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Polymer additives mixture analysis using pulsed-field gradient NMR spectroscopy

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ABSTRACT: The analysis of mixtures is a problem commonly faced in analytical chemistry. In this work, pulsed-field gradient NMR (PFG-NMR) experiments were used to analyze mixtures of polymer additives and simple polymer solutions. PFG-NMR experiments were also utilized to determine diffusion coefficients of the individual components of a mixture and in this way facilitate resonance assignments. This strategy is particularly useful for molecules containing isolated protons that are not amenable to the standard two-dimensional NMR experiments based on *J*-coupling. PFG-NMR was also used to edit the NMR spectra of polymer solutions by eliminating the resonances of fast-diffusing components such as low molecular weight additives or residual solvent. Diffusion ordered spectroscopy (DOSY) was used for the analysis of the PFG-NMR data. The DOSY method produces a two-dimensional spectrum that correlates chemical shift with the calculated diffusion coefficient, and simplifies the analysis of many complex mixtures. For well resolved resonances, the correct diffusion coefficient is unambiguously determined. The DOSY analysis was able to resolve the diffusion coefficients of most of the components in the mixtures examined. However, in some cases of overlapped resonances and components with similar diffusion coefficients, a single diffusion coefficient was determined which was the weighted average of the two components.

KEYWORDS: NMR; pulsed-field gradient; diffusion ordered spectroscopy; polymers; polymer additives; mixture analysis

INTRODUCTION

Pulsed-field gradient nuclear magnetic resonance (PFG-NMR) spectroscopy is a well established method for the measurement of self-diffusion coefficients.[1–3] This methodology is a powerful analytical tool because it combines the high specificity and information content of NMR spectroscopy with the size selectivity of diffusion coefficients. The added information content of relative molecular size can be of enormous benefit in the analysis of complex mixtures.[1,4–6] A variety of interesting approaches have been used to extend this methodology by incorporating PFG-NMR into two-dimensional NMR experiments,[7–9] or to utilize one-dimensional spectral editing methods in combination with PFG-NMR.[10,11] An added advantage of PFG-NMR is that it can be employed to simplify complex NMR spectra. This simplification is achieved by attenuation of resonances based on the differential diffusion properties of components present in the mixture. One of the more obvious and useful applications of this approach is the use of PFG-NMR for suppression of the water resonance in the ^{1}H NMR spectra of aqueous solutions.[1,12] Resonance suppression can be achieved through careful optimization of experimental parameters including the gradient amplitude, gradient duration or the length of the diffusion period. In this paper we demonstrate the utility of PFG-NMR as a tool for the spectral analysis of mixtures of polymer additives with different diffusion coefficients.

EXPERIMENTAL

2,6-Di-*tert*-butyl-4-methylphenol (BHT), deca-1,9-diene and tetramethylsilane (TMS) were obtained from Aldrich Chemical. Irganox 1330, Irganox 1098 and Tinuvin P were supplied by Ciba Geigy. Polystyrene was obtained from Polysciences ($M_p = 113\,000$, $M_w/M_n = 1.06$). Polyethylene was synthesized by S. Arthur at DuPont.

Samples were prepared by dissolving 1–20 mg of the components in chloroform-*d* ($CDCl_3$) or 1,1,2,2-tetrachloroethane-d_2 (TCE-d_2). The samples were then injected into a 270 µl cell. The cell was placed into a 5 mm NMR tube containing the same deuterated solvent. For clarity, the samples described in the Results and Discussion section are identified numerically as follows: sample 1, Irganox 1098, BHT, Tinuvin P in TCE-d_2; sample 2, Irganox 1098, Irganox 1330, Tinuvin P in

