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Detection of Interchain Proximity and Segmental Motion of Polymer Glass

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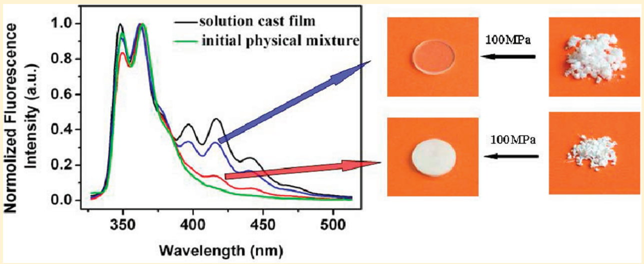
ABSTRACT: We used fluorescence nonradiative energy transfer (NRET) to detect the interchain distances *r* at the overlapping regions of polymer chains. Freeze-dried polystyrene (PS) is found to have an increased *r* value and thus a reduced chain packing density, which shows an increased segmental mobility under uniaxial compression. We clarify that it is the interchain coupling that restricts the chain motion in a glassy oligomer in which chain entanglement is absent.



INTRODUCTION

It has been known that the chain molecules are copiously overlapped and intertwined together. The interchain coupling between the overlapping chains provides topological constrains on segments and limits their motions. Consequently, the manufacturing of thermoplastics traditionally involves melt processing at temperatures well above the glass transition temperature (T_g) to enable molding under pressure into desired forms. Ngai points out that the intermolecular coupling at the overlapping regions has been particularly important in considering the local segmental motion and controlling the final mechanical properties of the materials.[1] Within a range of distances (r) of several angstroms to 2 nm, the interaction between chains is governed by van der Waals attraction that dies off as $1/r^6$ at larger separation or by hydrogen bonds which are slightly longer than a covalent bond. Investigation of intermolecular proximity on short length scales is especially promising for understanding the local motion of chain segments, supermolecular assembly, and biomimetics.[1−4] Figure 1a shows a typical chain of polystyrene copiously intertwined with other chains. Assuming that there are ~1000 styrene units covalently bonded together to give an overall molecular weight of $M_n \sim 10^5$, the chain pervades a volume of $\sim 10^6$ Å^3, whereas the molecule itself occupies a volume of only $\sim 10^4$ Å^3. It follows that the space penetrated by the molecules is shared with hundreds of other chains, all of which are copiously intertwined together. Thus, a typical segment can in principle interact with each of 1000 segments of the sample chain and also with hundreds of other chains, each of which contains another 1000 segments! This illustrates the difficulty of calculating that chain trajectory, which is truly a many-body problem that would be hard to address, even with the massive computing power which is available today. The intermolecular coupling on short scales is still a challenging problem that remains in considering the dynamics of local segmental relaxation.[2] Here we simplify this question as the detection experimentally of the distances r between chain segments at the overlapping regions, as shown in Figure 1b,c. For polymer glasses, the major segmental interactions within short length range of 0.3−2 nm involves van der Waals attraction forces, hydrogen bonding, etc.[3,4] Controlling interchain proximity on short range of scales will be able to control the local dynamics and chain motion of the polymer.[1−4] Figure 1d shows the topological entanglement, which appears when the polymer molecule is larger than the critical entanglement molecular weight (M_c).

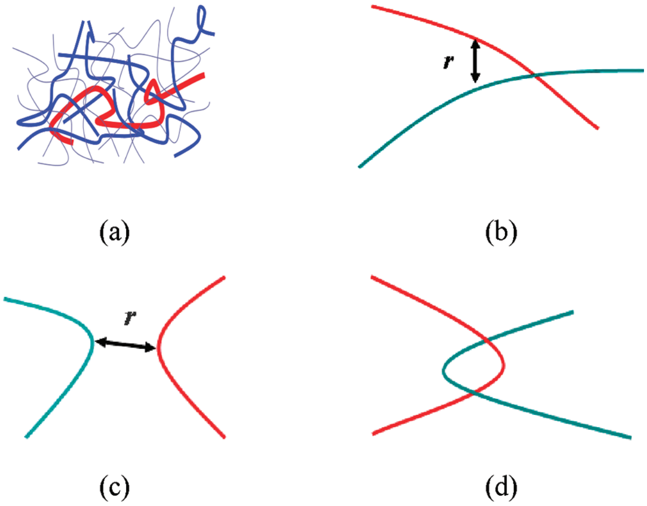


Figure 1. Schematic diagrams of (a) a PS chain (red line) coupled with numerous others, (b, c) proposed segmental distance *r* of neighboring chains at the overlapping regions, and (d) topological entanglement.[5]

