Probing Chain Interpenetration in Polymer Glasses by ^{1}H Dipolar Filter Solid-State NMR under Fast Magic Angle Spinning

Xiaoliang Wang,[†] Fangfang Tao,[†] Pingchuan Sun,*[,‡] Dongshan Zhou,[†] Zhaoqun Wang,[†] Qiang Gu,[†] Jinlei Hu,[†] and Gi Xue*[,†]

Department of Polymer Science and Engineering, School of Chemistry and Chemical Engineering, State Key Laboratory of Co-ordination Chemistry, Nanjing University, Nanjing 210093, P. R. China, and Key Laboratory of Functional Polymer Materials, Ministry of Education, College of Chemistry, Nankai University, Tianjin 300071, P. R. China

Received January 1, 2007
Revised Manuscript Received May 27, 2007

Introduction. The concept of chain entanglement provides the basis of our current understanding of the flow behavior of polymer melts and solutions.[1,2] The interpenetration process is a very important step for polymer chain condensation from the dilute solution to the aggregation state. Such a condensed multiple chain systems possess a structure where polymer chains form an entangled network, which thus establishes the mechanical property of polymers.[1−3] Information about interpenetration regions would provide significant insight into intermolecular coupling and the dynamics of local segmental relaxation, which issues remain unclear for glassy polymer physics. However, compared to those in solution and in the rubber state, an intriguing question concerning the characterization of the degree of interpenetration below and around the glass transition temperature (T_g) of a polymer has still not been tackled.[4−7] Atomic force microscopy, differential scanning calorimetry, dynamic mechanical thermal analysis, and scattering methods (visible light, X-ray, neutron) are frequently used to investigate chain interpenetration.[8−10] One drawback of these methods is that they yield information on length scales of a few to tens of nanometers; thus, they cannot be used to directly identify the individual structure in the interpenetration regions at a molecular level. Nonradiative energy transfer (NET) fluorescence spectroscopy has been used to observe the memory of the chain interpenetration that had existed in the original solution, and many interesting conclusions have been reported.[11,12] On the other hand, ^{13}C solid-state NMR and small-angle neutron scattering (SANS) studies have cast doubt on the conclusions regarding the memory of the chain interpenetration for the freeze-dried polymer reported by NET.[13−16] Developing new strategies to characterize the chain interpenetration in polymer glasses on a short length scale of 0.5 nm is still a challenge.

Solid-state NMR (SSNMR) spectroscopy is a powerful method for characterizing the structure and dynamics of bulk polymers. In particular, the SSNMR experiment based on the dipole−dipole interaction reflects interactions occurring over distances of 0.5−1.0 nm.[17] Therefore, SSNMR is an ideal technique for probing local information on the chain interpenetration regions at a molecular level. Among various nuclei, ^{13}C SSNMR has been widely applied for its excellent resolution. Intermolecular cross-polarization in a polymer blend in which one of the components is deuterated was used to investigate the intimate mixing of two chains and was successfully used to characterize the miscibility of different polymers with distinguishable chemical shifts.[9,10] However, this method will not work for some polymer blends where the chemical shifts and/or the proton relaxation times of the two components are not well distinguished.[18] Furthermore, compared with the ^{1}H NMR methods, ^{13}C SSNMR requires longer experimental time and larger amounts of sample due to the poor sensitivity arising from the low abundance of ^{13}C. Thus, ^{1}H SSNMR is still an attractive alternative to ^{13}C due to its high sensitivity.[17,19] The strong ^{1}H−^{1}H dipolar interaction, however, masks many other smaller interactions of interest and limits the use of ^{1}H SSNMR. Until now, few NMR methods have been reported to effectively characterize the degree of interpenetration in the polymer glasses.[14−16,20]

