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Quantitative Measurement of Polymer Compositions by NMR Spectroscopy:Targeting Polymers with Marked Difference in Phase Mobility

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ABSTRACT: A novel scheme that combines the cross-polarization (CP) with a single-pulse (SP) experiment is developed to quantitatively analyze compositions of multiphase polymers with marked difference in phase mobility. The CPSP method is able to record both CP and SP spectra in one experiment and avoid excessive long relaxation delay, saving considerable experimental time. The quantification of CP spectrum is done by measuring the enhancement factor of CP with a reciprocity relation, while the quantification of SP is derived directly from the Boltzmann distribution in thermo equilibrium. The relative mole composition obtained from a poly(styrene)−poly(isoprene) diblock copolymer matches well with the known value.

Introduction

Based on the cross-polarization (CP),[1,2] magic angle spinning (MAS),[3,4] and high power dipolar decoupling techniques, solid-state high-resolution ^{13}C NMR spectroscopy has been widely and successfully applied to the study of both physical and chemical structures of organic and inorganic solids.[5−10] While it can lead to a significant gain in sensitivity, the CP spectrum possesses an inherent shortcoming: nonquantitative. Such a drawback has limited the applications of the method, especially to the quantitative characterization of molecular structures. To overcome the problem, quantitative CP has been a research topic for several decades and a number of elegant schemes have been developed. They used the effects of spin diffusion,[11] dipolar recoupling,[12−14] Lee Goldburg spin-locking,[15] variable contact time,[16] cross depolarization,[17] etc. Most of the schemes were effective to their corresponding systems. Recently, a novel scheme based on the reciprocity relation[18] between cross-polarization and cross-depolarization (CDP)[19] was reported.[20] It was able to determine the enhancement factors of CP peaks from the reciprocity relation. Given these enhancement factors, conventional CP/MAS NMR spectra can be quantified. The experimental scheme is simple, general, and accurate, and it can be applied to different types of molecular structures. However, for some multiphase polymers with extremely mobile components the scheme of CP itself may fail as described bellow.

Multiphase polymers, including copolymers, polymer blends, semicrystalline polymers and polymeric composites, constitute a large family of polymer materials. The phase composition is fundamental for understanding the structure−property relations of these multiphase polymer systems.[21] In addition to the conventional techniques, such as DSC, X-ray diffraction, etc., the experimental scheme[20] we developed is apparently a useful method for acquiring this crucial information, especially for amorphous systems. Nevertheless, we find that there exist a number of multiphase polymers that are not suitable to employ the scheme of CP alone. One typical example is polystyrene-polyisoprene (SI) block copolymers. At room temperature, the SI block copolymers possess of one rigid phase of polystyrene (PS) and one extremely mobile phase of polyisoprene (PI). Because of the high mobility of PI chains, the signals of PI are almost invisible in a ^{13}C CP/MAS spectrum because the ^{1}H−^{13}C heteronuclear dipolar interactions are nearly averaged to zero by the fast molecular tumbling. As a result, the NMR methods based on CP alone are not suitable for these polymer systems. To combine the toughness and high modules of plastic polymer and the high resistance impact of rubber is a widely used strategy in polymer industry, in order to improve the macroscopic properties of the polymers. Multiphase polymers with similar characteristics of SI, i.e., the rigidness of different phases are distinctively different, are not rare. Developing suitable NMR techniques for characterizing them is therefore requisite.

In practice, single pulse (SP) experiment is often used for rubbers. It may also be applied to a PS system with a rigid phase. Since the ^{13}C spin−lattice relaxation for a rigid phase is usually very long, the relaxation delay in experiments should be sufficiently long to ensure fully recovery of the magnetization before each scan, leading to an experiment extremely time-consuming.

In this paper, we describe a new method that combines CP and SP in one experiment, which gives both the CP and SP spectra. For the PS spectrum, the CP enhancement factor is derived with the reciprocity relation; for the PI spectrum, a sufficiently long relaxation delay (in the order of seconds) relative to its ^{13}C spin−lattice relaxation time T_1 is given in the experiment so that the peak intensity can be calculated based on the Boltzmann distribution in thermo equilibrium.