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Table 1. Characterization of Polystyrenes Used in This Study

polymer	M_n (g/mol)	M_w/M_n	mol % of label
PS-An	2.14×10^5	1.03	0.272
PS-Cz	2.14×10^5	1.03	0.425
PS-An1	1300	1.63	0.102
PS-Cz1	1400	1.61	0.370

Polymer glasses can be in different states of overlap (shown in Figure 1b−d) of chains by special "manipulation" methods, such as freeze-drying solutions and controlled synthesis.[6−8] However, the manipulation and detection of intermolecular proximity on short length scales and the completely understanding of its effect on chain motion are not yet available.[1,8,9] There has been a great deal of interest in detecting chain entanglement and monitoring polymer interdiffusion with fluorescence nonradiative energy transfer (NRET), which is also called Forster resonance energy transfer or fluorescence resonance energy transfer (FRET).[10−16] In the present work we report that the interchain distances ranging from 0.5 to 3 nm can be detected by the use of NRET techniques.[15] We observed that controlling chain proximity for polystyrene glass gives a rise to an accompanying change in local segmental motion at temperatures well below the bulk T_g.

We used a fluorescent probe to investigate the extent to which macromolecular chains are coupled with each other as in the models shown in Figure 1b,c in freeze-dried polymers and in bulk polymer. This method is a powerful and efficient technique that uses the response of a probe molecule to provide information on the microenvironment at the molecular level.[10−16] We employed two types of PS molecules as our probes: PS-Cz, which has a carbazolyl (Cz) moiety, and PS-An, which has an anthryl (An) moiety. The fraction of each moiety of PS-Cz and PS-An was almost 1 unit per polymer molecule. We prepared freeze-dried powders from the PS-Cz, the PS-An, and a mixture of the two. When the PS films prepared from the mixture of the two PSs were excited at 294 nm, which is preferentially absorbed by Cz rather than An, the Cz fluorescence was found to be quenched dramatically while the An fluorescence increased significantly. This effect is due to the proximity of the Cz to the An, which permits the transfer of excitation energy between them. The average distance between Cz and An can be calculated using the Förster mechanism.[17] By measuring the energy transfer efficiency, we were able to determine the average distance between the Cz and the An in the powders prepared using a mixture of the two molecules. If the PS chains are coupled with one another, this average distance should be short. Alternatively, if the distance between the probe molecules is much larger than the range at which van der Waals type forces act, this would imply that the segments of the neighboring chains are not significantly coupled.

EXPERIMENTAL SECTION

Materials. PS samples with two molecular weights were studied. Table 1 summarizes their properties. The samples with a number-average molecule weight of 2.14×10^5 g/mol were bought from Polymer Source. These 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 elsewhere.[18] The oligomers were prepared by the copolymerization of styrene with 2-(*N*-carbazolyl)ethyl methacrylate and 9-anthrylmethyl methacrylate in tetrahydrofuran(THF) at 60 °C using benzyl chloride as initiator. More details about the synthesis of the labeled polymer could be found elsewhere.[11] 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. THF was commercially available and purified by filtration before use. The concentrations of chromophores in the labeled polymers were measured with a Perkin-Elmer Lambda 35 UV−vis spectrophotometer. The molecular weights of the oligomer were determined by gel permeation chromatography (GPC).

NRET Measurements. The freeze-dried samples were prepared by dissolving equal weights of PS-An and PS-Cz in benzene of the desired amount at room temperature to get a homogeneous solution. Then the solution was dropped into a large amount of liquid nitrogen with stirring and frozen in a fraction of a second. The freeze-dried samples were carried out at −35 °C for 2 weeks under vacuum.