In this work, we developed a new strategy to characterize the chain interpenetration in 50/50 hydrogenous polystyrene (PS-H)/deuterated PS (PS-D) blends. In principle, this strategy includes three important steps. First, deuterated and hydrogenated polymers are mixed at a certain ratio, typically 50:50 wt %. In normal hydrogenous chains of polymer glasses, there is always strong ^{1}H−^{1}H dipolar interaction, typically 30−50 kHz, severely broadening the ^{1}H signal. When the deuterated chain interpenetrates with the hydrogenous one within a distance of 0.5 nm,[20] the strong ^{1}H−^{1}H dipolar interaction of the hydrogenous chains will be decreased in the chain interpenetration region. This effect is known as the ^{2}H-induced “^{1}H dipolar dilution” effect. Second, fast MAS (25 kHz) is used to further average out the ^{1}H−^{1}H residual dipolar interaction to less than 25 kHz in the interpenetration regions. Theoretically, MAS can average out all anisotropic interactions that can be described by second-rank tensors, if the rotation frequency exceeds the largest coupling of the spin species considered. However, faster MAS (>40 kHz) is not useful here because it may eliminate the difference of the ^{1}H−^{1}H dipolar interaction between interpenetrated and noninterpenetrated regions. Third, a dipolar filter pulse sequence (Figure 1a) developed by Schmidt-Rohr et al.[21,22] is used to suppress the signals from protons with strong dipolar interactions that are far from the deuterated chain. On the basis of the above three steps, a unique “isolation” of ^{1}H signal was achieved for protons that are sufficiently close to the deuterated chains. This can be used as a sensitive probe to characterize the degree of chain interpenetration in a homopolymer or the miscibility in various polymer blends on a molecular level.

Experimental Section. 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. The sample consists of a mixture of hydrogenated polystyrene (PS-H, Polymer Source Inc., sample P3915-s) and deuterated polystyrene (PS-D, Polymer Source Inc., sample P2404-dPS). Their number-average molecular weights are 112 000 and 103 800, with polydispersity indexes of 1.06 and 1.38, respectively. The residual level of protonation in the PS-D is about 3.5%, as determined by liquid-state ^{1}H NMR (Varian UNITYplus 400 MHz). The intrinsic viscosity of PS-H was 0.544 dL/g, which was determined using an Ubbelohde viscometer at 25 °C.[11,12] Equal weights of the

---

* To whom correspondence should be addressed: Tel +86-25-83593432; Fax +86-25-83317761; e-mail xuegi@nju.edu.cn, spclbh@nankai.edu.cn.
[†] Nanjing University.
[‡] Nankai University.

10.1021/ma0700025 CCC: $37.00

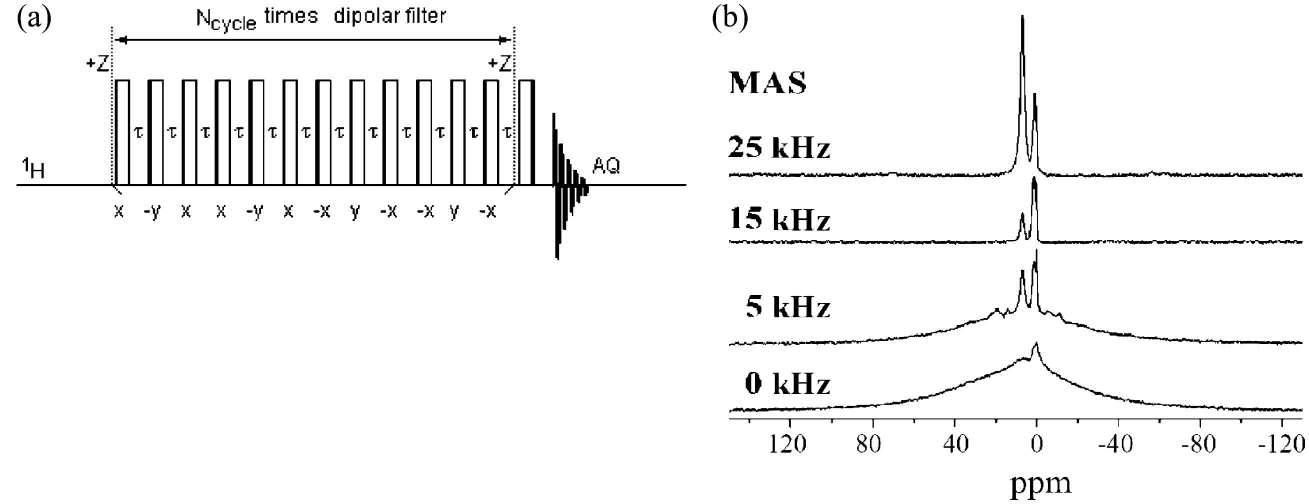

Figure 1. (a) Pulse sequence with a 12-pulse dipolar filter experiment. (b) Spinning frequency dependence of dipolar filtered ^{1}H MAS spectra of the 50/50 PS-H/PS-D blend, freeze-dried from 4.40 g/dL benzene solution, with $N_{cycle} = 8$. The MAS frequency is indicated in the figure. The small narrow peak at 0 Hz MAS is due to the residual aliphatic protons of the PS-D.