Experimental Section

A diblock copolymer of polystyrene and polyisoprene (Figure 1) with very narrow molecular weight distribution for both components is used in the NMR experiments. Due to the large difference in molecular motion, the two components appear to have quite different spin−lattice relaxation times T_1, about 10−60 s for PS and less than 1 s for PI. The NMR spectrum and molecular structure are shown in Figure 1, where the peaks labeled with a prime belong to the trans isomer of the PI

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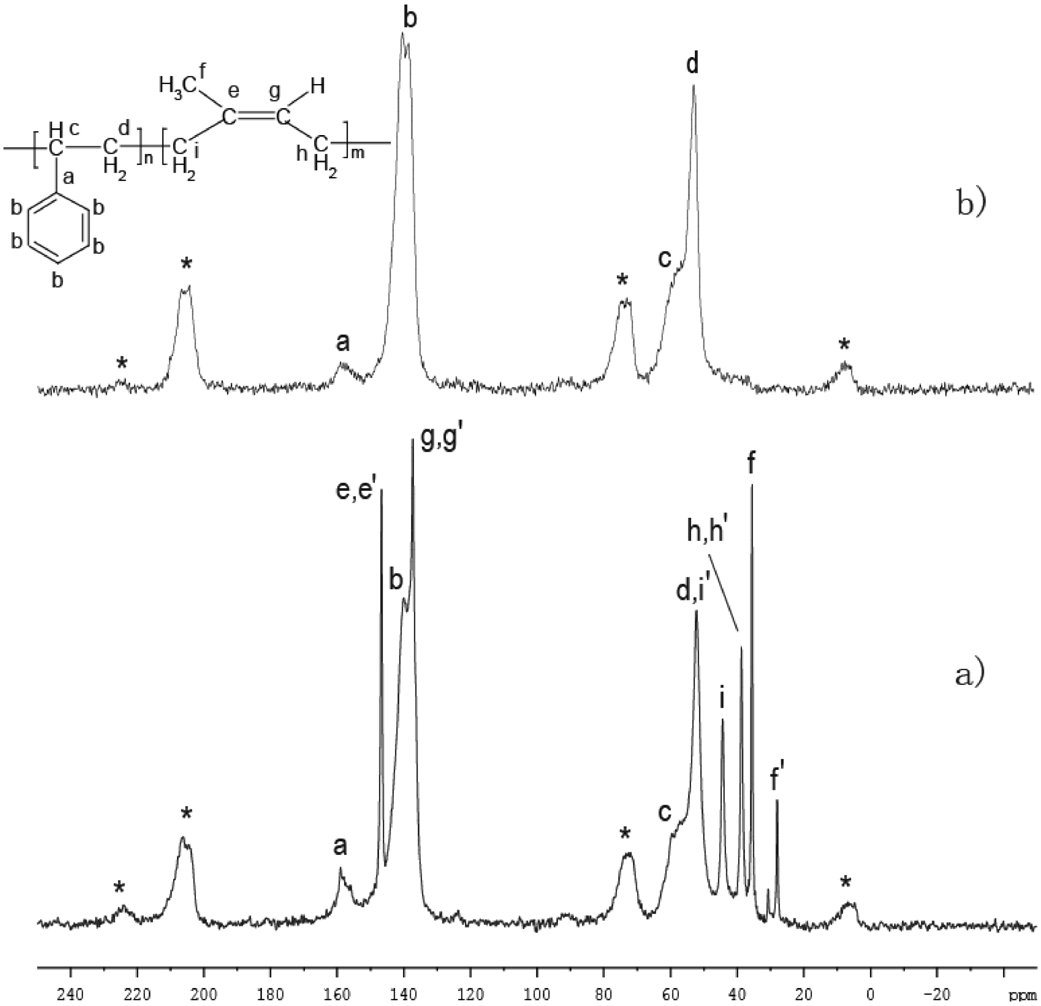

Figure 1. ^{13}C NMR spectrum of a copolymer of polystyrene and polyisoprene obtained with a single pulse sequence (bottom) and a Hartmann−Hahn CP sequence (top) (contact time t = 50 μs). In CP spectrum, all the peaks from the PI component are missing due to fast molecular motion. The structure of the molecule is shown on the top-left corner and the spinning sidebands are marked with an asterisk. All the peaks labeled with a prime come from the trans isomer of the PI component (not shown in the structure). For single pulse experiment, the acquisition delay is 300 s and number of scans are 512, but for CP experiment, the acquisition delay is 5 s and number of scans are 1024.

component (not shown). All the experiments were performed on a Bruker AVANCE III 300 MHz NMR instrument with a 4 mm MAS probe. The MAS speed was 5 kHz and pulse strength was 62.5 kHz for all the pulses, including the TPPM decoupling.[23] In the CP experiments, Hartmann−Hahn match condition was always fulfilled.

