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polymers are generally characterized by a distribution of motional frequencies, this assumption is expected to have a small effect on the reported integrals.[39]

(27) SAXS measurements of lamellar thickness and diffuse phase boundary thickness were carried out by analyses described in previous communications.[1,8] For the present study, bulk polymerized samples prepared from unlabeled butanediol[28] were employed in the SAXS studies. The samples were molded under vacuum at 180 °C and 4000 psi and slow cooled under pressure. The urethane exchange reaction is rapid at this temperature[17,18] and should correct for any nonrandom sequence length distribution which may have resulted during polymerization.[29,30]

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Characterization of Heterogeneous Polymer Blends by Two-Dimensional Proton Spin Diffusion Spectroscopy

Techniques providing information on disorder in solids are of particular importance for the study of synthetic polymers and of biopolymers. The physical properties of polymer blends depend to a large extent on miscibility and on the resulting heterogeneous structure,[1-3] which often results in new interesting mechanical properties of the blends. Disorder has been studied by traditional techniques such as diffraction methods,[4-8] thermal analysis,[9] and electron microscopy.[10] It has also been recognized that spin diffusion in nuclear magnetic resonance can provide information on heterogeneity of polymers.[11-18] Spin diffusion is induced by the dipolar interaction of nuclear spins and leads to a transfer of magnetization between neighboring spins. Because of the $1/r_{ik}{}^6$ distance dependence of the spin diffusion rate,[19] magnetization transfer is restricted to close neighborhood and delivers information on the spatial proximity of different molecules in a solid.

It is well-known that spin diffusion is of central importance for relaxation in solids by providing relaxation pathways via efficient relaxation centers like paramagnetic inpurities[19,20] and rotating methyl groups.[11-14] Polymeric systems are frequently heterogeneous either with respect to local order (e.g., crystalline and amorphous domains), leading to different mobility of the polymeric chains, or with respect to chemical composition in polymer blends. In heterogeneous systems, spin diffusion between components in different domains is strongly dependent on domain size, and the measurement of cross-relaxation between different domains provides insight into the domain structure of polymers.[13-15]

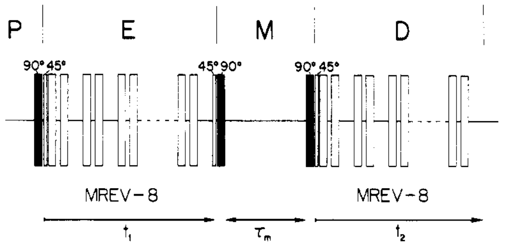

Figure 1. Pulse sequence for 2D proton spin diffusion spectroscopy with magic angle sample spinning. P, preparation by a $\pi/2$ pulse; E, evolution for time t_1 under MREV-8 multiple-pulse decoupling; M, spin diffusion during mixing time τ_m; D, detection in the presence of MREV-8 multiple-pulse decoupling.

In the case that the domains differ in mobility and correspondingly in their transverse relaxation rates, the spin diffusion rate between domains can be measured by the Goldman–Shen experiment[21] or by modified versions of it, including multiple-pulse line-narrowing sequences.[22,23] A more direct approach is possible if the resonance lines of the various components in the domains are spectrally resolved. Then selective polarization transfer experiments can be applied for the measurement of the spin diffusion rate. This is particularly easy for heteronuclear spin systems such as ^{1}H and ^{19}F[24-26] or for nuclear species with large chemical shift ranges such as ^{13}C. In the latter case, however, isotopic enrichment is necessary to render spin diffusion measurable[27] unless the system has exceptionally slow spin–lattice relaxation so that the spin memory is preserved for a sufficiently long time.[28,29] For practical measurements the techniques of two-dimensional (2D) spectroscopy[30,31] are predestinate. They permit high spectral selectivity and the simultaneous exploration of all cross-relaxation pathways.

