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Correlation of Structure, Mobility, and Morphological Information in Heterogeneous Polymer Materials by Two-Dimensional Wideline-Separation NMR Spectroscopy

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ABSTRACT: A novel version of the two-dimensional heteronuclear experiment, achieving ^1H wideline separation (WISE), is presented. It allows for the correlation of mobility and structure in organic solids. Differences of molecular dynamics are probed by ^1H wideline shapes, which are separated in the second dimension by ^{13}C chemical shifts. With a mixing time inserted before cross polarization from ^1H to ^{13}C, ^1H spin diffusion allows one to determine the mobility at interfaces and to measure domain sizes approximately. The technique is demonstrated on poly(styrene)-poly(siloxane) block copolymers and on a blend of poly(styrene) and poly(vinyl methyl ether), where nano-heterogeneity with respect to the mobility is found. The detection of phenyl flips in glassy polymers is also demonstrated.

Introduction

Many polymer materials are known to be heterogeneous on a length scale of a few tens of nanometers. Often, the various components exhibit different mobilities at the application temperature, which can result in desirable combinations of properties like hardness and impact strength; see, e.g., refs 1 and 2. For a detailed understanding of these properties on a microscopic level, it is essential to obtain knowledge on the distribution of the mobility in the material. In particular, this includes dynamic heterogeneities on the scale of few nanometers and the dynamics at the interfaces between rigid and mobile components. Though of considerable interest, such information is in general not directly accessible by classical methods.

Nuclear magnetic resonance (NMR) spectroscopy of solids offers many possibilities to probe molecular dynamics. In homopolymers, multidimensional exchange-NMR techniques have elucidated several important details of the slow dynamic processes responsible for the softening of polymers above the glass-rubber transition.[3-5] At higher rates, these processes have been followed by the measurement of various NMR relaxation times.[6,7] Another long-standing method for the qualitative characterization of molecular mobility is proton wideline NMR spectroscopy. Here, large-amplitude motions with rates exceeding the dipolar coupling of protons, typically 50 kHz, are detected through the reduction of the dipolar line width. For homogeneous systems, this simple experiment can even today provide valuable information.[8]

For advanced composite materials, however, one-dimensional proton line shapes leave many questions open. When a broad and a narrow spectral component are found to be superimposed, their relation to the respective structural components can only be established if one knows a priori which component is hard and soft, respectively. Segments of the "soft" component that are immobilized due to strong contacts to the hard phase cannot be distinguished from the "hard" component in the conventional 1D spectrum. Hard segments dispersed in the soft region are only recognized if their mobility is very high.

More often, the ^1H wideline spectrum cannot even be decomposed into few components in a convincing fashion. In many cases, this is due to gradients of mobility in the material, and though of considerable interest, this information cannot be extracted from the spectrum.

Two approaches have been developed in the past to increase the selectivity of solid-state NMR spectroscopy: pulsed ^2H NMR spectroscopy on selectively labeled systems[9] and separated local field NMR spectroscopy.[10,11] The first is often chemically demanding; the second, experimentally difficult to implement. Nevertheless, our knowledge of local motions in glassy polymers as well as chain motions above the glass transition has largely increased in recent years due to studies using these techniques, in particular ^2H NMR spectroscopy. Both methods, however, do not provide information about the sizes of domains with different mobilities. Here we describe a novel version of the heteronuclear two-dimensional (2D) experiments, which is straightforward to perform, allowing, e.g., temperature variation and providing the desired information. For every resolved ^{13}C resonance, it yields a proton wideline spectrum which reflects the dipolar couplings of the protons in the proximity of the respective ^{13}C nuclei. Thus, one achieves *wideline separation* (WISE) in the ^{13}C dimension, in contrast to related heteronuclear experiments, where essentially *correlations* of resolved ^{13}C and ^1H lines are established.[12,13] Nevertheless, in separating proton wideline spectra for different ^{13}C positions, the WISE experiment does establish a correlation, namely of chemical structure and segmental mobility, as reflected in the ^{13}C chemical shifts and the ^1H line shapes, respectively.

