WIM/WISE NMR Studies of Chain Dynamics in Solid Polymers and Blends

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Wideline separation (WISE) NMR with windowless isotropic mixing (WIM) is developed as a method to study the dynamics of polymers and blends. This experiment is designed to measure the dynamics of polymers through the proton lineshapes that are correlated with the carbon chemical shifts in two-dimensional NMR experiments. If the atoms experience large amplitude fluctuations that are fast compared to the dipolar broadening, then the proton lines will be narrowed relative to rigid solids. We have modified the WISE experiment by replacing the cross polarization step with WIM to quench spin diffusion during the cross polarization so that the proton linewidths can be directly related to the chain dynamics. Two-dimensional WIM/WISE has been used to measure the main-chain and side-chain dynamics in poly(n-butyl methacrylate) and blends of polystyrene and poly(vinyl methyl ether). © 2000 Academic Press

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INTRODUCTION

NMR has long been used as a method to measure the molecular dynamics of molecules both in solids and solutions (*1*), particularly in polymers where the dynamics are often directly related to the macroscopic properties (*2*). NMR provides information about the amplitude and frequency of molecular motion over a wide range of time scales from measurements of signal intensities, relaxation times, and the lineshapes. The experiment of choice depends on amplitude and rate of atomic fluctuations, since some measurements are sensitive to fluctuations on the MHz frequency or faster time scale while others are sensitive to mid-kHz or slower fluctuations (*2*). More recently, multidimensional NMR methods have been used to measure ultra-slow exchange in polymers (*3*).

Wideline separation (WISE) NMR was introduced some years ago as a simple and elegant method to measure the chain dynamics of solid polymers by correlating the proton lineshape with the carbon chemical shift (*4*). This experiment yields information about the dynamics by measuring the degree to which the proton lineshapes are averaged by molecular motion. The proton lines are broadened in solids by hetero- and homo-nuclear dipolar interactions, and motionally averaged lineshapes are observed if the atoms experience large amplitude fluctuations that are fast on the time scale of the dipolar linewidths (ca. 50 kHz). The heteronuclear contribution to the proton linewidth can be removed by carbon decoupling during the evolution period (*5*). Although the proton lineshapes are not amenable to the same detailed analysis as the deuterium lineshapes (*6*), they provide qualitative information about the dynamics without isotopic labeling. The WISE experiment can also be used to study the mixing of polymers by placing a spin diffusion delay between the proton evolution and cross polarization periods (*4*).

The WISE spectrum measures the proton lineshape following magnetization transfer from protons to carbons (or other nuclei) by cross polarization (*4*). This experiment provides information about the dynamics of chains rather than for individual groups because spin diffusion can average the lineshapes for protons that are close in space during the cross polarization period (*3*). In these experiments, we replace the cross polarization step with the 24-pulse windowless isotropic mixing (WIM) sequence that quenches spin diffusion during cross polarization (*7, 8*). This allows us to use the WISE experiment to measure the proton lineshapes in the absence of spin diffusion, so that the linewidths can be directly related to the molecular dynamics. We demonstrate the applicability of this experiment by measuring the lineshapes for the main chain and side chain atoms of poly(n-butyl methacrylate) as a function of temperature and for the individual chains in a polystyrene/poly(vinyl methyl ether) blend. We anticipate that many materials will be amenable to analysis by 2D WIM/WISE NMR.

MATERIALS AND METHODS

Poly(n-butyl methacrylate), polystyrene, and poly(vinyl methyl ether) were obtained from Aldrich. The polystyrene/poly(vinyl methyl ether) blend was prepared from a 10% solution in toluene made from equal molar mixtures of the

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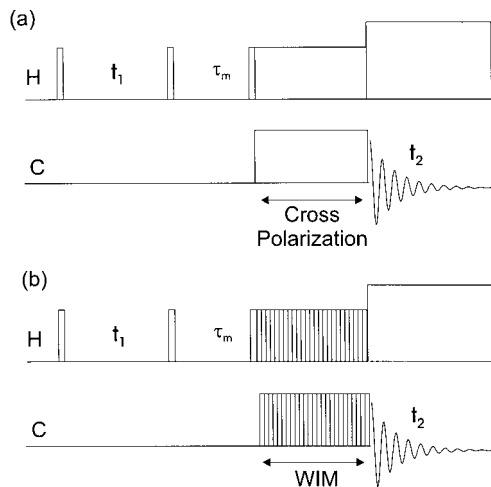
FIG. 1. The pulse sequence diagrams for 2D (a) WISE and (b) WIM/WISE NMR. In the WIM/WISE experiment the cross polarization is replaced with the windowless isotropic mixing sequence.