In this communication we propose the usage of proton spin diffusion in a two-dimensional (2D) spectroscopy experiment for the study of heterogeneity. Because of the larger gyromagnetic ratio and because of the higher natural abundance, proton spin diffusion is faster than carbon-13 spin diffusion by orders of magnitude. Typical time constants are 100 μs to 10 ms. Even for very short spin–lattice relaxation times, spin diffusion among protons can easily be observed.

A handicap of protons in this application is their small chemical shift range paired with very strong homonuclear dipolar interactions which entirely mask the different chemical shifts. It turns out, however, that by a combination of homonuclear multiple-pulse decoupling and magic angle sample spinning a sufficient resolution can be attained to resolve the relevant chemical shifts in many systems of practical interest.[32-34]

The experimental technique is an extension of the well-known two-dimensional (2D) exchange experiment.[30,31] The pulse scheme is shown in Figure 1. After preparation of transverse magnetization by a $\pi/2$ pulse, the precession in the presence of multiple-pulse decouping labels the magnetization components by their isotropic chemical shifts. A further $\pi/2$ pulse restores longitudinal magnetization which may diffuse in the following mixing time of length τ_m. A third $\pi/2$ pulse is used to monitor the diffusion process. The precessing magnetization, again in the presence of a multiple-pulse sequence, is finally de-

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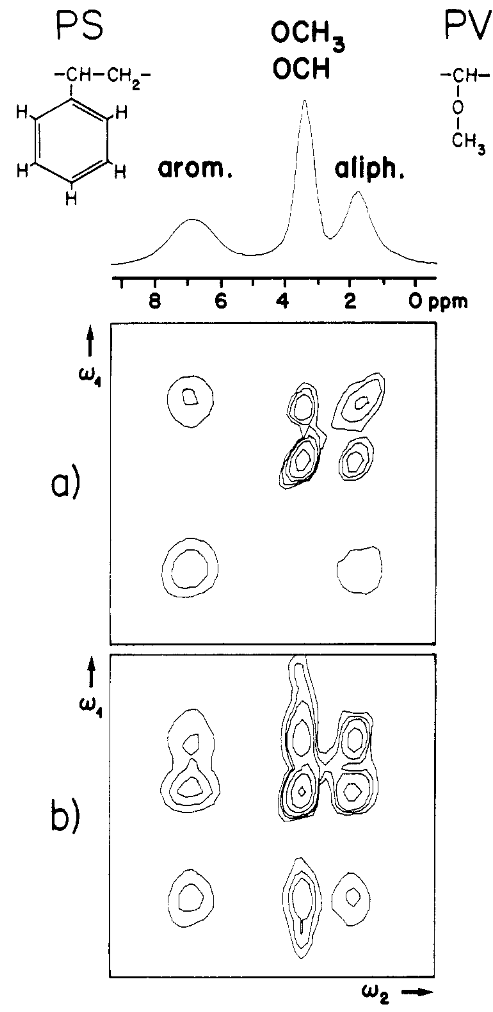

Figure 2. Two-dimensional proton spin diffusion spectra of blends of polystyrene and poly(vinyl methyl ether): (a) cast from chloroform; (b) cast from toluene. Note the absence of cross-peaks between signals belonging to different polymers when cast from chloroform in (a) while strong cross-peaks appear in (b) in the blend cast from toluene. The magic angle spinning frequency was 2.8 kHz, the temperature was 328 K, and the mixing time τ_m = 100 ms. The spectra were recorded on a Bruker CXP300 spectrometer.

tected and treated according to standard procedures of 2D spectroscopy.