Three types of films were solution-casted on to silicon wafers from solutions of THF with PS concentration of 4.0% (w/w) separately: a PS-Cz film made with a mixture of 50% (w/w) PS-Cz and 50% (w/w) PS, a PS-An film made with a mixture of 50% (w/w) PS-An and 50% (w/w) PS, and a PS-blend film made with a mixture of 50% (w/w) PS-Cz and 50% (w/w) PS-An. The films were dried under vacuum for more than 3 days at room temperature. The approximate film thickness was 2 μm.

Next, we measured the Cz fluorescence intensities of all three film types by exciting them at a wavelength readily absorbed by Cz, but not by An. Finally, by comparing the intensities of the Cz fluorescence, we were able to examine whether the Cz fluorescence is quenched in a PS-blend film. In these experiments, the film thicknesses and anthry concentrations are low enough that radiative energy-transfer effects are negligible.[19] The reflectance fluorescence was determined with a Jasco FP6500 fluorometer at excited wavelength of 294 nm.

NMR Measurements. ^1H solid-state NMR 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 ^1H chemical shifts were referenced to external TMS. More details of NMR experiments could be found elsewhere.[7]

Cold-Compression Test. PS-Cz powder and PS-An powder had been recovered by freeze-drying concentrated solutions. Then equal weights of them were physically mixed. The mixture were processed by a compression molding at 20 °C using a pressure of 100 MPa for 5 h. During the nonuniformly compression process, the polymer chains are subjected to shearing.[20]

RESULTS AND DISCUSSION

Fluorescence Behavior of PS-Cz, PS-An, and PS-Blend. Figure 2 shows the fluorescence spectra of solution-cast films from PS-Cz, PS-An, and PS-blend (1:1 ratio in weight) solutions. In order to get the same chromophores concentration, we diluted the chromophores concentration in PS-Cz film and PS-An film by mixing 50% (w/w) labeled PS and 50% (w/w) unlabeled PS. All the spectra shown in Figure 2 were recorded with an excitation wavelength of 294 nm. The excitation wavelength was chosen because it was the peak wavelength for Cz absorption but was not readily absorbed by An. We expected the An spectrum, therefore, to be visible but lower in intensity. From the combined results, it was clear that the fluorescence peaks for both Cz (which occurs at 348 and 362 nm) and for An (at 392, 414, and 440 nm) are in fact readily identifiable. As expected, the intensity of the fluorescence spectrum for PS-An was quite low.

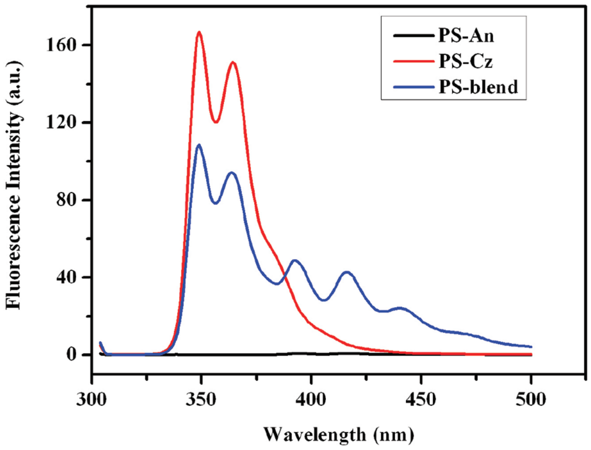

Figure 2. Fluorescence spectra recorded from solution-cast films from PS-Cz, PS-An, and PS-blend (1:1 ratio in weight) on silica wavers. The excitation wavelength was 294 nm in each case.

