Control of Solid-State Nuclear Overhauser Enhancement in Polyurethane Block Copolymers

David T. Okamoto, Stuart L. Cooper, and Thatcher W. Root*

Department of Chemical Engineering, University of Wisconsin—Madison, 1415 Johnson Drive, Madison, Wisconsin 53706-1691

Received October 3, 1991
Revised Manuscript Received January 27, 1992

Introduction

Relaxation times obtained by nuclear magnetic resonance (NMR) experiments have been used widely to characterize polymer morphology and determine magnitudes of segmental motion. We report here the observation and control of a solid-state nuclear Overhauser enhancement (NOE) that complicates the measurement of ^{13}C spin–lattice relaxation times of the highly-mobile soft-segment carbons in two block copolymer systems. The first system is a poly(ether urethane) composed of 4,4′-methylenebis(*p*-phenyl isocyanate) (MDI) as the hard segment and poly(tetramethylene oxide) (PTMO) as the soft segment, chain-extended with 1,4-butanediol (BD). The second system is solution-grade Biomer, which is an MDI/PTMO poly(urethane urea) with ethylenediamine (ED) as the chain extender. In both systems, the hard and soft segments are incompatible and form a microphase-separated domain morphology. The observed Overhauser enhancement is a consequence of motion in the soft segment. While it may be used to obtain an enhancement of the soft-segment signal, it may also complicate determination of carbon relaxation times, and we address this latter issue.

The NOE effect is used in solution-state NMR to obtain direct through-space information to determine the structure or conformation of the molecule.[1-3] The nuclear Overhauser enhancement occurs between two spins that are coupled together when one spin transition is perturbed and the other spin is observed. Cross-relaxation between coupled spins is described by

$$\frac{dI_z}{dt} = \frac{I_{eq} - I_z}{T_{II}} + \frac{S_{eq} - S_z}{T_{IS}} \qquad (1)$$

$$\frac{dS_z}{dt} = \frac{I_{eq} - I_z}{T_{SI}} + \frac{S_{eq} - S_z}{T_{SS}} \qquad (2)$$

where I and S spins are H and C, respectively, and expressions for the time constants (T_{ij}) can be obtained from details of molecular motions. The maximum effect is seen in solutions at the extreme narrowing limit ($\omega_L\tau_c \ll 1$), provided the only source of relaxation is the dipolar interaction. When I spins are saturated, the S magnetization approaches a larger steady state value

$$\frac{S_z}{S_{eq}} = 1 + \frac{T_{SS}\,I_{eq}}{T_{SI}\,S_{eq}} = 1 + \frac{\gamma_I}{2\gamma_S} \qquad (3)$$

These conditions are not usually valid for solid-state samples, so the increase will be less than the theoretical maximum of 2 possible for ^{1}H/^{13}C systems.

NOE measurements on solid samples of elastomers such as polyisoprene,[4,5] polybutadiene,[6] and polyethylene[7,8] have been reported. A careful study of solid benzene has described the orientation dependence of the NOE.[9] Solid-state NOE effects have been reported recently for plastic crystals and rigid crystalline solids[10] in experiments with long (tens of seconds) proton saturation pulses. Enhancements for backbone methylenes in polymeric films ranging from 0.86 to 1.24 have also been observed when a train of 90° pulses was used to maintain proton saturation.[11]

Several NMR experiments are available for measuring the spin–lattice relaxation time T_1. The most common are steady-state saturation–recovery and inversion–recovery.[12] When a wide range of T_1 values exists, such as in the multiphase systems studied in our laboratory, inversion–recovery experiments require excessive amounts of spectrometer time because the recycle delay is usually set at 5 times the longest T_1. Samples with long T_1 values or a wide range of T_1 values are best studied with the saturation–recovery sequence. T_1 values for different sites in polyurethane samples typically span 5 orders of magnitude (10 ms to 100 s).[13] When collecting a single data set spanning this range that will be used to characterize both hard and soft domains, the total experiment time required is decreased by a factor of 2 by using the saturation–recovery experiment instead of the more common inversion–recovery sequence.