polymers. Clear films were obtained by casting under nitrogen, and the samples were heated to 65°C under vacuum to remove all traces of the solvent.

Solid state NMR spectra were obtained on a Varian Unity NMR spectrometer operating at 125 MHz for carbons and 400 MHz for protons. The spectra were acquired with 4.25-μs carbon and proton pulses using a Chemagnetics 7.5-mm probe with magic-angle spinning at 3–4 kHz. Phase-sensitive 2D spectra were recorded using time-proportional phase incrementation (9) of the first proton pulse and sweep widths in the carbon and proton dimensions of 30 and 400 kHz.

RESULTS

Since its introduction several years ago, 2D wideline separation (WISE) NMR (4) has been used to study the dynamics of many classes of polymers via the correlation of the carbon chemical shifts with the proton lineshapes. The 2D WISE experiment (Fig. 1a) begins with a proton 90° pulse followed by the t_1 evolution period during which the proton signals evolve under the influence of the chemical shift and the dipolar interactions. Another 90° pulse tips the magnetization along the $-z$ axis for an optional spin diffusion time τ_m, before the signal is detected in the t_2 dimension following cross polarization. Two-dimensional Fourier transformation yields a data matrix with the carbon frequency along one axis and the proton frequency along the other. It is typically most informative to view the data as cross sections through the 2D matrix. Since the chemical shift range for protons (5 kHz) is much smaller than the linewidths (ca. 50 kHz), wideline spectra are observed in the t_1 dimension.

The 2D WISE experiment does not provide an unambiguous measure of the proton dynamics because the lineshapes can be partially averaged by spin diffusion during the cross polariza-

tion. The rate of spin diffusion is a factor of two less than for the exchange of z magnetization (3), but significant spin diffusion can occur during the cross polarization contract times (1–2 ms) that are typically used in the solid state NMR analysis of polymers (2). The distance over which spin diffusion can lead to lineshape averaging is approximately given by (4)

$$\langle |x| \rangle = \sqrt{\frac{D\tau\pi}{4}}, \qquad [1]$$

where D is the spin diffusion rate constant and τ is the cross polarization contact time. For a glassy polymer below T_g the spin diffusion coefficient is of the order of 0.8×10^{-15} m^2/s (10), and with a contact time of 1 ms, this gives a spin diffusion length scale of ca. 5 Å. For polymers above T_g, the spin diffusion coefficients are much smaller (0.05×10^{-15} m^2/s) (11), but longer cross polarization times are required to achieve the same signal intensity. It is well known that librations and methyl group rotations in otherwise rigid solids can partially average the proton lineshape (1). Protons that are within 5 Å of a methyl or some other rapidly fluctuating group may therefore appear with a motionally narrowed lineshape in the WISE spectrum, not from molecular motion, but from spin diffusion. This makes the WISE experiment more suited to the study of entire chains, rather than the dynamics of individual groups.

Poly(n-butyl methacrylate)
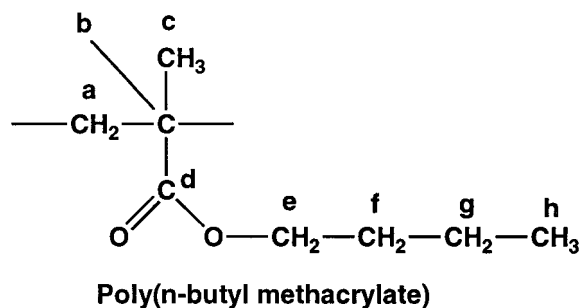
The effect of cross polarization time on the WISE lineshape has been studied for poly(n-butyl methacrylate), an amorphous polymer with a T_g of 27°C. Figure 2 shows the cross polarization spectra acquired with 3.5 kHz magic-angle sample spinning and dipolar decoupling during acquisition. Poly(n-butyl methacrylate) shows several well-resolved resonances, including the carbonyl, the methylenes in the main chain and side chain, and the main chain quaternary resonance. The only overlapping resonances are the main-chain and side-chain methyl peaks at 12.5 ppm.