Description of Experiment

The pulse sequence and principle of the WISE experiment (without ^1H spin diffusion) are displayed in Figure 1a. It starts with an 90° pulse on the protons, followed by an incremented proton evolution period (t_1). By means of Hartmann-Hahn cross polarization (CP)[14] from protons to carbons, the proton magnetization at the end of the evolution period[15] is transformed into amplitude modulation of the ^{13}C signal, which is probed in the t_2 domain of the experiment. Pulse sequences to manipulate the ^{13}C signal can be applied in the t_2 domain without the problems arising when ^{13}C magnetization is evolving in the evolution period.[16] Indeed, for all the spectra shown below, the TOSS sequence[17] was used to suppress ^{13}C spinning sidebands. In the resulting 2D spectrum, the chemical structure is reflected in the signal position on the ^{13}C chemical shift axis. For each of these resolved signals, corresponding to certain molecular moieties, the molec-

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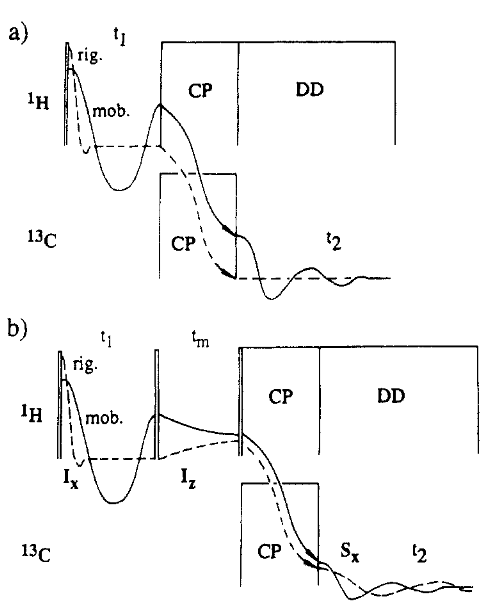

Figure 1. Pulse sequence and principle of the heteronuclear 2D WISE-NMR experiment. (a) Basic version with proton evolution, cross polarization (CP), and ^{13}C detection with dipolar decoupling of protons (DD). Typical magnetization decays are sketched. For simplicity, just two components, a "rigid" and a "mobile" one, are considered. At the start of the detection period, the four 180° pulses of the TOSS sequence[17] (not shown here) can be applied to suppress ^{13}C spinning sidebands. (b) Extension by a mixing time before cross polarization. The decrease of the difference between proton magnetization levels by proton spin diffusion during the mixing time is indicated.

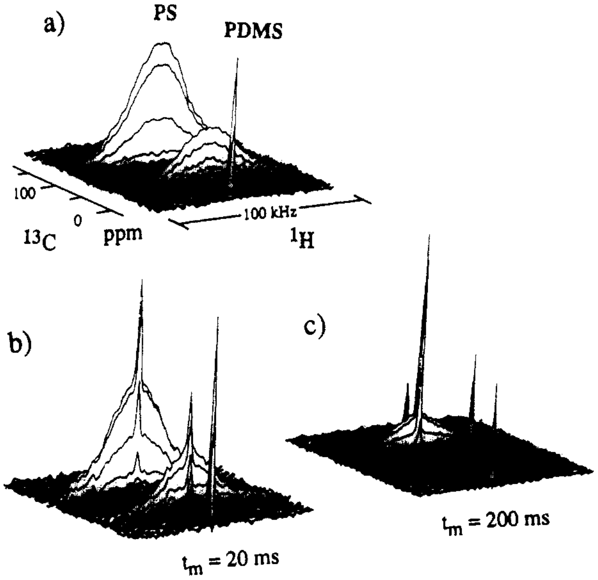

Figure 2. WISE-NMR spectra of PS-*b*-PDMS (50:50 mol %) for a series of mixing times. (a) Minimum effective t_m of 0.5 ms, due to the CP contact time of 1 ms. The PDMS (line near 0 ppm) is highly mobile but does not induce significant mobility in the PS (lines at 40, 127, and 144 ppm; the ^{1}H line width averaged between phenyl and methylene protons is 40 kHz). (b) t_m = 20 ms. The PDMS within 1 nm from the PS–PDMS interface is detected in the sharp components on the PS signals. (c) Within a mixing time of t_m = 200 ms, the ^{1}H magnetization is approaching spatial equilibration.

ular mobility is characterized by the line shape parallel to the ^{1}H axis, with narrow lines indicating high segmental mobility.