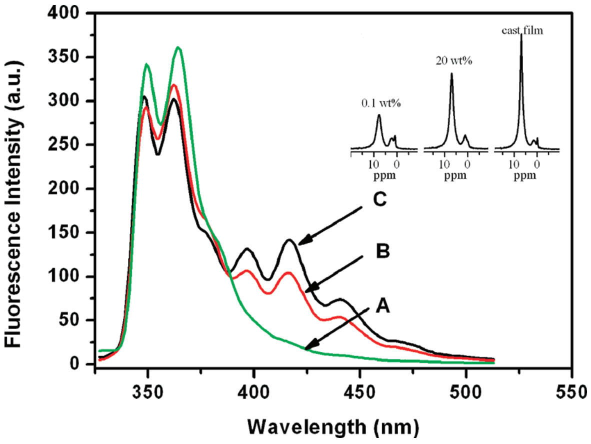

Figure 3. Reflectance fluorescence spectra for polymer PS-blend glasses recovered by freeze-drying solution of PS-Cz and PS-An (1:1 ratio in weight) from (A) 0.1 wt % benzene, (B) 20 wt % benzene, and (C) a cast film. Samples were irradiated at 294 nm, and the changes in the nonradiative energy transfer were characterized by the relative emission intensity of the carbazole label at 365 nm to the anthracene label at 414 nm. Inset: solid-state ^{1}H NMR spectra of isotopic blends of PS recovered by freeze-drying PS/benzene solutions. The original concentration for each solution for freeze-drying is indicated at each peak of the spectra.[7]

It was clear that the Cz fluorescence in the PS blend mix spectrum in Figure 2 is weaker than that in the spectrum from the pure PS-Cz film of the same thickness. This indicated that the Cz fluorescence was significantly quenched in the ultrathin films created from the mixture of PS-Cz and PS-An. In contrast, the An fluorescence increased in the film with the mixed composition. We contend that these changes in the spectra are due to a singlet energy transfer from the Cz to the An in the PS-blend film. The relative emission intensity of donor (Cz) and acceptor (An) when the system was irradiated in the donor absorption band may be used as a "spectroscopic ruler" to estimate the separation (r) of these two moieties.[21]

Interchain Segment Separation in Freeze-Dried Polymers. The fluorescence spectra for the blend of PS chains labeled with Cz and An have been used to measure interchain distances over 0.2−3 nm.[10] In Figure 3, the spectrum C is for the cast film of the labeled blend. In this blend, all chains are in close proximity so that the excitation energy of the donor molecules at 365 nm could partially transfer to the acceptor groups in proximity (within a distance of ∼3 nm) by NRET, which resulted in a new emission peak at 414 nm. For the PS glass recovered from very dilute solution the peak at 414 nm was very weak in intensity as shown in Figure 3, spectrum A, indicating that NRET efficiency between the labeled chains is very low.

In the previous report,[18] the extent of flexible chain interpenetration as a function of solution concentration using the following approach: Two portions of polymer labeled by donor and acceptor were dissolved in benzene and frozen within a fraction of a second. It was assumed that the extent of chain overlapping remained unchanged during the rapid freezing so that after removal of the frozen benzene by sublimation, the material should retain a memory of the chain interpenetration that had existed in the original solution. Increasing chain overlapping was then expected to increase nonradiative energy transfer by the Förster mechanism, leading to a decreasing ratio of emission intensity from the carbazole and anthracene, $I_{\mathrm{Cz}}/I_{\mathrm{An}}$, when the sample was irradiated in the carbazole absorption band. The data agreed with this expectation and the transition from a low to high energy transfer efficiency seemed to correspond to the concentrations of the original solution from which the PS samples were prepared. The fluorescence spectra indicates that the interchain distance is rather large ($r > 3$ nm) for samples prepared from very dilute solution, implying that the interchain van der Waals force should be very weak in the freeze-dried dilute solutions.