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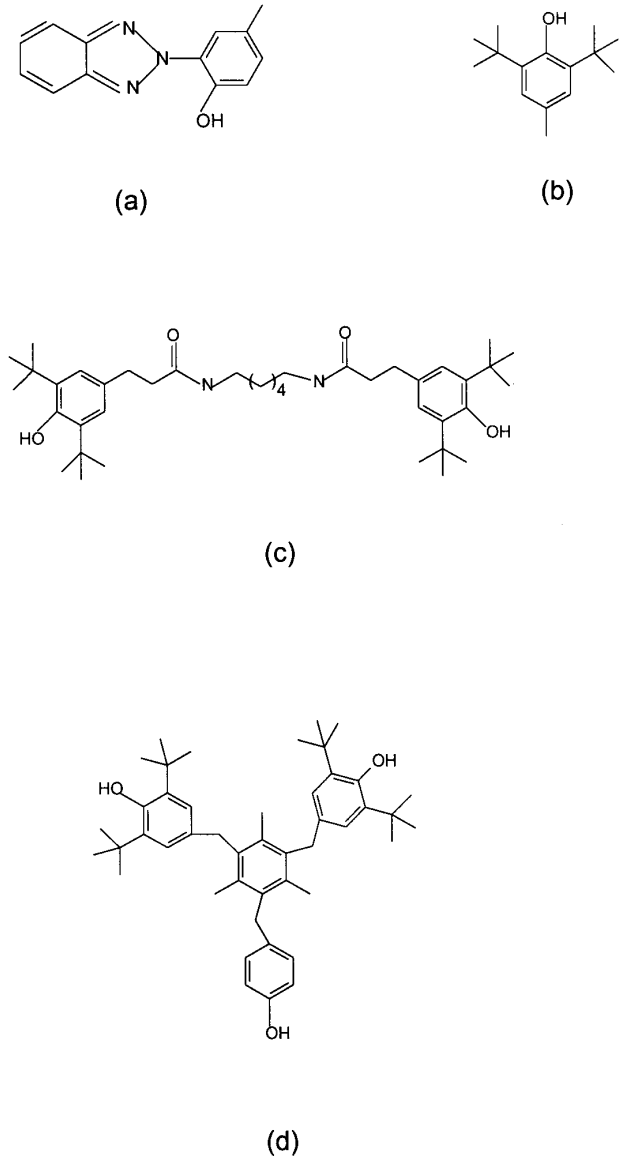

Figure 1. Structures, names and molecular weights of the polymer additives used: (a) Tinuvin P, M_n 225; (b) BHT, M_n 220; (c) Irganox 1098, M_n 637; (d) Irganox 1330, M_n 775.

TCE-d_2; sample 3, polystyrene, TMS, trace water in TCE-d_2; sample 4, polyethylene, deca-1,9-diene in $CDCl_3$.

All NMR spectra were measured at 298 K with a Bruker AM360 NMR spectrometer using a 5–mm *z*-gradient Bruker inverse probe with a coil constant of 0.057 T m^{-1} A^{-1}. The rectangular gradient pulses were generated using a PC-controlled 25 A gradient driver built by Digital Specialists (Chapel Hill, NC, USA). The timing of the gradient pulses was controlled in the spectrometer pulse sequence by generating trigger pulses at the spectrometer console, which were delivered to the PC. Diffusion coefficients were extracted from a series of ^{1}H NMR spectra measured using the bipolar pulse longitudinal encode–decode (BPPLED) pulse sequence as a function of gradient amplitude.[13] In each experiment, 2 ms gradient pulses and a diffusion delay of 0.5–1.0 s were used with a 15 ms delay at the end of the pulse sequence for the elimination of residual eddy currents. The amplitudes of the gradient pulses ranged from 0.026 to 0.30 T m^{-1}, with an approximately 90% decrease in the resonance intensity achieved at the largest gradient amplitudes. For most experiments, 12–15 different gradient amplitudes were used in each experiment. The spectral editing experiments, the results of which are shown in Fig. 4 and 5, used 20 different gradient amplitudes in each experiment. The FIDs were acquired with an Aspect 3000 computer and transferred to a Silicon Graphics workstation for data processing using Felix version 95.0 (Biosym). The modulation of the NMR signal amplitude in the BPPLED pulse sequence is related to gradient strength as described by the equation

