

Diffusion-Ordered NMR Spectroscopy of Poly([ethylene-co-vinyl acetate]-graft-vinyl chloride) in Solution

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Two-dimensional nuclear magnetic resonance (2D-NMR) spectroscopy employed pulsed-field gradient (PFG) techniques has become one of the most important tools for studying the structure and dynamics of all types of chemical and biological compounds in solution states. Very recently, a newly developed 2D technique, diffusion-ordered 2D-NMR spectroscopy (DOSY) has generated significant interest because it produces NMR spectra of mixtures to be resolved on the basis of the size and shape of components present in the mixture.^{1,2} As the gradient strength increases, in DOSY experiments, signals decay exponentially according to the translational diffusion coefficients of individual molecules which largely depend on physical parameters like temperature, solvent viscosity, and size and shape of the molecule. Effective data inversions of the decay curves depending on the gradient strength produce a two-dimensional NMR spectrum that shows correlations between chemical shifts in the directly observed dimension and the calculated diffusion coefficients in the indirectly observed dimension.¹ There have been many reports suggesting its potential applications because this 2D experiment permits a noninvasive chromatographic separation of components in a mixture solution without need to any preliminary physical separation.³⁻¹¹ By coupling of DOSY to the other conventional NMR techniques, such as COSY-DOSY, INEPT-DOSY, HMQC-DOSY, HMBC-DOSY, and *etc.*, all structural units in a mixture can be examined simultaneously.^{1,12} DOSY NMR can also be used as a powerful tool to distinguish between the complexed and noncomplexed forms in a mixture of host and guest compounds due to the differences in their diffusion coefficients reflecting the changes in their size and mass accompanied by complex formation.^{6,13-15}

NMR spectroscopy is also an invaluable tool for the quantitative and qualitative analysis of polymers.¹⁶ Differing from relatively well resolved ¹³C NMR spectra of polymer solutions, proton NMR spectra are usually not well resolved due to the fast relaxation and molecular weight distributions of the polymers. This frequently makes it quite difficult to perform complete peak assignments in polymer mixture samples by ¹H NMR spectroscopy. DOSY NMR has been introduced to solve such kinds of problems in polymer mixture systems (*e.g.* polymer-polymer mixtures and polymer-additives mixtures).^{8,10,17,18} In this work, a new potential of the 2D-DOSY technique for the analysis of graft

copolymer solutions has been investigated by comparing the diffusional behavior of the target copolymer with the mixture of constituent polymers. By conventional ¹H NMR spectroscopy, some graft copolymers are not distinguished from the mixtures of their constituent polymers.

Experimental Section

A commercial graft copolymer ethylene-vinyl acetate-graft-vinyl chloride (EVA-g-VC, $M_w = 138000$, $M_w/M_n = 3.2$) manufactured by Shin Dai-Ichi Vinyl Corporation (Japan) containing 55 wt.% of EVA has been used. This polymer has hardness equivalent to ~50 part per hundred resins (phr) plasticizer can be obtained, and was synthesized by grafting vinyl chloride onto EVA copolymer. For a mixture sample, a commercial PVC (LG Chem. Korea, $M_w = 83000$, $M_w/M_n = 2.1$) polymer and EVA copolymer (Sumitomo, Japan, $M_w = 49000$, $M_w/M_n = 3.4$) were used. A soft PVC eraser with ~40 phr dioctylphthalate (DOP) as a plasticizer was used for a control experiment to separate the additive signals from the PVC peaks. Solutions of polymer mixture (PVC : EVA = 45 : 55 wt %) and graft copolymer in tetrachloroethane-*d*₂ containing 6 mg of samples in 1 mL of solvents were prepared and were heated to 373 K for a day. The control solution was prepared by dissolving 20 mg of eraser sample (PVC with DOP) in 1 mL tetrahydrofuran-*d*₈.

All NMR experiments were performed at 298 K on a Bruker Avance 600 spectrometer equipped with a Bruker 5mm micro-imaging PFG probe and a strong gradient amplifier, which provides a z-direction gradient strength of up to 200 G/cm. The temperature was maintained constant within ± 0.1 °C by means of the BVT-2000 unit. All DOSY experiments were performed using the bipolar pulse longitudinal eddy current delay pulse sequence (BPPLD).^{1,19} The spoil gradients were also applied at the diffusion period and the eddy current delay. Typically, a value of 0.5-1 ms was used for the gradient duration (δ), 100-120 ms for the diffusion time (Δ), and the gradient strength (g) was varied from 4 G/cm to 100-180 G/cm in 32-128 steps. Each parameter was chosen to obtain ~95% signal attenuation for the slowest diffusion species at the last step experiment. The pulse repetition delay (including acquisition time) between each scan was larger than 10 s. Data acquisition and analysis were performed using the Bruker xwinnmr software (version

3.5). The DOSY processing program as implemented in the xwinnmr was used to calculate the diffusion coefficients and to create two-dimensional spectra with NMR chemical shifts along one dimension and the calculated diffusion coefficients along the other.