To illustrate the technique, Figure 2a displays a typical spectrum for a simple case. The sample is a block copolymer of polystyrene (PS) and poly(dimethylsiloxane) (PDMS), to be fully described below. PS yields a ^{13}C spectrum with lines near 42, 128, and 146 ppm relative to TMS, while the methyl groups of PDMS have their resonance close to 0 ppm. At room temperature, pure polystyrene is below its glass transition temperature T_g. This is reflected by the wide lines in the ^{1}H dimension, corresponding to a fast decay of the t_1 amplitude modulation of the corresponding ^{13}C lines. In contrast, PDMS is more than 150 K above its T_g and therefore highly mobile. This is reflected in the small ^{1}H line width of the line near 0 ppm of ^{13}C, which is equivalent to a slow decay of this signal component with increasing t_1.

To probe the relative spatial position of components with different mobilities, ^{1}H spin diffusion can be introduced into the experiment. For this purpose, the ^{1}H magnetization remaining after the evolution period is flipped to the z-axis for the subsequent mixing period of duration t_m (Figure 1b). If regions with different mobilities (proton line shapes) are sufficiently close in space, they exchange ^{1}H magnetization by spin diffusion during t_m. This results in a transfer of t_1 modulation between slow and fast decaying ^{1}H components (cf. Figure 1b), equivalent to a transfer of ^{1}H line shape in the ω_1 frequency domain. This is best understood in the limit of complete spatial equilibration of ^{1}H magnetization during very long mixing times. Then, all ^{13}C signals are modulated by the same ^{1}H decay and therefore exhibit the same ^{1}H line shape along ω_1. Thus, the signals of rigid components, defined by their ^{13}C chemical shift and the absence of narrow components in the spectrum without spin diffusion, acquire, through the spin diffusion, narrow ^{1}H peak contributions from the mobile segments (cf. Figure 2b,c). Likewise, the signals of the mobile segments show broad ^{1}H wideline features of the rigid components. For relatively short mixing times, the signals of the rigid components can acquire ^{1}H line shape features only from the soft segments that are closest by; i.e. the line shape changes then selectively probe the mobility at the rigid–mobile interface.

^{1}H Wideline Spectra in the WISE Experiment. As is quite well-known, the proton line shape for immobile CH or CH$_2$ segments in hydrocarbons is hardly affected by sample rotation at rates below 5 kHz, which are equivalent to only one-tenth of the dipolar line width. This can be understood by considering that the FID decays within a time in which the rotor does not rotate by an appreciable angle and, more importantly, the many-particle dipolar interactions within the proton system keep the Hamiltonian from commuting with itself at different orientations, and therefore rotational echoes, or, equivalently, spinning sidebands, do not occur.

It is interesting to note that the indirect detection of the proton signal in the WISE experiment makes it possible to measure wide proton lines without a receiver dead-time problem. Moreover, the 2D experiment provides the ^{1}H line shapes of rigid segments in the presence of very mobile components, since the intensity of the latter is decreased due to their reduced cross polarization efficiency. In the PS-*b*-PDMS sample, fully discussed below, the PDMS proton line is so narrow and high in the conventional 1D proton spectrum that the broad and low PS signal, though of similar integrated intensity, is hardly detectable at all. In the 2D spectrum (Figure 2a) the broad lines are clearly separated from the narrow one.