$$I = I_0 \exp\left[-D(\Delta - \delta/3 - \tau/2)\gamma^2 g^2 \delta^2\right]$$

where I_0 is the intensity of the signal in the absence of the gradient, γ is the gyromagnetic ratio, Δ is the length of the delay during which diffusion occurs, g and δ are the amplitude and duration of the gradient pulses, respectively, τ (1.4 ms in our experiments) is a short delay between the gradient pulse and the subsequent r.f. pulse and D is the diffusion coefficient. In this pulse sequence, the magnetization undergoes T_1 relaxation during the diffusion and eddy current delay times and T_2 relaxation during the time period defined by $4(\delta + \tau)$. Diffusion coefficients were extracted from the NMR spectra with the diffusion-ordered spectroscopy DOSY methodology.[14] The data inversion program SPLMOD was used to calculate the diffusion coefficients.[15,16] The result of the DOSY method of analysis is a two-dimensional spectrum with NMR chemical shift along one axis and calculated diffusion coefficients along the other.

RESULTS AND DISCUSSION

PFG-NMR can be used to identify in a mixture those components that have similar (or overlapping) chemical shifts but different diffusional properties. Commercial polymers generally contain a mixture of additives, including antioxidants, UV stabilizers and slip agents. It is often of interest to determine or verify the components present. This determination is performed by extracting the polymer of interest using methanol or chloroform and analyzing the resulting mixture of additives and polymer oligomers. These mixtures frequently contain compounds with similar functional groups and overlapping resonances, or CH_n groups separated by non-protonated heteroatoms such as may occur in esters, ethers, polycyclic heteroaromatics and amides. Without authentic samples of the additives, total identification can be difficult using routine NMR correlation methods. However, these additives often cover a range of molecular weights and sizes, making them amenable to separation and identification by PFG-NMR. Two

examples of polymer additive mixtures will be discussed in this paper. The chemical components of these mixtures and their molecular weights are shown in Fig. 1. In addition, results are presented for polystyrene dissolved in TCE-d_2 and for a mixture of polyethylene and deca-1,9-diene in $CDCl_3$.

Fig. 2 shows the DOSY spectrum of sample 1, which contains Tinuvin P, BHT and Irganox 1330, with the resonances of each component indicated in the single-pulse ^{1}H NMR spectrum drawn at the top of the DOSY contour plot. Each of the resonances in the spectrum has associated with it a diffusion coefficient, summarized in Table 1. Additional DOSY correlations from the solvent, TCE-d_2, and silicone grease contaminant can be observed. The errors reported in Table 1 are fitting errors, as these results were calculated from a single experimental trial. Comparison of the diffusion coefficients calculated for the resolved components in Table 1 indicate that the fitting errors underestimate the experimental error which is likely in the range 2–3%.

Because the diffusion coefficients of the components of sample 1 are significantly different, most of the resonances in the DOSY spectrum can be identified by simple inspection of the peaks which are aligned with a particular diffusion coefficient, or horizontal row, in the contour plot. This differentiation is especially useful when an unknown component contains one or more isolated protons, as is the case with these compounds, since singlet resonances often hinder the process of complete spectral assignment and identification.