An MREV-8 pulse sequence[35,36] proved efficient for line narrowing (sequence of $\pi/2$ pulses: $x, y, y, -x, x, -y, -y, -x$) with $\pi/2$ pulses of 2 μs and windows between the pulses of 1 and 4 μs, leading to a chemical shift scaling factor of 0.51. The effective precession of the magnetization occurs about the axis $2^{-1/2}(\mathbf{e}_z - \mathbf{e}_x)$ in the rotating frame. $(\pi/4)_{\pm y}$ pulses are needed before and after the multiple-pulse train to place the magnetization perpendicular to the effective rotation axis to prevent spin locking. The $(\pi/2)_x$ pulse starting the mixing period is phase-alternated ($\pm\pi/2$) together with the receiver reference frequency to suppress leakage of unwanted transverse magnetization. Synchronization of the multiple-pulse sequence with the magic angle sample spinning proved to be unessential.

For demonstration of the technique, it is applied to the study of mixtures of atactic polystyrene (PS) (supplied by BASF) and atactic poly(vinyl methyl ether) (PVME) obtained from Aldrich-Chemie (Steinheim), BRD. Both polymers are disperse with respect to molecular weight. The sample of PS is characterized by M_η = 279 000 (toluene, 25 °C) and M_w/M_n = 2.5, and the sample of PVME by M_η = 53 500 (benzene, 30 °C) and $M_w/M_n \sim 2.0$ as estimated from GPC measurements. The blending was achieved by precipitation from a homogeneous ternary solution of the two polymers in chloroform or toluene (containing 2.5% of each polymer) in a large excess of cooled (−60 °C) petroleum ether. The precipitate was filtered off and vacuum dried for 48 h. The mole ratio of monomeric units [PS]/[PVME] in the mixture was 0.61. It is well-known from thermal analysis[37,38] and from proton NMR relaxation studies[39] that the physical properties of the blends depend on the solvent from which they are precipitated or from which films are cast.

The 2D proton spin diffusion spectra of the two blends are shown in Figure 2. The one-dimensional spectrum included in Figure 2 demonstrates resolved lines for the aromatic protons of PS at 6.9 ppm and for the methyl and methine protons of PVME at 3.5 ppm while the methylene proton signals of both species overlap at 1.9 ppm. The residual line widths are caused by the spread in isotropic chemical shifts due to chemical and conformational inequivalence and packing effects as well as by incomplete dipolar decoupling. The narrow central line profits from the enhanced mobility of the methoxy group in PVME.

Figure 2a shows that the cross-peaks between the aromatic PS protons and the methyl and methine PVME protons are missing when the blend is cast from chloroform. This indicates the absence of spin diffusion between the two polymers and there is no evidence for mixed domains in the blend. However, when cast from toluene, strong cross-peaks become apparent in Figure 2b between the above-mentioned protons, indicating the existence of mixed domains in which the component polymers are in close contact on a microscopic scale.

The question remains whether it is possible to deduce more quantitative information from the intensity of the cross-peaks. By using short mixing times where the initial rate approximation can be applied it is possible to measure the spin diffusion rates which may be interpreted in terms of a domain model. For mixing times long compared to the spin diffusion time, but short with respect to T_1 (typically $\tau_m \simeq$ 100 ms), the system reaches an internal equilibrium and the off-diagonal peaks assume their maximum relative amplitudes which are indicative for the fraction of the components in the various domains.

We use in the following a model of a polymer blend with N_A moles of component A and N_B moles of component B which exhibits three coexisting phases: phase a with pure component A, phase b with pure component B, and a mixed phase c with a composition of $f_A N_A$ moles of A and $f_B N_B$ moles of B. Such a three-phase model is supported by differential thermal analysis (DTA) in the case of PS and PVME mixtures.[37]

We treat at first a simplified situation where each of the two components A and B show a single resonance line. The signal intensities in the 2D spectrum for a sufficiently long mixing time (τ_m) can then be computed as follows. Phases a and b contribute exclusively to the diagonal peaks with contributions proportional to $(1 - f_A)N_A$ and $(1 - f_B)N_B$, respectively. The A magnetization of phase c before spin diffusion takes place is proportional to $f_A N_A$. It is distributed during the mixing time between the two components in proportion to the number of moles of A and B in phase c. Thus the corresponding contribution to the diagonal peak intensity I_{AA} is proportional to $(f_A N_A)^2/(f_A N_A + f_B N_B)$ and the cross-peak intensity I_{AB} is given by $f_A N_A f_B N_B/(f_A N_A + f_B N_B)$. Similar expressions for the B magnetization lead to the following total peak intensities:

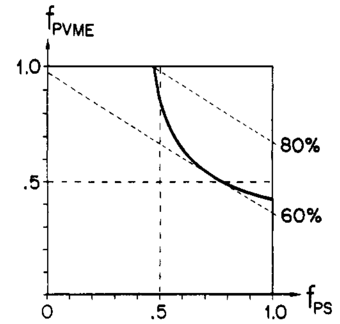

Figure 3. The solid curve represents the possible fractions of polystyrene (f_{PS}) and of poly(vinyl methyl ether) (f_{PVME}) in the mixed phase compatible with the measured peak intensities of the 2D spectrum in Figure 2b for the blend cast from toluene. The mixed phase must contain 60–80% of the total polymer (dashed limits).

$$I_{AA} = N_A - \frac{f_A f_B N_A N_B}{f_A N_A + f_B N_B}$$

$$I_{BB} = N_B - \frac{f_A f_B N_A N_B}{f_A N_A + f_B N_B}$$

$$I_{AB} = I_{BA} = \frac{f_A f_B N_A N_B}{f_A N_A + f_B N_B}$$

From these intensities it is not possible to fully determine both unknown concentrations of the mixed phase; however, the intensity ratio

$$\xi = \frac{I_{AB}}{I_{AA} + I_{BB}} = \frac{f_A f_B}{(r + 1)(f_A + f_B/r) - 2 f_A f_B} \qquad (r = N_A/N_B)$$

permits limits to be set upon the fractions f_A and f_B.

Rather than discussing in more detail this simplified situation, we treat the case of the PS/PVME mixture where both components show two distinct resonance lines between which additional spin diffusion occurs. A similar, although more elaborate expression can be derived from the signal intensities:

$$\xi = \frac{I_{AB}}{I_{AA} + I_{BB}} = \frac{240 f_A f_B}{(256 + 300r - 481 f_B) f_A + (192/r + 225) f_B}$$

The intensities refer here to the diagonal and cross-peaks of the aromatic PS protons (A) and the methine and methyl protons of PVME (B). With the mole ratio $r = 0.61$ and with the measured intensity ratio $\xi = 0.22$ for the blend obtained from toluene solution, the values for f_A ($=f_{PS}$) and f_B ($=f_{PVME}$) compatible with the spin diffusion measurement are represented by the curve in Figure 3 showing the limits $0.47 \leq f_A \leq 1$ and $0.42 \leq f_B \leq 1$. The percentage f of the total polymer contained in the mixed phase

$$f = \frac{f_A N_A + f_B N_B}{N_A + N_B} = \frac{r f_A + f_B}{1 + r}$$

is however better determined than the individual fractional contributions and lies between 60% and 80% as indicated by the dashed limits in Figure 3.

In conclusion, the advantage of proton spin diffusion for the investigation of heterogeneity is based on the high sensitivity and on the fast spin diffusion. Although the spectral resolution is restricted, two-dimensional spin diffusion measurements are promising for application to a wide class of systems. The same technique can also be used with other abundant nuclei. Particularly promising seems to be fluorine-19 where the larger chemical shift range eases the spectral distinction of the various species. While this 2D experiment requires spectral resolution, it can also be applied when the domains exhibit similar relaxation times, a situation which cannot be handled by the Goldman–Shen experiment. The 2D experiment described is designed for a semiquantitative characterization of heterogeneity. At present investigations are in progress for the design of fully quantitative spin diffusion experiments in polymer systems with spectrally resolved resonance lines.

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Registry No. PS (homopolymer), 9003-53-6; PVME (homopolymer), 9003-09-2.

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