Results and Discussion

Graft copolymerization has been used as a very important technique for modifying the chemical and physical properties of polymers to meet specialized industrial needs. In general, the formation of the graft copolymer can be confirmed with NMR, IR spectroscopy, and size-exclusion chromatography. In NMR spectroscopy, however, frequently it is very difficult to confirm the grafting due to the similarity of the NMR spectra with those of the polymer blends. In view point of this, 2D-DOSY NMR could be a valuable and potential technique to distinguish between graft copolymers and the polymer blends of their constituents since the translational diffusion coefficients reflect the changes in the shape and/or size of polymers.

In DOSY experiments using the BPPI.ED pulse sequence, the signal intensity is generally given as^{1,19}

$$I(q) = I_0 \exp[-Dq^2(\Delta - \delta/3 - \tau/2)] \quad (1)$$

where, I_0 is the intensity of the signal in the absence of the gradient, D is the translational diffusion coefficient, τ is the time between bipolar gradients, and $q = \gamma g \delta$ is the effective gradient where γ is the gyromagnetic ratio of the observed nucleus, g and δ are the amplitude and duration of the gradient pulses, respectively. By use of z -gradient, molecules can be spatially labeled, *i.e.* marked depending of their position in the sample tube, and if they move during the diffusion time (Δ) a second gradient is used to decode their new position. The receiver integrates over the whole sample volume and the result is an intensity attenuation of NMR signal depending on the diffusion coefficients of molecules in the sample as described in Eq. (1). A good and detailed review about diffusion and DOSY experiments can be found in elsewhere.¹

Figure 1(a) shows the 2D-DOSY spectrum (diffusion coefficient vs. ¹H chemical shift) of the plasticized PVC sample (eraser) with the single-pulse ¹H NMR spectrum drawn at the top of the DOSY contour plot. A typical diffusion decay curve for a DOP proton signal by varying the gradient strength is also shown in Figure 1(b). Since translational diffusion coefficients of all protons belonging to a single molecule also become identical, NMR signals from each component in a mixture appear parallel to the F_2 axis and are separated by each component on F_1 axis. Therefore, the results are similar to chromatographic separation. As shown in Figure 1(a), it is clear that the DOP and the solvent (THF) exhibited much larger diffusion coefficients than the PVC, as might be easily expected on the basis of their large differences in molecular sizes compared with the polymer. This implies that the NMR

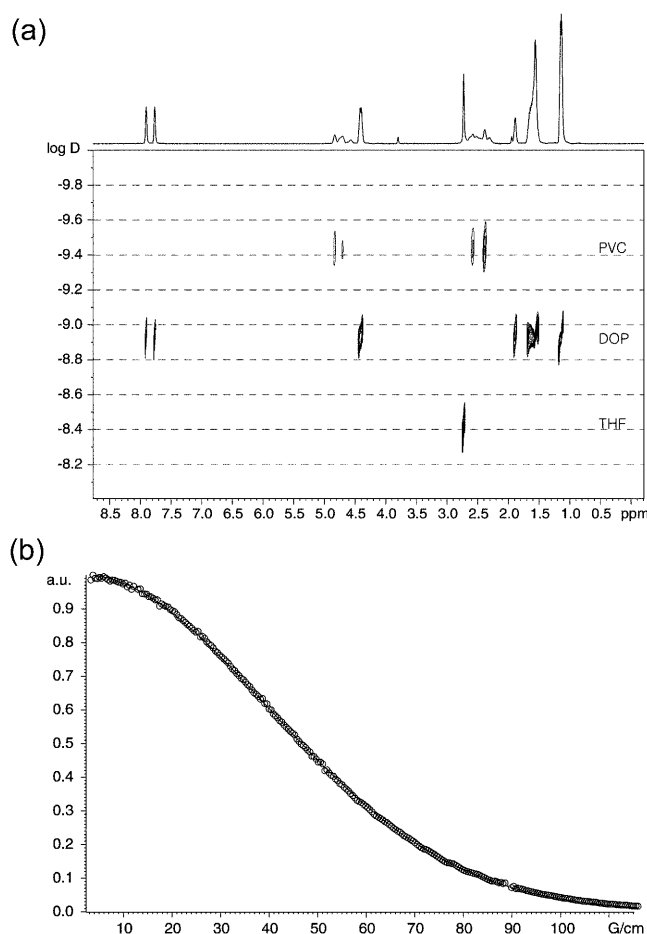


Figure 1. (a) ¹H DOSY spectrum of the eraser sample showing resolution of the individual components - PVC, DOP, and THF along the diffusion dimension and (b) diffusion decay curve for the DOP methyl proton peak (-1.1 ppm) by varying the gradient strength

signals of polymer additives can be identified from the polymer signals by DOSY technique without physical separation procedures. The resultant diffusion coefficients were 4.0×10^{-10} , 1.3×10^{-9} , and $4.1 \times 10^{-8} \text{ m}^2\text{s}^{-1}$ for the PVC, DOP, and THF signals, respectively. Because exact measurement of the diffusion coefficients is not the purpose of this experiment, the values shown in all Figures must be treated relatively.

