DOP solution prevent the collision between PS chains. As a result, the collision time ($\tau_c$) is too long to establish enough contact between chains. Under the time scale of the cooling experiment, these single chains aggregated together with little interchain overlapping.

In order to confirm the single and multichain association of PS in different solvent, the polymer glasses recovered from solutions were investigated by a new strategy using dipolar filter $^1$H solid-state NMR under fast magic angle spinning. 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.[1] The MAS at about 25 kHz induces crucial changes in spin dynamics for organic solids by eliminating the majority of $^1$H$-$$^1$H and $^1$H$-$$^{13}$C dipolar couplings. If the deuterated PS (PS-D) chains were blended with PS-H, the so-called "deuterium induced $^1$H 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. Faster spinning may eliminate the strong chemical anisotropy for the detected species. A dipolar filter pulse sequence together with fast magic angle spinning were 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 an isotopic blends of PS glasses. When the protons are in close proximities less than 0.5 nm, the $^1$H$-$$^1$H dipolar-dipolar interaction was very strong. When the length scale of the distances is larger than 1 nm, the dipolar interaction signals were dramatically reduced in intensity. Parts a and b of Figure 5 show the concentration dependence of $^1$H solid state NMR spectra of PS isotopic blends freeze-dried from benzene solution (small-sized solvent, easier to remove from solution than decalin) and from DOP respectively. In Figure 5a, the peaks of aromatic ring protons at 7 ppm increase in intensity with an increase of the prepared concentrations. On the contrary, the 1.5 ppm peak of protons from the main chain changes in intensity slightly with concentrations. A glassy film cast from a solution consists of the isotropic mixture in benzene shows the strongest $^1$H NMR signal at 7 ppm and is regarded as fully interpenetrated sample. Figure 5b shows the NMR spectra for PS recovered from DOP. The intensity of the aromatic peak are low and keep almost constant independently on the prepared solutions. Figure 5c illustrated the integration of the peaks of aromatic protons versus $[\eta]c$. One can see that the intensity changed slowly with concentration in the semidilute region but increased dramatically above 4.8 ($[\eta]c$). Our $^1$H solid state NMR results clearly indicate that: the original state of the chains in solution could be partly restored by freeze-drying, which was according to the results reported by Morawetz et al.[23,25] It is worth noting that the NMR intensities keeps almost constant for the PS glasses recovered from DOP in spite the prepared concentrations, and the intensity level of PS recovered from a 20 wt % solution in DOP is as low as that from a 0.1 wt % solution in benzene. These results strongly support our argument that PS chains are in less overlapped state in DOP, and they became aggregated single chains after the temperature changed from the above to below the Θ temperature.

From the experiments and results above, we found that the chains comformation in solvents with various molecular sizes are different even at the same concentraion region. Polymer freeze-extrating from a solution in larger molecular size has low level of chain interpenetration and larger intersegmental distances on a short length scale of 0.5 nm. Since the van der Waals attractive interaction forces for nonpolar chains work within this length, the local segmental mobility must be increased for chains with the controlled segmental proximity. This exactly explains why polymers prepared from middle-sized solvents are easier to form highly ordered $3_1$ helix and to crystallize under annealing.[15−19] This interchain proximity also showed an important effect on the structural relaxation near the glass transition.[37]

## Conclusion

NET and rheology studies showed that the polystyrene chains in semidilute solution of middle-sized solvent (DOP) followed single chain aggregation as the temperature decreasing from above to below $\Theta$ temperature, while in the same concentration of normal small-sized solvent (decalin or cyclohexene) followed multichain association and collapse. The difference of the hysteresis in the reheating process is consistent with the different collapse process. These experiments were performed just around $\Theta$ temperature and we can observe clearly the single or multichain association by NET. And polymer chains freeze-extracted from solutions in middle-sized solvents may supply an easier way to get single chain particles in the use of studying polymer crystallization, protein folding, and DNA packing.

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