two components were dissolved in benzene of the desired amount at room temperature. Then the homogeneous solution was dropped into a large amount of liquid nitrogen with stirring and frozen in a fraction of a second. Freeze-drying of the sample was carried out at −35 °C, which was below the melting point of the solution and was well below the glass transition temperature of polystyrene, typically for 2 weeks. As a comparison, equal weights of PS-D and PS-H were separately dissolved in benzene at a concentration of 0.5 g/dL and frozen in liquid nitrogen. Then two frozen isotopic solutions were poured into liquid nitrogen; finally, the mixture was freeze-dried as mentioned above. This freeze-dried sample was regarded as physically noninterpenetrated. A cast film was prepared from a benzene solution consisting of equal weights of PS-D and PS-H at a total concentration of 5 g/dL. Then the film was further dried under vacuum at 120 °C for 24 h, and this sample was regarded as fully interpenetrated.

Solid-state NMR spectra were recorded 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.

For the ^{1}H dipolar filter experiments (Figure 1a), several cycles (N_{cycle}, typically value 8) of a 12-pulse dipolar filter sequence were used to select the ^{1}H magnetization with a weak ^{1}H−^{1}H dipole−dipole interaction which has relative longer transverse relaxation times than those of the strong ^{1}H−^{1}H dipole−dipole interaction. The 90° pulse width was 1.5 μs, and the interpulse spacing of τ was typically 10 μs, which was carefully adjusted so that the rotor period was not an integer multiple of the filter cycle.[22] A detailed discussion of the relationship between signal intensity and the rotor period is given in the Supporting Information. Recycle delays or intervals between two scans were adjusted to 5 times the ^{1}H T_1 values. The spectra were obtained with 32 scans for each spectrum. It is noteworthy that spectra with high sensitivity and good resolution can be obtained typically only in as little as 3 min, and the signal-to-noise ratio is good about 200 in a 2.5 mm rotor with about 8 mg sample weight. The remaining background signal was separately collected under the same condition without sample. Then the background signal was subtracted from the spectra acquired with a sample to obtain all the spectra data used in the subsequent analysis. The sample weight in each experiment was accurately measured, and the all signal intensities were normalized by the weight of PS-H.

Results and Discussion. It is very common to use deuterated samples in ^{13}C solid-state NMR to study certain interactions between different polymers or different parts of the same polymers,[18] but a deuterated sample is seldom used in ^{1}H SSNMR.[16,20] VanderHart et al. reported pioneering ^{1}H SSNMR work at low MAS spin frequency (2.2 kHz) to determine the intimate mixing of an isotopically enriched blend. They found that the residual proton signal from the aromatic rings of PS-D disappeared when the isotopic PS-D was intimately mixed with PS-H. That experiment succeeded because the ^{1}H−^{1}H dipolar interactions involving those residual protons on PS-D were augmented by the insertion of nearby protons of PS-H to the point that MAS at 2.2 kHz was no longer able to narrow their resonances.[20] Instead of using that slow MAS technique, we herein use fast MAS in combination with a dipolar filter method to probe the protons in the chain interpenetration region. To obtain the most effective content of the deuterated chains in the dipolar filter ^{1}H MAS experiments, we prepared five benzene solution-cast PS-H/PS-D blends with different PS-D content, and it was found that the largest dipolar filtered signal intensity can be achieved in the 50/50 PS-H/PS-D blend (see Supporting Information). Figure 1b shows the spinning frequency dependence of the dipolar filtered ^{1}H MAS spectra of the 50/50 PS-H/PS-D blend freeze-dried from the 4.40 g/dL benzene solution, which is well above c* (critical overlap concentration). With increasing spinning frequency, the peaks are narrowed, and the peak of aromatic ring at 7 ppm and that of the aliphatic protons at 1.5 ppm can be well distinguished. The signal at 7 ppm is isolated (dramatically increased) when the spinning frequency increases up to 25 kHz. Meanwhile, the signal at 1.5 ppm is only slightly increased above 5 kHz MAS. It should be mentioned that the increase of the aromatic signal is not monotonic with increasing MAS frequency, and this can be understood as the recoupling effect of anisotropic interactions at special spinning frequencies. On the other hand, a proper N_{cycle} should be selected to achieve enough signal intensity and desired isolation of the protons in the interpenetration region. An example of the effect of N_{cycle} values on the signal intensities and line shapes can be found in the Supporting Information.