Figure 3 compares cross sections through the 2D WISE spectra of poly(n-butyl methacrylate) at the frequency of the side chain methylene nearest the oxygen (e) and the methyl signals (c/h) for cross polarization contact times of 0.054 and 5 ms. Very different proton linewidths (40 and 17 kHz) are observed for the two peaks with the shortest cross polarization
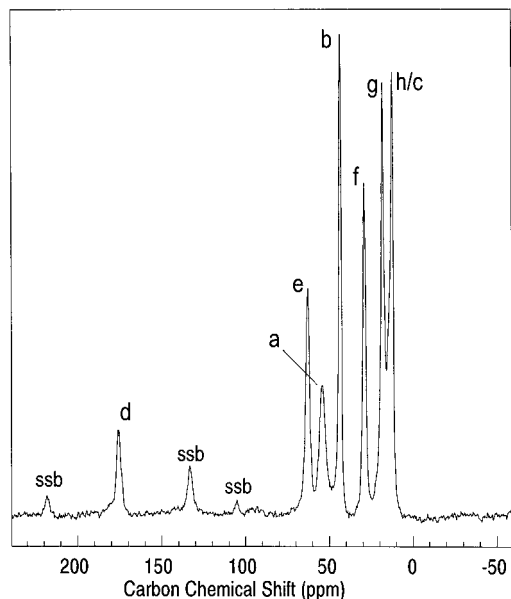
FIG. 2. The 125-MHz carbon spectrum of poly(n-butyl methacrylate) recorded with cross polarization and 3.5-kHz magic-angle sample spinning.

lineshapes measured by 2D WISE NMR depend on the cross-polarization time.

Windowless isotropic mixing (WIM) was introduced as a pulsed alternative to cross polarization (7, 8). Instead of using matched carbon and proton spin-locking fields, cross polarization is accomplished with a series of 24 pulses applied simultaneously to the carbon and protons to transfer magnetization from protons to carbons while quenching spin diffusion. The WIM pulse sequence has been extensively used to measure heteronuclear correlations in rotating solids (8, 12, 13), and we have been using WIM for cross polarization in the 2D WISE experiment using the pulse sequence shown in Fig. 1b. By using WIM in place of simple cross polarization, we can correlate the carbon chemical shifts with the proton linewidths without the complications of spin diffusion, and the lineshapes can be related to the dynamics of individual groups in polymer chains.