To get quantitatively the PS or PI mole composition, a single pulse experiment with a long acquisition delay is often used. The spectrum shown in Figure 1a was done in this way and it took about 42.7 h with an acquisition delay of 300 s. Experimental time would be greatly shortened if the Hartman-Hahn CP could be employed. Unfortunately, the CP gives nearly no PI signal due to the fast molecular tumbling at room temperature. As a matter of fact its dipolar interactions between ^{1}H and ^{13}C are completely averaged out, resulting in the peaks from PS only (Figure 1b).

To effectively analyze this and some similar samples, we used a conventional CP combined with a SP sequence as shown in Figure 2, which is referred to CPSP in short. The initial ^{13}C 90° pulse rotates the PI magnetization to the $x-y$ plane in the rotating frame and the magnetization is then spin-locked by the subsequent ^{13}C CP pulse. Here, the ^{13}C spin-locking pulse plays two roles: one is to hold the PI magnetization so that it will not dephase during the contact time t and the other to transfer polarization from ^{1}H to ^{13}C for PS. For this sample, polarization transfer will not occur in PI component because of the fast molecular motion. For some other samples, it may occur partially due to the residual dipolar couplings. In this case the polarized ^{13}C signal will have the same phase as the spin-locked one with the

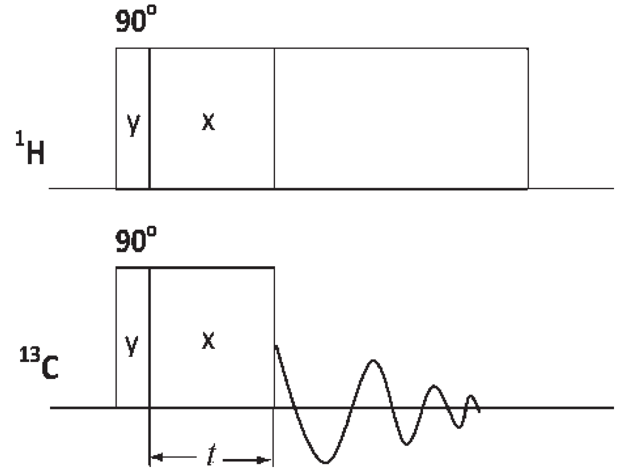

Figure 2. CPSP sequence with the following phase cycles: y, $-y$ (^{1}H 90°); x (^{1}H CP); y, $-y$, $-y$, y, $-x$, x, x, $-x$ (^{13}C 90°); x, x, $-x$, $-x$, y, y, $-y$, $-y$ (^{13}C CP); and x, $-x$, $-x$, x, y, $-y$, $-y$, y (receiver phase). The CYCLOPS phase cycle[22] is included to remove the RF imperfections.