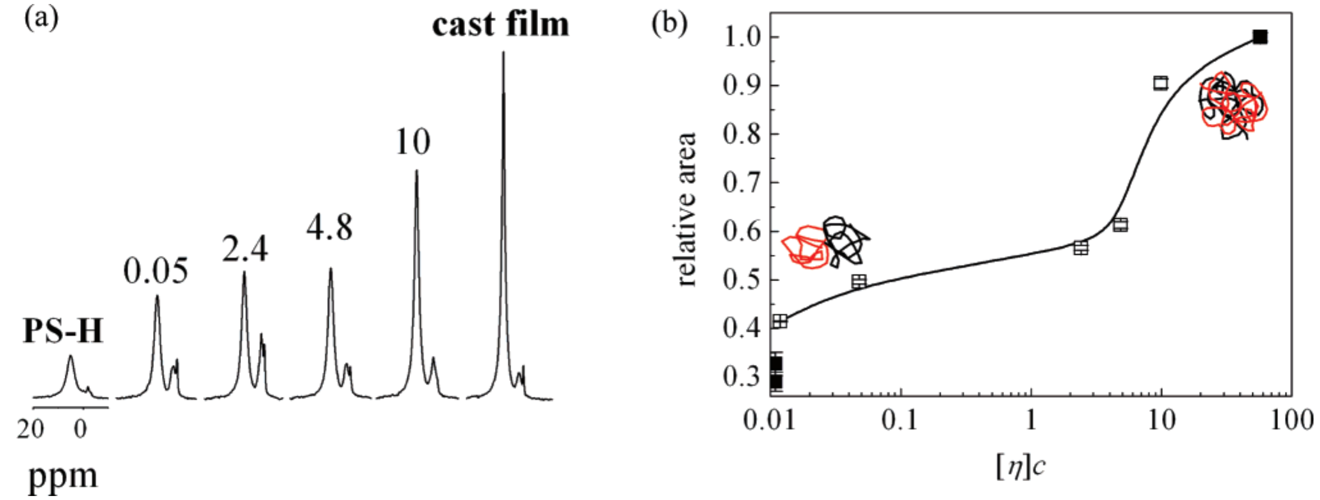

Figure 2. (a) Concentration dependence of ^{1}H dipolar filter MAS spectra of 50/50 PS-H/PS-D blends with dipolar filter ($N_{\text{cycle}} = 8$) at 25 kHz spinning frequency. The spectra are for the pure PS-H, 50/50 PS-H/PS-D blends freeze-dried from 0.05, 2.4, 4.8, and 10 $[\eta]c$ and solution-cast film, respectively. The cast film is regarded as a fully interpenetrated sample. (b) Area of the aromatic ring peak at 7 ppm vs concentration. The intensity of the cast film was taken as 1. The filled black square data corresponds to PS-H, physically noninterpenetrated PS-H/PS-D, and film cast from bottom to top, respectively.

Figure 2 shows the concentration dependence of the dipolar filtered ^{1}H MAS spectra of 50/50 PS-H/PS-D blends freeze-dried from the benzene solutions. The fraction of protons survived after the dipolar filter depends strongly on the degree of chain interpenetration and the strength of the dipolar filter (selection of N_{cycle}) employed. For example, for the physically noninterpenetrated sample, only 1% of the proton signal is retained at $N_{\text{cycle}} = 8$ when compared with the signal without the dipolar filter. While for the fully interpenetrated sample (cast film), about 3% of the proton signal can be retained (see Supporting Information). In Figure 2a, the peaks of the aromatic ring protons at 7 ppm increase in intensity with the increase of the sample concentrations, clearly indicating a gradual increase of the proximity of different aromatic groups on hydrogenous and deuterated PS chains, which results in the enhancement of the "^{1}H dipolar dilution" effect. Since "^{1}H dipolar dilution" resulting from the segmental mixing of a hydrogenous polystyrene chain with deuterated polystyrene chains only occurs within 0.5 nm (the characteristic distance of ^{1}H−^{1}H dipolar interaction), therefore, the isolated signal is a clear evidence of segmental mixing within a distance of 0.5 nm.