The concentration dependence of r on the original concentration for freeze-dried polymer can be verified by ^{1}H solid-state NMR studies. Solid-sate NMR experiment based on the dipole−dipole interaction reflects interchain coupling occurring over short distances about 0.2−1 nm.[7,22] We recently developed a new strategy applied a dipolar filter pulse sequence together with fast magic angle spinning to suppress line broadening induced by the strong dipolar interaction to characterize the chain proximity at a distance within 1 nm in an isotopic blends of polymer glasses.[7] When the deuterated PS (PS-D) chain is in a close proximity to the hydrogenous PS (PS-H) within 0.5 nm, a unique ^{1}H signal was selectively isolated. 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. The solid-state ^{1}H NMR spectra of isotopic blends of PS freeze-dried from benzene are shown in Figure 3, inset. One can see that the signal from isolated aromatic protons (7 ppm) is very strong for the cast film and for that recovered from concentrated (20 wt %) solution, indicating that the chains are in closer proximity (less than 0.5 nm) in these PS glasses. On the contrary, the aromatic peak is very weak for the PS glass recovered from very dilute PS/benzene (0.1 wt %), indicating that the chains are isolated with each other. The NMR results are in good coincident with NRET experiment shown in Figure 3.

Molecular Weight Effect on Fluorescence Spectroscopic and NMR Measurements. Entanglement is an important factor that influences the physical properties of polymers. The investigation of polymer entanglements is very important not only for fundamental research but also for industrial applications of polymer materials. In several publications, the fluorescent probe was used to investigate the extent to which macromolecules are entangled in polymer bulk, freeze-dried polymers, and ultrathin films.[10,11,16] By measuring the energy transfer efficiency, the

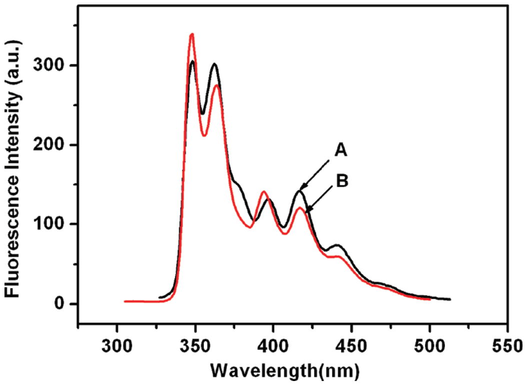

Figure 4. Reflectance fluorescence spectra for solution-cast film of polymer PS blends of PS-Cz and PS-An (1:1 ratio in weight). Spectrum A from PS-blend with M_n = 2.14 × 10^5 g/mol; spectrum B from PS-blend with M_n = 1.3× 10^3 g/mol.

average distance between the Cz and the An in those samples were detected. If the polymer chains are entangled with one another, this average distance should be short. Alternatively, if the distance between the probe molecules is much larger than the radii of gyration for these molecules, this would imply that the polymer molecules are not significantly entangled. In our experiments, the interchain distances at the overlapping regions for polymers with various molecular weights were investigated using NRET and NMR methods. It is well accepted that there is critical molecular weight (M_c) for chain entanglement, above which the chains are entangled together. For PS, this critical M_c is about 3 × 10^4 g/mol. The PS samples used in Figure 4 have molecular weight of 2.14 × 10^5 and 1.3× 10^3 g/mol, respectively. It is confirmed by viscoelastic study that PS with M_n < 30 000 g/mol show no rubber plateau in its diagram, indicating that it is entanglement free.

Both fluorescence spectras in Figure 4 show significant NRET efficiency, indicating that the interchain coupling is in a high level for both two samples. Although there are no chain entanglements in the oligomer, obviously interchain overlapping do exist.

The interchain distances on shorter scales for PS with various molecular weights can also be characterized by proton solid state NMR. The M_c of polystyrene is about 3 × 10^4 g/mol; we prepared three solution-cast films of PS with molecular weights higher and lower than 3 × 10^4 g/mol. Then we use the above-mentioned ^{1}H solid-state NMR strategy to characterize the chain proximity of these PS films. We found that the PS films were very fragile when the molecular weight was below M_c. In Figure 5, the ^{1}H dipolar filtered NMR signal intensities of all these three samples were very strong, indicating that large amounts of chain overlapping within 1 nm existed even when the molecular weight was lower than the M_c. This kind of close contacts could form van der Waals interactions. However, these low molecular weight polymer films with poor mechanical strength will not show rubbery plateau; thus we should not call this kind of chain contacts as "entanglements".