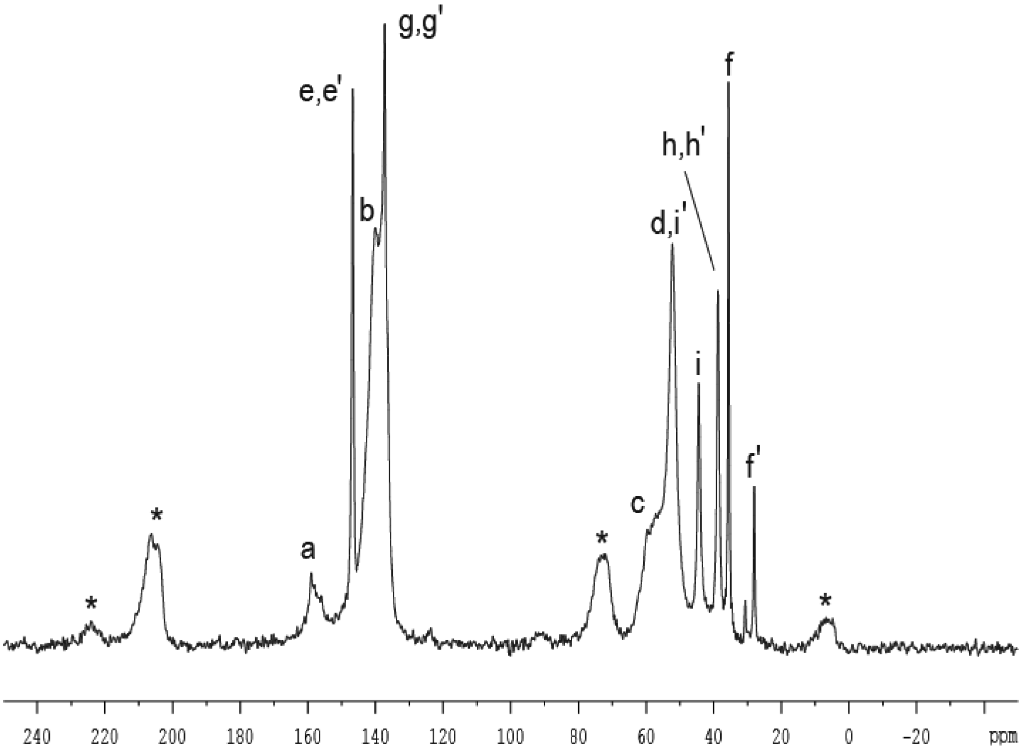

Figure 3. ^{13}C NMR spectrum of a copolymer of polystyrene and polyisoprene obtained with the CPSP sequence as shown in Figure 2, where the PS peaks come from the CP while the PI peaks come from the single pulse. The contact time, acquisition delay, and number of scans are 50 μs, 5 s, and 1024, respectively.

phase cycles shown in Figure 2, leading to an enhanced rather than destructive magnetization.

The CPSP spectrum of a copolymer of polystyrene and polyisoprene is shown in Figure 3, where the peaks from both PS and PI phases appear, resembling the spectrum obtained with a single pulse (Figure 1a). This spectrum, however, takes only about 1.4 h, considerably shortened compared to the one by a single pulse. Therefore, this method provides a quick measurement of the copolymers with marked difference in phase mobility.

The question arises: How does one derive quantitative information from such hybrid spectrum peaks, partly from CP and partly from a SP? This problem seems rather different from the quantitative CP since it involves a signal directly from the Boltzmann equilibrium. Nevertheless, quantification of CPSP spectrum can still be achieved quite naturally if the enhancement factor of CP can be determined.

Quantification of CPSP Spectrum

In general, the relative peak intensities of the CPSP spectrum are no longer comparable, especially for those from the two different phases. To overcome the problem, both signals from CP and SP need to be quantified. If the acquisition delay is so long compared to the T_1 of PI that the corresponding ^{13}C nuclei are fully relaxed before each scan, the SP signal can be calculated based on the Boltzmann distribution in thermo equilibrium (the same condition is required for ^{1}H in the CP experiments). In addition, the CP signal also needs to be quantified and it can be done by measuring the enhancement factor of relevant peaks with the reciprocity relation. Quantification of CPSP is therefore made possible.

A CDP experiment is required to get the enhancement factor, where polarization is transferred from the ^{13}C to its surrounding ^{1}H. According to the reciprocity relation, the dynamics of CP(t) and CDP(t) follows the equation,

$$\mathrm{CP}(t) + \mathrm{CDP}(t) = 1 \qquad (1)$$

where the spin−lattice relaxation in the rotating frame ($T_{1\rho}$) is neglected. It is valid for a contact time t that is much smaller than $T_{1\rho}$. A relaxation compensated reciprocity relation may be employed for a longer t.[20] Unlike CP(t), CDP(t) is normalized decay curve with CDP(0) = 1. From eq 1, it is straightforward to derive the enhancement factor

$$\eta(t) = [1 - \mathrm{CDP}(t)]\,\frac{\gamma_{\mathrm{H}}}{\gamma_{\mathrm{C}}} \qquad (2)$$

where γ_{H} and γ_{C} are the gyromagnetic ratios of the ^{1}H and ^{13}C, respectively. In eq 2, the ratio ($\gamma_{\mathrm{H}}/\gamma_{\mathrm{C}}$) = 3.977 is included since we are comparing CP signal with the one from Boltzmann equilibrium.

To compare peak intensities from PS and PI components, the one from CP needs to be divided by the enhancement factor $\eta(t)$. A contact time t = 50 μs is chosen in both the CP and CDP experiments. This time is short enough to neglect the $T_{1\rho}$ effect, yet it is sufficiently long for a rigid ^{13}CH (or ^{13}CH$_2$) group to transfer polarization. The ^{13}CH group from the benzene ring (labeled b) in PS and other ^{13}C (labeled h, h′, f, and f′) in PI (Figure 1a) are used for the measurements. From the CDP experiment we get CDP(50 μs) = 0.417 and it leads to the enhancement factor η(50 μs) = 2.319 (eq 2).