Table 1. Diffusion coefficients of the individual components of sample 1

Sample 1 for Fig. 2	^{1}H chemical shift (ppm)	Diffusion coefficient $\times 10^6$ (cm^2 s^{-1})
Irganox 1330	1.34	1.86 ± 0.02
BHT	1.61	3.63 ± 0.01
BHT	2.30	3.01 ± 0.05
Irganox 1330	2.33	2.13 ± 0.02
Tinuvin P	2.44	4.10 ± 0.02
Irganox 1330	4.02	1.78 ± 0.01
Irganox 1330	4.97	1.90 ± 0.05
BHT	5.03	3.55 ± 0.01
TCE (solvent)	6.00	7.42 ± 0.01
Irganox 1330	6.88	1.86 ± 0.02
BHT	6.98	3.63 ± 0.03
Tinuvin P	7.13	4.26 ± 0.05
Tinuvin P	7.14	4.27 ± 0.02
Tinuvin P	7.20	4.30 ± 0.02
Tinuvin P	7.22	4.27 ± 0.03
Tinuvin P	7.53	4.37 ± 0.01
Tinuvin P	7.97	4.36 ± 0.02
Tinuvin P	8.24	4.40 ± 0.03
Tinuvin P	11.17	4.45 ± 0.02

There is some scatter in the exact diffusion coefficients determined for the different protons of each molecule. This scatter can be reduced if desired by using a greater number of gradient increments in the diffusion

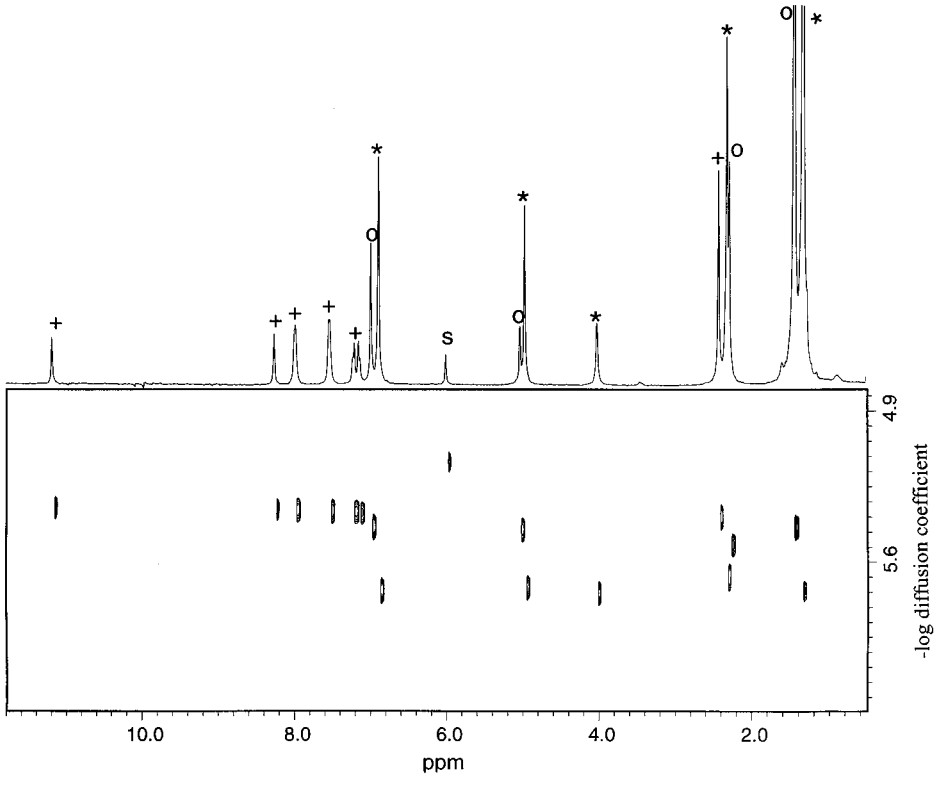

Figure 2. ^{1}H DOSY spectrum of sample 1 showing resolution of the individual components along the chemical shift and diffusion dimensions. The single pulse ^{1}H NMR spectrum is shown along the top of the 2D DOSY plot. The resonances of the different components are as follows: +, Tinuvin P; *, Irganox 1330; ○, BHT.