Overlapping Effect on Segmental Motion. We investigated the molecular motion and glass transition dynamics for freeze-dried polymers with different interchain segment distances. The PS-Cz and PS-An glasses were prepared by freeze-drying concentrated solutions in benzene. Then the freeze-dried PS-Cz glass was physically mixed with PS-An glass. A cold-compression test was performed under 100 MPa in a commercial compressing-mold at 20 and 120 °C, respectively. Their reflectance fluorescence spectra were recorded and are shown in Figure 6.

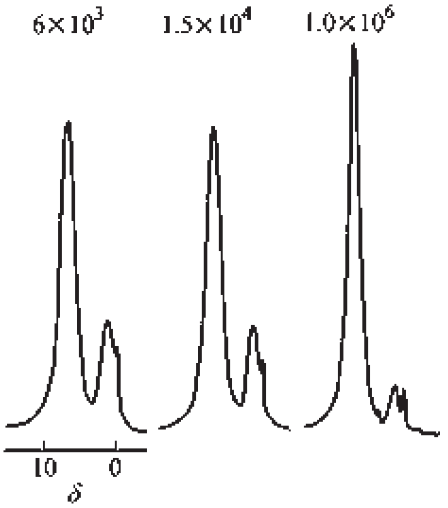

Figure 5. Molecular weight dependence of ^{1}H dipolar filtered NMR spectra of 50/50 PS-H/PS-D blends at 25 kHz spinning frequency. The spectra are for the solution-cast film of oilgomers with M_n of 1.3 × 10^3 and 1.5 × 10^4 g/mol and for polymers with M_n of 1.0 × 10^6 g/mol.

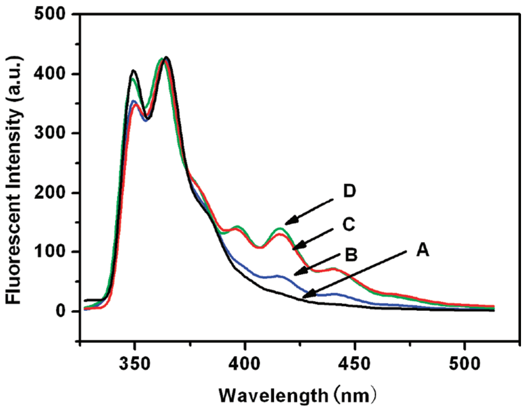

Figure 6. Reflectance fluorescence spectra for a physical mixture of PS-Cz powder and PS-An powder which had been recovered by freeze-drying concentrated solutions (20 wt %), respectively: (A) the initial physical mixture; (B) the mixture after compression at 20 °C for 5 h under 100 MPa; (C) the mixture after compression at 120 °C for 5 h under 100 MPa; (D) the melting cast film of PS-blend.

The reflectance fluorescence spectra B in Figure 6 show lower NRET efficiency for the initial mixture of PS-Cz and PS-An powdered glasses freeze-dried from concentrated solutions after being compressed at 20 °C for 5 h under 100 MPa. After compression at 120 °C, which is above the glass transition temperature of PS glass (T_g = 105 °C), one can see the significant increase in the band at 414 nm as shown in Figure 6C, indicating the approaching of PS-Cz and PS-An chains. The interchain distance is nearly the same as the melting cast film of PS-Cz and PS-An blend. These experimental results indicate that the PS chains from concentrated solution are heavily interchain coupled. They can hardly move to approach each other in the glassy state. Only hot-compression at a temperature above T_g could blend the PS chains at molecular levels.

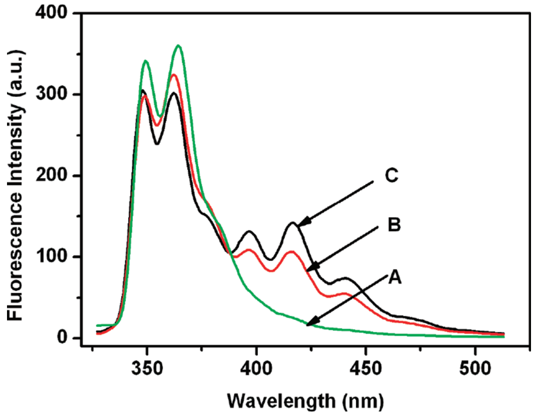

Figure 7. Reflectance fluorescence spectra for mixture of PS-Cz and PS-An glasses recovered by freeze-drying concentrated solutions (0.1 wt %): (A) the initial physical mixture; (B) compressed mixture at 20 °C; (C) solution-cast film.