Figure 4 shows cross sections through the WIM/WISE 2D spectra for the main chain methylene (a), the side-chain methylene nearest the oxygen (e), and the methyl signals (c/h) of poly(n-butyl methacrylate). The important feature to note is that large differences in the line widths are directly observable from the WIM/WISE cross sections. Although the signal-to-noise is low for the main-chain signal, the full width at half maximum is greater than 50 kHz. This demonstrates that there is little averaging of the dipolar interactions for the main chain at 27°C for poly(n-butyl methacrylate). The side-chain methylene (e) shows a partially reduced line with a width of 39 kHz, demonstrating that the side chain experiences substantial mo-
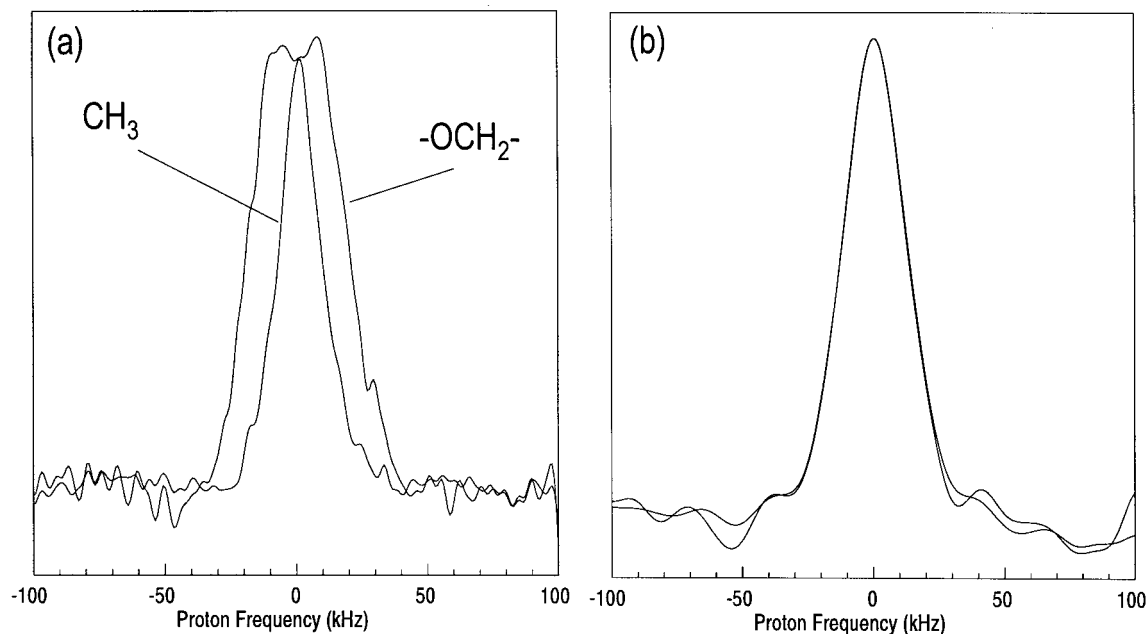
time, reflecting the difference in chain dynamics for these two kinds of groups. Cross-polarization spectra are usually recorded with longer contact times because the signal-to-noise is very low with such a short period for carbon–proton magnetization transfer. Figure 3b shows that identical lineshapes are observed for these carbons when a longer (5 ms) cross-polarization period is used. These data clearly demonstrate that the

FIG. 3. Cross sections through the 2D WISE spectra of poly(n-butyl methacrylate) at the frequencies of the side-chain methylene and methyl signals for cross polarization times of (a) 0.054 and (b) 5 ms.
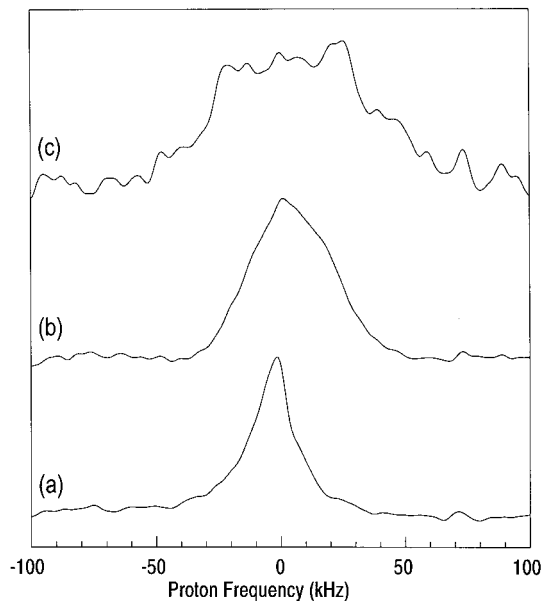
FIG. 4. Cross sections through the 2D WIM/WISE spectrum of poly(*n*-butyl methacrylate) at the frequencies of the (a) methyl, (b) side-chain methylene, and (c) the main-chain methylene carbons.
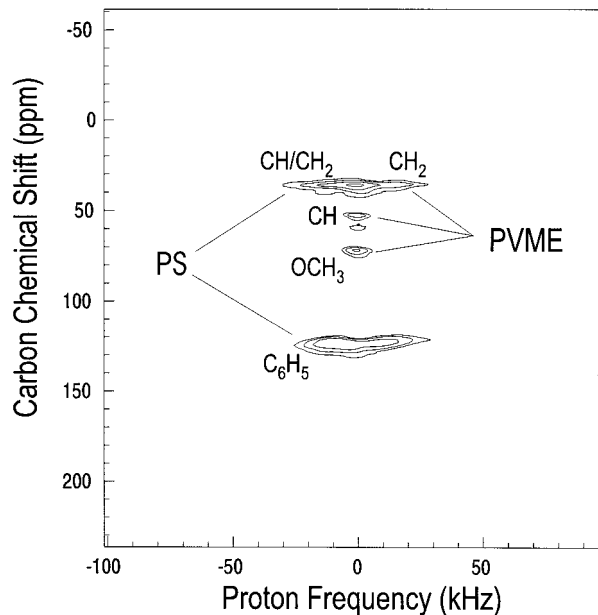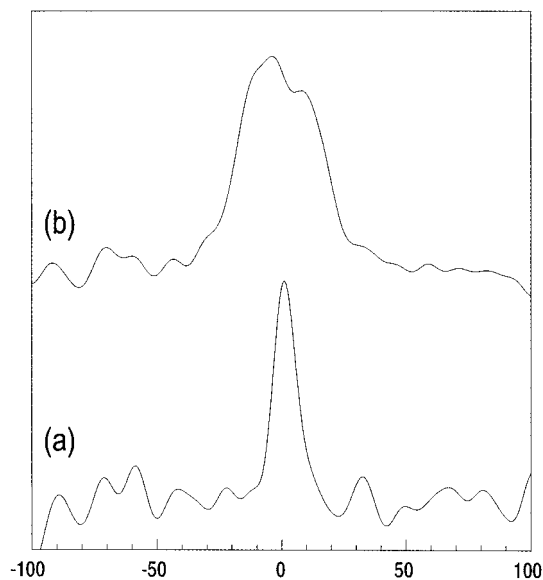