For a SP spectrum derived from the Boltzmann equilibrium (Figure 1a), these pairs of peaks (h, h′, f, f′, e, e′, and g, g′) have the same intensity. Due to partial overlap of the peaks, h, h′, f, and f′ are integrated together and the average value of the four peaks (×2) is used as the peak intensity of PI component. The peak labeled b (÷5) is used as the PS peak intensity, which includes one center band and four spinning sidebands. One of them is not shown in the spectrum and the intensity of the second sideband on the right is counted twice. The four peaks, e, e′, g, and g′, which belong to PI, are also integrated together with the peak b (Figures 1a and 3). The sum of four peaks, which is the same as the sum of e, e′, g, and g′, then needs to be subtracted from the integrated value.

Given the enhancement factor (eq 2), it is convenient to calculate the mole fraction (MF) of PS (or PI)

$$\mathrm{PS}_{\mathrm{MF}} = \frac{I_{ps}}{I_{PS} + I_{PI}\eta} = 45.2\% \qquad (3)$$

where the PS peak intensity $I_{\mathrm{PS}} = 1.113$ and PI peak intensity $I_{\mathrm{PI}} = 0.583$ are derived from the integrals of the relevant peaks mentioned above. This value (45.2%) agrees well with the one (43.8%) obtained from a SP experiment with a long acquisition delay of 300 s and total acquisition time of 42.7 h (Figure 1a). However, the overall time for the CPSP and two CDP ($t = 0$ and $t = 50$ us) experiments is only 4.3 h, almost 10-fold less than the single pulse experiment.

It is worth mentioning that for some other samples a 50 μs spin-locking time may introduce a small polarization transfer for the mobile component due to the residual dipolar interactions. It will affect the accuracy of the method. In this case, $t = 0$ can be used for obtaining only the PI spectrum, which avoids the problem and ^{13}C $T_{1\rho}$ effect. In addition, the spectrum is much simpler because no peaks from the rigid component are present. The cost is, however, one more experiment with a short acquisition delay.

Conclusion

For multiphase polymers with both rigid and very mobile (or rubber) phases, neither CP nor SP is effective in the quantitative determination of each composition due to the fact that CP is not effective to the mobile phases and SP is too time-consuming. This problem can be solved with a CPSP method. It combines both CP and SP in one experiment, leading to a hybrid NMR spectrum. This method avoids a very long ^{13}C relaxation delay (up to tens of minutes) required by the SP experiment for the rigid phases, while in the CPSP experiment the corresponding spectrum is obtained by the CP, where only the proton T_1 (up to several seconds) needs to be taken into account. Therefore, the CPSP saves considerably the experimental time.

The CPSP spectrum can be quantified using the reciprocity relation to derive a CP enhancement factor for the peaks of rigid phases and integrating directly from the peaks of mobile phases under the condition of Boltzmann distribution in thermo equilibrium. The CPSP experiment is simple and it requires only one more ^{13}C 90° pulse applied just before the ^{13}C spin-locking pulse. With proper phase cycles, both the CP and SP signals are accumulated together. To calculate the CP enhancement factors of rigid phases, several additional CDP experiments are required with relatively short relaxation delay.

Under high MAS speed, the Hartmann−Hahn match conditions are shifted to $\omega_{\mathrm{I}} - \omega_{\mathrm{S}} = n\omega_{\mathrm{R}}$ ($n = \pm 1, \pm 2$),[4] but the reciprocity relation still holds as conformed by computer simulation.[20] Under high magnetic field, the relative spin−lattice relaxation times may change moderately and as a result, the experimental conditions may need to alter accordingly, but the overall results will not be affected. Therefore, the scheme of CPSP will work under both high MAS speed and magnetic field.

In general, the CPSP scheme can be applied to sample systems with marked difference in phase mobility, in which the CP efficiency of the mobile component becomes significantly lower than the SP experiment. On the other hand, the relative rigid phases may have a very long ^{13}C T_1 relaxation, making the SP experiment unreasonably time-consuming, yet the CP method is perfect to such phases. This method may also be applied to ^{29}Si or other low γ nuclei containing molecules with a similar nature.

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