We have next carried out the 2D-DOSY experiments on the graft copolymer and a mixture of PVC and EVA with composition of 45 : 55 wt %. Because two polymers, PVC and EVA, have different molecular weights and hydrodynamic radii, the NMR resonances in the DOSY spectrum can be identified by careful inspection of the peaks which aligned with a particular diffusion coefficient in the contour plot. The diffusion coefficient of the PVC was found to be smaller than that of the EVA by ~40% as shown in Figure 2(a), and the difference could be large enough to distinguish two components in 2D-DOSY spectra. In the case of the graft copolymer, however, all the NMR signals (from the graft copolymer) should have same attenuation patterns resulting in a single diffusion coefficient since both units

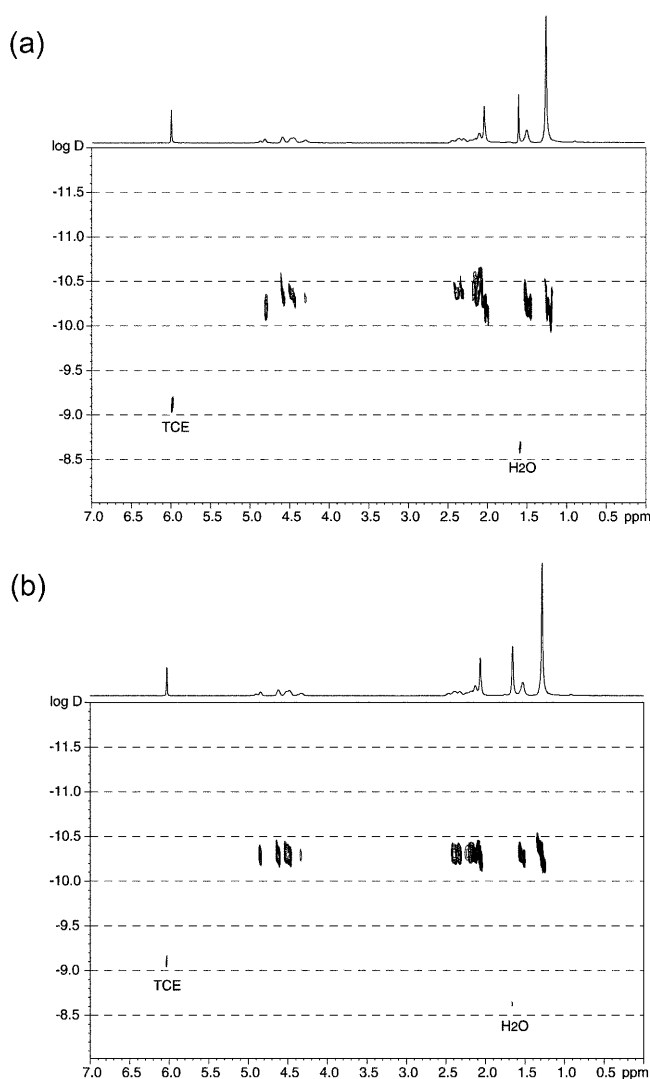


Figure 2. ^1H DOSY spectrum of (a) the polymer mixture of PVC and EVA, and (b) the graft copolymer.

(EVA and PVC) are present in a single molecule by grafting. Figure 2(b) shows that all NMR peaks from the graft copolymer appeared parallel to the x-axis with the diffusion coefficient of $5.1 \times 10^{-11} \text{ m}^2\text{s}^{-1}$. Although the 1D ^1H NMR spectra of the polymer mixture and the graft copolymer drawn at the top of the corresponding 2D-DOSY contour plots are too similar to be distinguished each other, the different translational diffusion properties of the polymers ultimately showed up in different diffusion coefficients of

each constituent polymer unit. Therefore well resolved 2D-DOSY spectra would permit the confirmation of the grafting of two polymer units. Additional DOSY correlations from the solvent (THF) and residual water contaminant can also be observed with very larger diffusion coefficients than those of the polymers.

In summary, we have demonstrated a new potential of the 2D-DOSY techniques for the analysis of grafting copolymers distinguished from the polymer mixture of the corresponding polymer units having an almost identical ^1H NMR spectrum. The DOSY NMR technique can also be applied to examine other related copolymer systems of important industrial applications such as block-copolymers with long repeating units in the same manner.

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