FIG. 5. A contour plot for the WIM/WISE spectrum of the polystyrene/poly(vinyl methyl ether) blend at 27°C. The assignments for the polystyrene aromatic and aliphatic peaks and the poly(vinyl methyl ether) methine and methoxy peaks are shown.

tion relative to the main chain. The methyl signal, which is a composite of the main-chain and side-chain methyl groups, shows a line width of 16 kHz, reflecting the averaging of the dipolar interactions by methyl-group rotation. The low signal-to-noise in for the main-chain signal is due to the difficulty in detecting this signal. The dynamics in the main chain are such that interference with either the decoupling or magic-angle sample spinning leads to linebroadening.

Poly(*n*-butyl methacrylate) has a DSC T_g of 27°C, and WIM/WISE NMR has been used to measure the effect of temperature on side chain motion above T_g. Table 1 shows the linewidths for the side chain methylene (e) and methyl (c/h) groups at 27, 50, and 80°C. At T_g, the side-chain methylene is reduced from the rigid lattice value of 50 to 39 kHz, and is further reduced to 36 kHz at 50°C and 32 kHz at 80°C. The composite methyl signal is reduced from 17 to 12 kHz over this same temperature range.

WIM/WISE NMR can also be used to investigate the dy-namics in polymer blends. The quenching of spin diffusion is particularly important for the study of blends with molecular level mixing, where the proton lineshapes can be averaged between the chains by spin diffusion. The dynamics of poly-mers in blends are of interest in light of recent studies dem-onstrating that even while mixed, the chains do not show identical dynamical behavior even though a single T_g is ob-served by DSC (*14*). It has also been shown that the dynamics of the chains in blends can be different from the pure compo-nent polymers (*15*).

Figure 5 shows a contour plot of the WIM/WISE spectrum of the 50:50 molar polystyrene/poly(vinyl methyl ether) blend at 27°C. Several well-resolved peaks are observed, including the polystyrene aromatic carbons at 125 ppm and the poly(vi-nyl methyl ether) methoxy and methine carbons at 67 and 54 ppm. The peak at ca. 40 ppm contains the overlapping poly-styrene methine and methylene carbons and the poly(vinyl methyl ether) methylene carbons. The contour plot shows that very different proton linewidths are observed for the polysty-rene and poly(vinyl methyl ether) chains, and Fig. 6 compares cross sections through the WIM/WISE spectra for the aromatic peak of polystyrene and the main chain methine peak of poly(vinyl methyl ether). The aromatic protons in pure poly-styrene have a full width at half maximum of 40 kHz while the same peak in the blend has a width of 36 kHz. This demon-strates that the aromatic rings are more mobile in the blend, and that they feel the effect of being dissolved in a matrix with the lower T_g poly(vinyl methyl ether). The opposite effect is ob-served for poly(vinyl methyl ether). Poly(vinyl methyl ether)