dimension and by signal averaging more scans at each increment to improve the signal-to-noise ratio. Improvements in spectral resolution, either by improved digital resolution or from the use of higher magnetic fields, will be translated into improved resolution in the diffusion dimension for overlapped resonances. The effects of resonance overlap on the diffusion coefficients calculated with SPLMOD can be seen by comparison of the diffusion coefficients determined for the closely spaced resonances of BHT at 2.30 ppm (3.01×10^{-6} cm^2 s^{-1}) and Irganox 1330 at 2.33 ppm (2.13×10^{-6} cm^2 s^{-1}) with those determined using the better resolved resonances of these components. Although these resonances are resolved in the one-dimensional spectrum plotted along the top of Fig. 2, the diffusion coefficients calculated using the resonances at 2.30 and 2.33 ppm produce diffusion coefficients of BHT and Irganox 1330 that are too fast or too slow, respectively because of overlap in the integrals of these resonances and the use of a single exponential fit for the determination of these diffusion coefficients.

The DOSY spectrum of a different additive mixture, sample 2, is shown in Fig. 3. Again the single-pulse ^{1}H NMR spectrum of this mixture is shown along the top of the 2D DOSY plot. Tinuvin P is well resolved from other peaks along the diffusion axis, but the Irganox components are not. Even though the two Irganox components of this mixture have different molecular weights, their shapes are different. Irganox 1098 has an extended linear shape whereas Irganox 1330 is star shaped. For two molecules of identical molecular weight, a star-shaped molecule should have a larger diffusion coefficient than a linear molecule. This expectation is in accord with the observation that the heavier but more globular Irganox 1330 has a diffusion coefficient which is experimentally indistinguishable from that of the lighter but more extended Irganox 1098. The shape difference compensates for the differences in molecular weight, and the diffusion coefficients measured for these two compounds are essentially identical.

Another interesting point to note in Fig. 3 is that the exchangeable OH protons (at 4.96, 5.08 and 11.15 ppm) have larger diffusion coefficients than the rest of the protons in their respective molecules. These OH protons are exchanging with the protons of water in the solvent during the diffusion period of the pulse sequence. Therefore, the diffusion coefficients determined from the OH resonances are a weighted average and are larger than those measured for the other non-exchangeable protons in the sample. This effect is a general phenomenon in PFG-NMR spectra.[17–19]

In cases where it is not necessary or desirable to determine numerically the diffusion coefficient, PFG-NMR allows the analyst to simplify mixture analysis through spectral editing based on the differential diffusional properties of the components of the mixture.[10–12] This approach has also been illustrated with sample 1 (Tinuvin P, BHT and Irganox 1330). The selective effect of gradient amplitude on resonance intensity can be seen from the spectra in the stacked