It should also be noted that the pulse sequence shown in Figure 1a,b provides no quadrature detection in ω_1; i.e. the spectra are symmetrized with respect to $\omega_1 = 0$. In all the cases discussed in this paper, this is no problem, as the spectra themselves exhibit this symmetry to a very good approximation, and the narrow components were set on resonance. While it is possible to measure the component that is antisymmetric in ω_1 just by changing the phase of the first pulse by 90°, this has unfavorable effects on the signal-to-noise ratio in the spectrum in two respects. First, it doubles the measuring time, and second, on being added to the symmetric spectrum, the antisymmetric part increases the noise by $\sqrt{2}$ without significant enhancement of the signal.

Special precautions must sometimes be taken if very highly mobile components with short ^{13}C T_1 and long T_2 times are present. These can produce signals by direct ^{13}C excitation, independent of the cross polarization. Consequently, the signal does not decay with increasing t_1, leading to very narrow lines at $\omega_1 = 0$ and the corresponding ^{13}C peak position. In fact, the PDMS signal near 0 ppm in Figure 2 is of such nature, as indicated by the lack of spin diffusion effects on this particular signal in Figure 2c. If required, one can reduce or eliminate these signals by a series of ^{13}C saturation pulses and delays before the actual WISE pulse sequence.

It is virtually impossible to calculate the proton line shapes resulting from specific motional processes for the multispin dipolar interaction. Therefore, one might argue that a ^{1}H wideline NMR spectrum contains only limited information about the motional process involved. In many cases, however, qualitative information, e.g. presence or absence of broad and narrow components or the appearance of spinning sidebands in the ^{1}H spectrum, is completely sufficient to unravel motional heterogeneities. This is demonstrated in the following sections. As a rough estimate, it can be said that a ^{1}H line narrowed to a width below 1 kHz must be due to motions resulting in nearly isotropic averaging with rates exceeding 1 MHz, whereas ^{1}H spinning sidebands indicate anisotropic motions of similar rates.

Experimental Section

The spectra were taken at ambient temperature on a Bruker MSL 300 spectrometer at a field of 7 T in a Bruker double resonance MAS (magic angle spinning) probehead, with rotation frequencies near 4.5 kHz. Between 128 and 256 t_1 increments with a t_1 dwell time of 5 μs were used for each spectrum. Measuring times ranged between 5 and 18 h. In all cases, the pulse sequence in Figure 1b was used. The minimum t_m value was 50 μs. The cross polarization contact times used in the acquisition of the WISE spectra are given in the respective figure captions. If not indicated otherwise, the spectra were taken at ambient temperature.

Results and Discussion

Phase-Separated Systems. As the first example Figure 2 displays a series of spectra of a 50:50 di-block copolymer of PS and PDMS[18] for increasing mixing times. This system, with total M_n = 60 000, is expected to exhibit a morphology of regularly alternating microphases of PS and PDMS, as is typical of symmetric di-block copolymers.[2] From the molecular weight and comparison with similar systems, the thickness of PS phases in this sample can be inferred to be smaller than 30 nm.[18] The PDMS is extremely mobile ($T_g \approx 150$ K), as indicated by the narrow proton line and low cross polarization efficiency of the peak near 0 ppm. This high mobility is, however, not imparted to any significant fraction of the polystyrene, as is indicated by the total absence of narrowed ^{1}H lines on the polystyrene signals. In fact, very highly mobile PS can be excluded directly by the lack of any sharp peak near 7 ppm in the 1D proton spectrum. Even with effects of $T_{1\rho}$ relaxation during the contact time and interference of motion and decoupling taken into account, the amount of mobile PS is estimated to be well below 5%. Thus, taking into account the estimated diameter of the PS domains of less than 30 nm, the thickness of a presumed dynamic interface must be below 1 nm, or three repeat-unit diameters. With 20 ms of spin diffusion (Figure 2b), the existence of a very steep gradient of mobility is corroborated. The mobile components communicating with the PS have very small line widths, with no detectable decay over 1 ms. From their intensity and the maximum thickness of the PS phases, they can be estimated to represent the PDMS side of the interfacial regions, within 1 nm from the PS. After 200 ms (Figure 2c), the ^{1}H magnetization has diffused further and approached, but not yet completely attained, spatial equilibration.