TABLE 1
The Linewidths of the poly(*n*-butyl Methacrylate) Side Chain Methylene and Methyl Groups as a Function of Temperature

	Linewidth (kHz)	
Temperature (°C)	$-OCH_2-$	$-CH_3$
27	38.9	16.8
50	35.7	17.5
80	32.4	12.4

FIG. 6. Cross sections through the WIM/WISE spectrum of the polystyrene/poly(vinyl methyl ether) blend at the frequency of the (a) poly(vinyl methyl ether) methine carbon and the (b) polystyrene aromatic carbon resonance.

has a T_g of $-31°C$ and chain motion at ambient temperature averages the proton lineshape to 6 kHz (not shown). WIM/WISE NMR shows that the methine motion is restricted relative to the pure poly(vinyl methyl ether) in the blend with polystyrene, where a 12-kHz linewidth is observed.

WIM/WISE NMR has also been used to study the effect of temperature on the chain dynamics for the polystyrene/poly(vinyl methyl ether) blend, and some of the results are shown in Table 2. The polystyrene aromatic proton linewidth is reduced from 36 kHz at 27°C to 30 kHz at 50°C to 9 kHz at 80°C. By contrast, the already averaged lineshape of poly(vinyl methyl ether) changes to a much smaller degree over this temperature range.

DISCUSSION

NMR is often the method of choice for studying polymer dynamics because the NMR spectrum and relaxation rates are sensitive to the chain dynamics over a wide range of frequencies (2). The range of frequencies that can be measured by NMR has recently been extended with the introduction of 2D NMR methods to investigate the molecular dynamics, including WISE NMR (4) and ultra-slow 2D exchange methods (16). In these studies we have introduced a modified version of the 2D WISE experiment that uses windowless isotropic mixing to quench spin diffusion, so that the lineshapes can be directly related to the molecular dynamics.

WIM/WISE was used in these studies to measure the dynamics of the well-resolved main-chain and side-chain atoms in poly(n-butyl methacrylate). Near the T_g detected by DSC we

found that the linewidths for the main-chain protons are close to the values expected for rigid polymers. This apparent discrepancy between the dynamics detected by DSC and NMR is due to the well-known difference in frequencies probed by the two methods, since the DSC transitions sensitive to low frequency motions (ca. $1 \ s^{-1}$) while much higher frequencies are required to average the NMR lineshapes. The lineshapes for the side-chain protons are partially averaged at the DSC T_g, demonstrating that the side chains are more flexible than the main chains. At higher temperatures we observed the further averaging of the lineshapes for the side chain protons.

Polystyrene/poly(vinyl methyl ether) blends have been extensively investigated as the prototypical miscible blend. It was observed in the early studies that optically clear films with a T_g intermediate between the two homopolymers could be observed for films cast from toluene or benzene, while phase-separated blends were observed upon casting from chloroform or trichloroethane (17). It was noted, however, that the T_g was broad compared to the T_g's of the component polymers, suggesting that the system is heterogeneous on some smaller length scale. Proton NMR studies showed that the blends were homogeneous on the length scale probed by T_1 (170 Å), but two-component T_2 relaxation was observed (18). This could be interpreted either as evidence for microphase separation or evidence that the component polymers have different dynamics in the miscible blend. Following these initial studies, several NMR experiments, including intermolecular cross polarization (19), NOE methods (20), and 2D multipulse exchange NMR (21), have shown that there are close contacts between the two chains. Other studies have shown that the blend contains heterogeneities on a length scale estimated to be 0.6–3.5 nm (4, 22). Results from the multiple-pulse NMR studies suggested a more complex structure with three phases that included a mixed phase and polystyrene and poly(vinyl methyl ether)-rich phases (23). Approximately 80% of the material was found in the mixed phase.