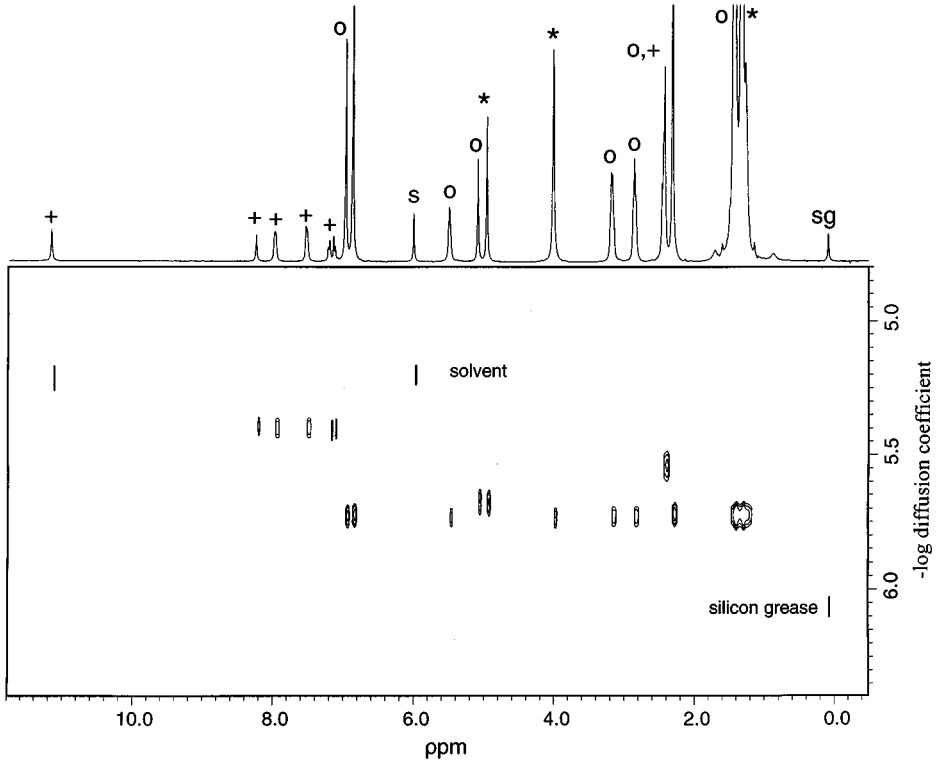

Figure 3. ^{1}H DOSY spectrum of sample 2 showing resolution of the individual components along the chemical shift and diffusion dimensions. The single pulse ^{1}H spectrum is shown along the top of the 2D DOSY plot. The resonances of the different components are as follows: +, Tinuvin P; *, Irganox 1330; ○, Irganox 1098. In addition, the solvent resonance (labeled S) and the silicone grease contaminant (labeled Sg) are indicated.

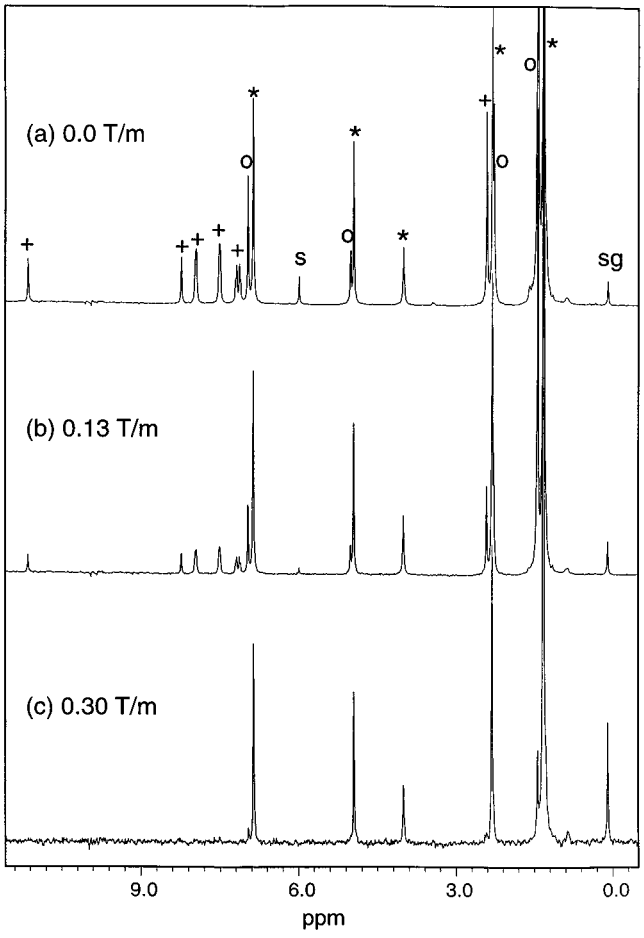

Figure 4. A stacked plot of selected individual single-pulse ^{1}H and BPPLED NMR spectra for sample 1. (a) Single-pulse ^{1}H NMR spectrum. The resonances of the different components are as follows: +, Tinuvin P; *, Irganox 1330; ○, BHT. BPPLED spectra are shown with gradient amplitudes of (b) 0.13 (c) 0.30 T m^{-1}.