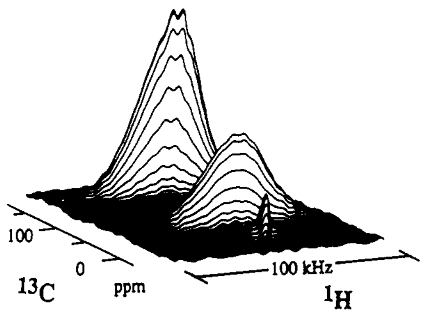

Figure 3. WISE-NMR spectrum for PS-*b*-PMPS (86:14 mol %), with a CP contact time of 0.6 ms. In the ^{1}H line shape of the PMPS methyl signal (close to 0 ppm of the ^{13}C scale), at least two components are distinguishable, indicating different degrees of immobilization of the PMPS. The horns on the phenyl signal (at 130 ppm) derive from the phenyl protons of the mobile PMPS, which are off resonance due to their ^{1}H chemical shift.

To indicate the sensitivity to small fractions of mobile components, and to a partial reduction of mobility of the soft segment, Figure 3 shows a spectrum of an 86:14 PS-*b*-poly(methylphenylsiloxane) (PMPS, T_g = 245 K) block copolymer, M_n = 48 000.[19] The 14 mol % of PMPS are clearly visible. One can even distinguish a narrow and a broad component in the proton line shape of the methyl signal near 0 ppm on the ^{13}C scale, indicating that about 50% of the PMPS exhibit a significantly reduced mobility, presumably due to their close contact to the PS. Thus, due to partial miscibility in this system the gradient of mobility is less steep than in the PS-PDMS copolymer.

Nano-Heterogeneous System: PVME/PS. Another interesting example of a material with close spatial proximity of components that possess very different mobilities as pure substances at room temperature is provided by the blend of poly(styrene) and poly(vinyl methyl ether) (PVME) cast from toluene. The composition is 50:50 wt %, the molecular weights are 200 000 (GPC) for the anionically polymerized PS, and 50 000 for the PVME (Aldrich).

To most classical techniques, this blend appears as homogeneous. It has also been studied in the solid state by a number of NMR techniques, e.g. ^{1}H multiple-pulse exchange experiments,[20] and extensively by $T_{1\rho}$ relaxation.[21] Dissolved in toluene, these two polymers show clear indications of interactions.[22] Pure PVME and pure PS have T_g's of 245 and 373 K, respectively, while in the 50:50 blend a single broad glass transition is detected around 260 K by differential scanning calorimetry (DSC).[23] At room temperature, the proton wideline spectrum shows components of large and intermediate widths without a clear separation, and becomes narrower gradually upon an increase of the temperature. Figure 4a displays the rather featureless ^{1}H spectrum at 320 K; Figure 4b, the spectrum of the most mobile components in the ^{1}H spectrum, selected by means of the "dipolar filter"