In contrast to the aromatic signal, the proton signal from the main chain at 1.5 ppm changes in intensity slightly with the sample concentrations. Using simulations based on the Gaussian correlation model for the experimental spin diffusion data, Karasz et al. found that a correlation length of 0.5−0.6 nm was favor for PS-d5/PS-d3 solution-cast blends.[23] Because of the spatial obstruction of the aromatic groups to the protons of the main chain,[24] the PS-D no longer has the chance to be near the aliphatic protons within the effective distance to induce "^{1}H dipolar dilution" in PS-H/PS-D blends. This result was in good agreement with the work of VanderHart, who found the proton from the aromatic ring of PS was very sensitive to dipole−dipole interaction from surrounding protons while the aliphatic proton was not.[20] A glassy film cast from a solution consists of the 50/50 PS-H/PS-D mixture shows the strongest ^{1}H NMR signal at 7 ppm and is regarded as a fully interpenetrated sample. It is clear that the NMR signal of the protons in close proximity to the deuterated chain (within a distance of 0.5 nm) was selectively isolated under MAS at 25 kHz. This selectively isolated signal in ^{1}H SSNMR can be used as a sensitive probe to characterizing the interchain interpenetration. Previous work using the intermolecular cross-polarization ^{13}C SSNMR technique indicated that the residual intensity from the predeuterated component considerably affects the experimental results.[14,15] However, the presence of a small amount of residual protons does not interfere with the experimental results of the ^{1}H SSNMR technique developed in the current study.[20] This is because the measured contribution of the residual protons of PS-D to the dipolar filtered signal of the cast film at $N_{\text{cycle}} = 8$ is less than 3%. It should be also mentioned that although the experiment at other N_{cycle} close to 8 can still give similar result, the experiment at $N_{\text{cycle}} = 8$ provides the best sensitivity to interpenetration.

Figure 2b shows the integration of the aromatic proton peaks vs $[\eta]c$. The product of intrinsic viscosity and concentration reflects the degree of chain interpenetration in solution.[25] One can see that the intensity of the proton signal increases slowly with the concentration in the semidilute region but dramatically when the concentration is above the critical overlap concentration c^* ($= 4\ [\eta]c$). In the literature there are still competing viewpoints between NET and ^{13}C SSNMR[11,14,15] concerning the transition of chain interpenetration in polymer glasses freeze-dried from dilute regions. Our ^{1}H SSNMR results clearly indicate that, on the one hand, the original state of the chains in solution could be partly retained by freeze drying, which is consistent with the results from NET.[11] On the other hand, chains do overlap in the polymer glasses prepared from solution which is even 10 times diluter than c^*. This chain overlap might be created by the collapse of chains during the freeze-drying process. The partial overlap created during the freeze-drying process was also the reason why the dipolar dephasing of ^{13}C failed to characterize the memory of the chain interpenetration that had existed in the original solution.[14,15] The large surface effect between hydrogenous and deuterated chain coils and the residual protons in the deuterated sample were the other two reasons. The curve obtained from ^{1}H SSNMR increases rapidly when $[\eta]c > 4$, which is similar to the curve of viscosity vs $[\eta]c$ in solution.[25] This suggests that, in a high concentration region, our strategy has a similar sensitivity to the interpenetration of chains in glassy state as the rheology experiment does in solution. Whereas the curve obtained from NET levels off at $[\eta]c > 3$, the difference between the two curves may originate from the technique itself: the SSNMR is sensitive to the local interaction within a range of 0.5 nm,[17] while the NET is sensitive with a range of 2−4 nm.[7,11,12] With the increase of the degree of interpenetration from the dilute range to concentrated range, the interchain interaction increases slowly from dilute region to semidilute region, while sharply from the semidilute region to the concentrated region.[1] The interchain interaction is on the length scale of 0.5 nm, which is suited to the characteristic detection range of SSNMR. The origin of the curve shape of NET was well illustrated elsewhere.[11]

Conclusion. In this work, we developed a new and general strategy to characterize the chain interpenetration in polymer glasses. Our method combines the preparation of the isotopically enriched polymer blends with ^{1}H dipolar filter solid-state NMR under fast magic angle spinning (MAS). This approach selectively isolates the signal of protons in close proximity to the deuterated chains and allows us to efficiently probe the chain interpenetration or miscibility in various polymer blends within a length scale of 0.5 nm. Chain interpenetration and the intimacy of segment mixing in polystyrene isotopic blends of hydrogenous and deuterated chains at different interpenetration degree were successfully and qualitatively characterized. Except for the application in homopolymer glasses, this novel NMR approach can also be expected to be used to elucidate the miscibility and structural relaxation in a variety of polymer blends at scale of 0.5 nm, and our research on these related topics is in progress.