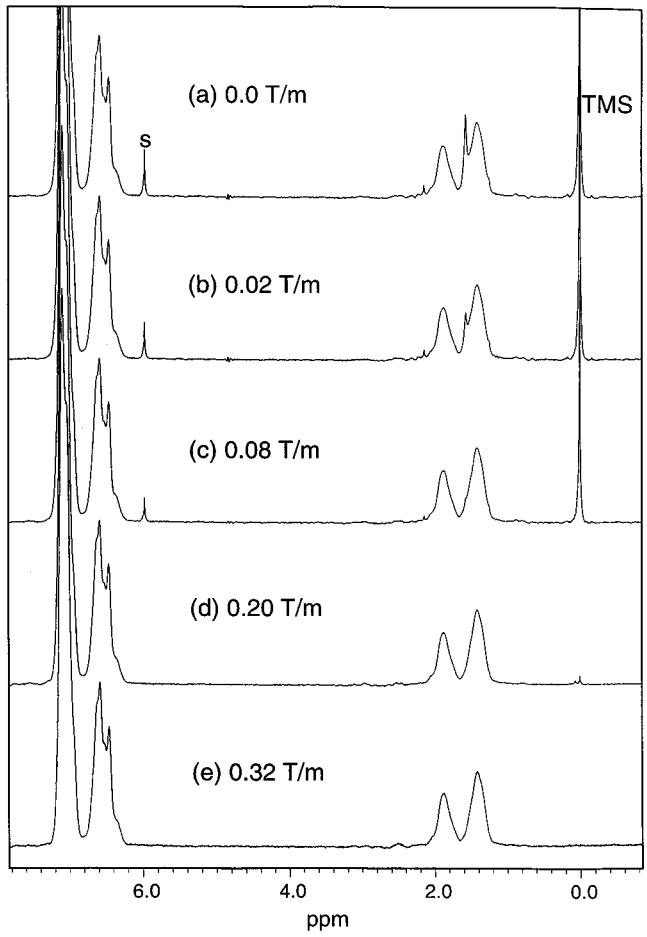

Figure 5. A stacked plot comparison illustrating spectral editing for the polymer sample of sample 3. (a) Single-pulse ^{1}H NMR spectrum and BPPLED spectra with gradient of strengths of (b) 0.02, (c) 0.08, (d) 0.20 and (e) 0.32 T m^{-1}.

plot in Fig. 4. At higher gradient amplitudes, the resonances of the faster diffusing components of the mixture have been eliminated from the spectrum, allowing the observation of a clean spectrum of the highest molecular weight component.

Similarly, Fig. 5 shows an example of spectral editing for a sample of polystyrene and TMS dissolved in TCE-d_2. Loss of magnetization due to T_1 relaxation during the diffusion delay is a potential problem when acquiring PFG-NMR spectra of polymers. However in this case, the losses of polymer magnetization due to T_1 and T_2 relaxation during the pulse sequence do not present a significant problem and ample signal is available for the determination of diffusion coefficients. The PFG-NMR spectrum was acquired using a gradient amplitude that eliminates the signals from the solvent, adventitious water and TMS, but not the polystyrene resonances. This gradient technique can be used to eliminate unwanted signals from the NMR spectrum of a polymer sample, such as those arising from residual monomers, small molecules remaining from unsuccessful grafting chemistry to the polymer and residual polymerization solvents.

Fig. 6 illustrates the DOSY spectrum of a mixture of polyethylene and deca-1,9-diene in chloroform-d_1. These results provide an example of how small molecules can be resolved in the presence of polymers. Most of the decadiene resonances occur along the diffusion axis at the point indicated with the arrow, whereas resonances of the polyethylene (PE), including some olefinic protons at about 5.3 ppm, occur at a much lower diffusion coefficient. The diffusion coefficient calculated for these olefinic protons is slightly faster than those determined from the other PE resonances. This resonance arises primarily from the unsaturated end groups of the polymer. Assuming that the end groups are equally distributed, on a molar basis the lower molecular weight polymers would have a higher percentage of olefinic end groups than the higher molecular weight components. Therefore, the measured average diffusion coefficient calculated from this resonance is weighted average with the faster diffusing, lower molecular weight components contributing relatively more on a molar basis than the higher molecular weight polymers.