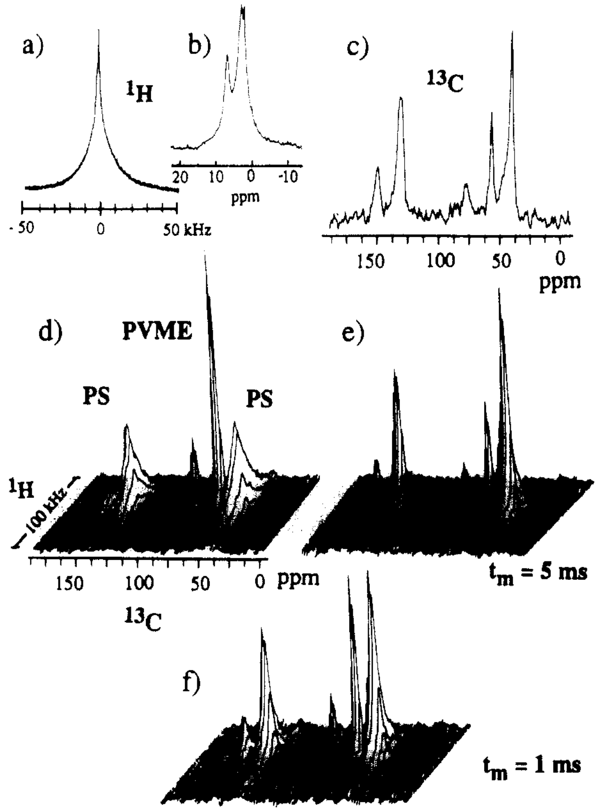

Figure 4. MAS spectra, ν_r = 4 kHz, of a 50:50 blend of PS and PVME cast from toluene, T = 320 K: (a) 1D proton wideline spectrum; (b) most mobile components in the ^{1}H spectrum of (a) selected by means of the "dipolar filter" pulse sequence (note the difference in scale relative to (a), 30 ppm = 9 kHz); (c) 1D ^{13}C spectrum; (d)–(f) WISE-NMR spectra. (d) Minimum effective t_m of 0.2 ms, due to CP contact time of 0.4 ms. The narrow ^{1}H lines of the PVME reflect its mobility, while the PS exhibits broad components, proving that a significant fraction exhibits still reduced mobility. (e) Already within t_m = 5 ms, the proton magnetization has essentially equilibrated, as can be inferred from the equivalence of the silhouette of the 2D spectrum with the 1D ^{13}C spectrum. This means that the hard and soft regions detected in the spectrum of (d) have typical smallest diameters of less than 5 nm. (f) t_m = 1 ms. ^{1}H spin diffusion is proceeding, but not yet close to equilibration. This sets lower limits for the size of the heterogeneities.

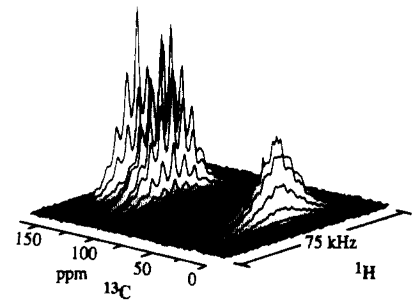

Figure 5. WISE-NMR spectrum of polycarbonate, CP contact time of 0.2 µs, ν_r = 4.5 kHz. The phenyl signals exhibit pronounced ^{1}H spinning sidebands, due to the phenyl flip motion, while the methyl protons show a simple ^{1}H line, with a width of 20 kHz.

sequence,[24] with a considerable phenyl signal at 7 ppm. The ^{13}C CP MAS TOSS spectrum is shown in Figure 4c. The results of these standard NMR methods seem to indicate homogeneity of the dynamics. On the other hand, some hints at dynamic heterogeneities have been found in other NMR studies.[20,21] These dynamic heterogeneities are definitely proved by the 2D WISE spectrum of Figure 4d, which clearly shows that the major portion of the PVME is mobile, while a considerable fraction of the PS exhibits neither significant motional averaging in the proton line width nor short $T_{1\rho}$ relaxation times. This indicates that most of the PS units move with rates below 10 kHz, although the blend is more than 50 K above its DSC glass-transition temperature. Portions of the PS that possess intermediate or high mobilities are detected in the cusps of the ^{1}H line shapes of the PS signals. The WISE spectrum demonstrates that a wideline spectrum as shown in Figure 4a must not necessarily imply homogeneity of a blend on a subnanometer scale.[25]