The dynamics of polystyrene/poly(vinyl methyl ether) blends have also been investigated by NMR methods (4, 15, 24). It has been reported that the linewidths for some of the carbons go through a maximum as a function of temperature due to interference of the chain motion with either the magic-angle sample spinning or the proton decoupling. From

TABLE 2
The WIM/WISE Linewidths for the Polystyrene Aromatic Protons and the poly(Vinyl Methyl Ether) Main Chain Methine Protons as a Function of Temperature

Temperature (°C)	Linewidth (kHz)	
	PS C_6H_5	PVME $-CH-$
27	35.7	12.4
50	29.5	11.0
80	9.0	11.1

this temperature-dependent linebroadening it has been shown that the dynamics of the component polymers are quite different from each other, and chain motion in polystyrene is much slower than the poly(vinyl methyl ether) in the miscible blend. Furthermore, chain motion in polystyrene is increased by mixing with the low T_g poly(vinyl methyl ether) and the molecular motions of poly(vinyl methyl ether) are retarded by mixing with the polystyrene. This behavior has also been observed for 1,2-polybutadiene/polyisoprene blends (*14, 25, 26*).

The proton lineshapes in the WIM/WISE NMR experiments provide a direct measure of the chain dynamics in the miscible blend. The results show that there is a large difference in the dynamics between the aromatic rings of polystyrene and the main chain of poly(vinyl methyl ether), consistent with the previous reports. The polystyrene aromatic protons have a linewidth of 36 kHz at 27°C, demonstrating that polystyrene retains considerable rigidity even when blended with a low T_g material. On the other hand, this linewidth is less than the 40 kHz measured for the polystyrene aromatic rings in the bulk material, showing that the rings in the blend are more mobile than in the pure material. It is also interesting to note that the aromatic linewidths are much more temperature dependent than are the main-chain signals for poly(*n*-butyl methacrylate) and poly(vinyl methyl ether). This reflects the additional modes, such as ring flips and librations, that become available to the polymer side chain at temperatures above T_g.

The behavior of the poly(vinyl methyl ether) main-chain signals is opposite of that observed for polystyrene. Poly(vinyl methyl ether) at ambient temperature is above T_g and the lineshape is averaged by chain motion from the rigid lattice value to 6 kHz for the bulk polymer. A value of 12 kHz is observed for the blend with polystyrene, demonstrating that the local environment is affected by blending with the more rigid polymer. Such a difference in chain dynamics might be expected based on the observation of nanoheterogenities in the blend discussed above.

The data presented from the WIM/WISE experiments are in agreement with the dynamics measured from the temperature dependence of the ^{13}C linewidths. The studies of the ^{13}C linewidths rely on the fortuitous interference of the chain dynamics and the line narrowing methods, since if the chain dynamics are on the same time scale as the magic-angle spinning or the decoupling, line narrowing becomes inefficient and broadening is observed (*27*). In polystyrene it was demonstrated that the line broadening is a consequence of interference with the decoupling (*24*), while in poly(vinyl methyl ether) it is more likely that the broadening is a consequence of interference with magic-angle spinning. One important advantage of the WIM/WISE approach is that the measurements are not dependent on the fortuitous interference of the chain dynamics with the line narrowing methods and should be applicable to more materials over a wider range of temperatures.

In summary, we have introduced 2D WIM/WISE NMR as a tool to study the dynamics of polymers in the solid state. This modified version of WISE uses windowless isotropic mixing to quench spin diffusion during cross polarization, so that the proton lineshapes can be directly related to the chain dynamics. The pulse sequence is more complex, but we find that WIM is easy to implement and has a signal-to-noise ratio only slightly lower than for cross polarization. Multipulse tune-up is not required for efficient cross polarization using WIM. WIM/WISE NMR has been used to study the effect of temperature on the dynamics of the main-chain and side-chain protons in poly(*n*-butyl methacrylate) and the effect of blending on the dynamics of polystyrene and poly(vinyl methyl ether). We anticipate that this method will be applicable to a wide variety of materials, including polymer blends and polymers at surfaces (*28*). The original WISE experiment remains a valuable tool for studying the length scale of mixing in phase-separated polymers and blends (*29*).

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