In our hands, the SPLMOD analysis program did not separate the resonance at 1.35 ppm into a separate

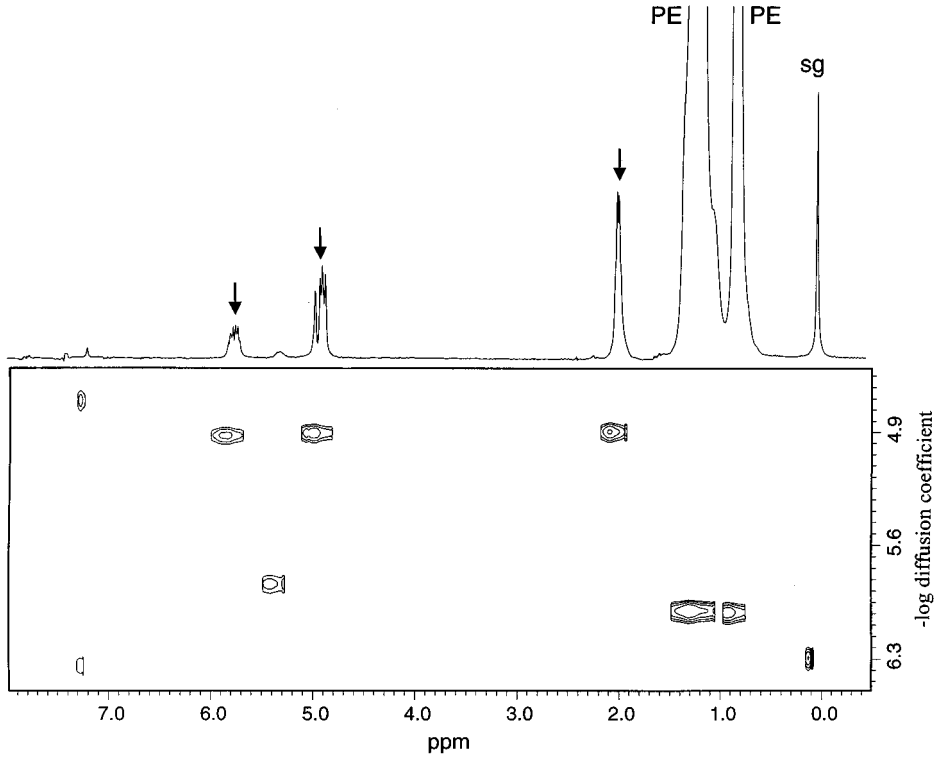

Figure 6. ^{1}H DOSY spectrum of sample 4 showing resolution of the individual components along the chemical shift and diffusion dimensions. The single-pulse ^{1}H NMR spectrum of the mixture is shown along the top of the 2D DOSY plot.

contribution from the polyethylene and the low molecular weight diene. This failure illustrates a general limitation of the DOSY approach in treating overlapping resonances with molecular weight distributions. Other researchers have found various solutions to address these problems, including, for example, the CONTIN approach of Johnson's group to polymers solutions,[14] the CORE method of Stilbs and co-workers[20,21] and the multivariate analysis approaches of Schulze and Stilbs[22] and Windig and Antalek.[23]

CONCLUSION

We have demonstrated the feasibility of using the DOSY method of NMR data analysis to separate the resonances of common polymer additives along the diffusion dimension and, more generally, to resolve small molecule resonances in the presence of polymers. In addition, spectral editing with PFG-NMR can be used to eliminate resonances of all but the highest molecular weight component (lowest diffusion constant) of a mixture, including elimination of residual solvent and monomer resonances in polymer NMR spectra.

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