In fact, the approximate diameter of the regions showing different dynamic behavior can be determined as described above, by ^{1}H spin diffusion before the cross polarization. From Figure 4e, which was taken with t_m = 5 ms, it is immediately apparent that after 5 ms of spin diffusion the silhouette of the spectrum has changed drastically. It is now identical to the 1D ^{13}C spectrum, which means that the proton spin diffusion has eliminated the differences in ^{1}H line shapes. This indicates that the magnetization has essentially equilibrated within 5 ms, while a mixing time of 1 ms is clearly too short for equilibration to occur (cf. Figure 4f). After 5 ms of spin diffusion, the magnetization has a mean absolute displacement from one phase ($x < 0$) into the other ($x > 0$)[26,27] of

$$\langle |x| \rangle = (D_{\mathrm{eff}} t_m \pi / 4)^{12}$$

where D_{eff}, the effective spin diffusion coefficient, is given by

$$D_{\mathrm{eff}}^{1/2} = (D_{\mathrm{PS}} D_{\mathrm{PVME}})^{1/2} / (D_{\mathrm{PS}}^{1/2}/2 + D_{\mathrm{PVME}}^{1/2}/2)$$

From comparisons with the diffusion coefficients established in systems with well-known domain sizes and similar proton line widths,[28] we estimate values of $D_{\mathrm{PS}} = 0.5 \pm 0.2$ nm^2/ms and $D_{\mathrm{PVME}} = 0.1 \pm 0.05$ nm^2/ms. For t_m = 5 ms this yields $\langle |x| \rangle = 0.9 \pm 0.3$ nm. In lamellar systems, equilibration in a domain of diameter d has essentially occurred when $\langle |x| \rangle \approx d/2$. For cylindrical or spherical domains[29] of diameter d, 85% of complete exchange is already reached for $\langle |x| \rangle \approx d/4$.[27] In the case of arbitrarily shaped domains, their smallest diameters are most relevant for the spin diffusion process. Thus, from the 2D WISE spectra, as well as one-dimensional dipolar-filter and spin-diffusion data, the smallest diameter of a typical heterogeneity in the PVME/PS system at 320 K is estimated to be 3.5 ± 1.5 nm. Note that in spite of such small sizes of the heterogeneities, significant differences in molecular mobility are clearly demonstrated by the spectrum in Figure 4d. All these findings prove that the system is neither homogeneous nor strictly phase separated, but in fact *nano-heterogeneous*.

Note that in the experiments for different mixing times always the same carbon atoms are detected; in fact, the projections on the ^{13}C axis are the same for all three WISE spectra shown in Figure 4.

Local Motion: Phenyl Flip in Polycarbonate. The spectroscopic relevance of the ω_1 dimension becomes particularly obvious in case of restricted molecular motions, in particular rotations about a single axis. Then, spinning sidebands can appear in the ^{1}H dimension. Characteristic broad spinning sidebands are found for flipping phenyl rings, which have been characterized in detail by deuteron[30] and ^{13}C NMR spectroscopy.[31] These proton spinning sidebands can be understood by considering that the intermolecular dipolar interactions are weakened, while the dipolar interactions of the phenyl protons along the flip axes are unchanged, and these relatively isolated proton pairs yield spectra with spinning sidebands. As an experimental example, Figure 5 shows the spectrum of bisphenol A polycarbonate at a rotation frequency of 4.5

kHz. The sidebands for the flipping phenyl rings are clearly seen, while the methyl protons exhibit only a simple proton line narrowed to 20 kHz by the methyl rotation and the phenyl flips.

Thus, the WISE method can detect phenyl flips in unlabeled samples in a straightforward way, in some respects similar to the experimentally much more demanding separated local field technique with MAS.[11]

Summary and Outlook

The heteronuclear 2D WISE experiment described in this paper allows the correlation of structure and mobility to an extent that in practice was so far achievable only by ^{2}H NMR spectroscopy on selectively labeled samples. In addition, the experiment with ^{1}H spin diffusion can provide information on the spatial arrangement of the regions of different mobility. The WISE experiment is easy to implement and widely applicable. Usually, overnight data acquisition provides a sufficient signal-to-noise ratio. The parameters to be adjusted in addition to standard CP-MAS spectroscopy are few and vary only slightly between samples. The 2D data processing is quite simple and can be accomplished in less than 3 min (VAX 3200 workstation). We are hopeful that the WISE technique will find wide application to a large variety of multicomponent polymer systems.

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