Acknowledgment. We are grateful to the referees for their detailed revisions of the manuscript. We are also grateful to Dr. A.-C. Shi for his critical reading of the manuscript. This work was supported by the National Science Foundation of China (No. 50533020, 90403013, 20504014, 20374031), the Foundation for the Author of National Excellent Doctoral Dissertation of P. R. China (No. 200528), and the Scientific Research Foundation of Graduated School of Nanjing University.

Supporting Information Available: Some detailed information about the 12-pulse dipolar filter NMR experiment for PS-H/PS-D blends. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) de Genes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.

(2) Mark, J.; Ngai, K.; Graessley, W.; Mandelkern, L.; Samulski, E.; Koenig, J.; Wignall, G. D. *Physical Properties of Polymers*, 3rd ed.; Cambridge University Press: New York, 2003.

(3) Liang, T. N.; Zhang, Z. Q.; Li, T.; Yang, X. Z. *Polymer* **2004**, *45*, 1365−1371.

(4) Porter, R. S.; Johnson, J. F. *Chem. Rev.* **1966**, *66*, 1−27.

(5) Rastogi, S.; Lippits, D. R.; Peters, G. W. M.; Graf, R.; Yao, Y. F.; Spiess, H. W. *Nat. Mater.* **2005**, *4*, 635−641.

(6) Lippits, D. R.; Rastogi, S.; Hohne, G. W. H.; Mezari, B.; Magusin, P. *Macromolecules* **2007**, *40*, 1004−1010.

(7) Morawetz, H. *Science* **1988**, *240*, 172−176.

(8) Dinelli, F.; Leggett, G. J.; Shipway, P. H. *Nanotechnology* **2005**, *16*, 675−682.

(9) Koenig, J. K. *Spectroscopy of Polymers*, 2nd ed.; Elsevier: New York, 1999.

(10) Guo, M. M. *Trends Polym. Sci.* **1996**, *4*, 238−244.

(11) Chang, L. P.; Morawetz, H. *Macromolecules* **1987**, *20*, 428−431.

(12) Liu, C. Y.; Morawetz, H. *Macromolecules* **1988**, *21*, 515−518.

(13) Brown, H. R.; Wignall, G. D. *Macromolecules* **1990**, *23*, 683−685.

(14) McGrath, K. J.; Roland, C. M. *Macromolecules* **1992**, *25*, 1366−1367.

(15) McGrath, K. J.; Roland, C. M.; Weiss, R. G. *Macromolecules* **1993**, *26*, 6127−6128.

(16) McGrath, K. J.; Roland, C. M.; Antonietti, M. *Macromolecules* **2000**, *33*, 8354−8360.

(17) Schmidt-Rohr, K.; Spiess, H. W. *Multidimensional Solid-State NMR and Polymers*; Academic Press: San Diego, 1994.

(18) Guo, M.; Zachmann, H. G. *Polymer* **1993**, *34*, 2503−2507.

(19) Schnell, I.; Spiess, H. W. *J. Magn. Reson.* **2001**, *151*, 153−227.

(20) VanderHart, D. L.; Manders, W. F.; Stein, R. S.; Herman, W. *Macromolecules* **1987**, *20*, 1724−1726.

(21) Egger, N.; Schmidtrohr, K.; Blumich, B.; Domke, W. D.; Stapp, B. *J. Appl. Polym. Sci.* **1992**, *44*, 289−295.

(22) Sun, P. C.; Dang, Q. Q.; Li, B. H.; Chen, T. H.; Wang, Y. N.; Lin, H.; Jin, Q. H.; Ding, D. T.; Shi, A. C. *Macromolecules* **2005**, *38*, 5654−5667.

(23) Li, S.; Rice, D. M.; Karasz, F. E. *Macromolecules* **1994**, *27*, 6527−6531.

(24) Mitchell, G. R.; Windle, A. H. *Polymer* **1984**, *25*, 906−920.

(25) Frish, H. L.; Simha, R. *Rheology Theory and Applications*; Academic Press: New York, 1956.

MA0700025