(a) $M_n = 2 \times 10^5$ g/mol ($r > 1$ nm) (b) $M_n = 4 \times 10^3$ g/mol ($r > 1$ nm)

(c) $M_n = 2 \times 10^5$ g/mol ($r < 1$ nm) (d) $M_n = 4 \times 10^3$ g/mol ($r < 1$ nm)

Figure 8. Photos of cold-compressed pellets of high molecular weight PS and low molecular weight oligomer: (a, b) from freeze-dried dilute solutions (0.5 wt %); (c, d) the raw powder bulk. The molecular weight is indicated on each photo. The compression is under 100 MPa in a commercial compression mold at room temperature.

Figure 7 illustrates an unexpected result: a fairly strong band at 414 nm appears in the spectrum for the cold-compressed mixture of PS-Cz and PS-An glasses which had been recovered from dilute solutions. The high NRET efficiency is due to the close proximity of the Cz to the An, which permits the transfer of excitation energy between them, clearly indicating the segmental movements during compression at room temperature, which is about 80 °C lower than the calorimetric T_g! The increased segmental mobility for the PS chains with reduced segmental coupling is the major cause of the segmental movements under compressive stress.

The segmental motion of the freeze-dried polymer can be verified by cold compression in a commercial compression mold tool. The photos for cold-compressed PS pellets are shown in Figure 8.

Figure 8a shows a transparent pellet was formed after compressing the freeze-dried PS at room temperature. The rigidity and transparency of this pellet (in Figure 8a) and its accuracy of the form are testimonies that the PS powder once flowed under cold-pressing to take the shape of its container.[20] Figure 8b is for the freeze-dried oligomer. The pellet of (b) is transparent but brittle, due to the lack of chain entanglements. Photos (c) and (d) are for the raw PS and oligomer. They are opaque. In raw bulk materials the strong interchain interaction provides strong restriction for the segmental motion in the glassy state. As expected, it needs hot-pressing at a temperature well above T_g to make the transparent pellets. Although the oligomer sample does not contain entanglements, its segments are still restricted even in local motion. We conclude that it is the short-range interchain coupling that restricts the chain segmental motion in the glassy state.

Recently, a theory of jamming and unjamming transition has been developed to characterize a wide variety of amorphous systems, such as foams, colloidal suspensions, granular media, and molecular glasses from a flowing state to a rigid yet disordered state.[22−25] When a glass is heated, it melts and begins to flow. The application of stress can also make a glass flow; soft glasses, including polymers, yield when subjected to sufficiently large stresses. The equivalence of these two routes to flow is a basic tenet of unjamming transition. In our experiment, the lowering of the interchain coupling by reducing the packing density makes the segmental flow under stress at the test temperature. This shear-induced flow is exactly what is expected within the jamming picture. These experiments provide strong evidence for the merit of the perspective, suggesting that the speculated jammed granular systems under shear may also provide new insight into the behavior of sheared polymer chains. A detailed understanding of the true evidence of the analogy must await confirmation by further studies, which will help us to learn more about the glass transition, one of the most widely studied, yet incompletely understood, phase transition.

■ CONCLUSION

We applied fluorescence nonradiative energy transfer (NRET) and proton solid-state NMR to detect interchain distance r at the overlapping regions on range of scales less than 2 nm. The increase of r in the freeze-dried polymer indicates a reduction of packing density and a reduction in interchain coupling. We clarified that NRET and NMR detected r is mainly due to the segmental distance at the overlapping point, not due to the chain entanglement in an oligomer with molecular weight below M_c. The freeze-dried polymer with lowered packing density can be compressed to transparent pellet at temperatures well below T_g. It is the reduction in packing density which increases the segmental mobility in the glassy state.

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