In solution-state NMR, the proton amplifier is operated continuously to decouple protons from carbons. To perform solution-state NMR experiments without the NOE effect interfering in peak intensities, gated decoupling is employed. This approach, where the proton amplifier is on only during signal acquisition, is invariably used for solid-state NMR because of the high power levels required to decouple dipole–dipole interactions. While it is usually assumed that this gating and the slow motions present in a solid will prevent any Overhauser enhancement, cross-relaxation can cause an NOE if one observe period is sufficiently close to the previous decoupling period. In particular, this may occur for a saturation–recovery experiment.

Experimental Section

The poly(ether urethane) sample was prepared from a 7/6/1 molar ratio of MDI/BD/PTMO-2000, resulting in a 50% hard-segment polyurethane by weight. The solution-grade Biomer sample was taken from the 30% solids suspension (in *N,N*-dimethylacetamide) as received from Ethicon, Inc. (Lot BNB 001). Both polymers were dried and redissolved in *N,N′*-dimethylformamide. Films of the polymers were prepared by spin-casting the solutions and drying in a vacuum oven to remove residual solvent.

NMR experiments were performed at room temperature on a Chemagnetics CMC-300A FTNMR spectrometer operating at 75.35 MHz for ^{13}C. Standard-phase cycling and quadrature detection were employed. Magic-angle spinning (MAS) and high-power proton decoupling were employed, with 7.5-mm zirconia rotor spinning speeds of about 6 kHz and a sweep width of 30 kHz. The proton amplifier is continuously enabled, and decoupling was controlled by gating on the 299.5-MHz carrier input only during the 34-ms acquisition period.

Results and Discussion

Typical saturation–recovery data for the PTMO soft-segment ether carbon in the 50% hard-segment poly(ether urethane) are shown in Figure 1. Normal saturation–recovery curves follow a (1 − exp(−t/T_1)) behavior, and such behavior is seen for slowly-relaxing sites in this sample. However, the intensity of the ether peak does not grow and recover to an equilibrium value, but instead appears to decay from a large initial value toward equi-

---

* Author to whom correspondence should be addressed.

0024-9297/92/2225-3301$03.00/0

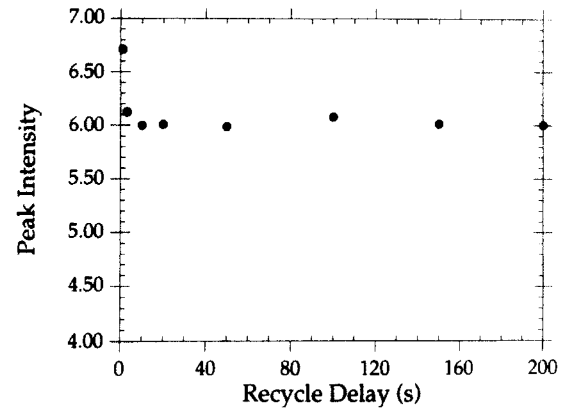

Figure 1. ^{13}C T_1 saturation–recovery data for the PTMO soft-segment ether carbon in a 50% hard-segment poly(ether urethane) exhibiting NOE effects.

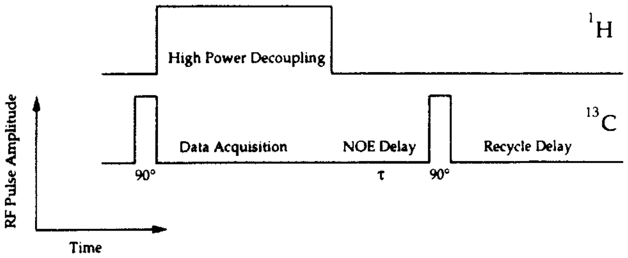

Figure 2. Radiofrequency pulse sequence for the direct-detection NMR experiment with an NOE–spoiler pulse following an NOE delay of duration τ. Neither axis is to scale.

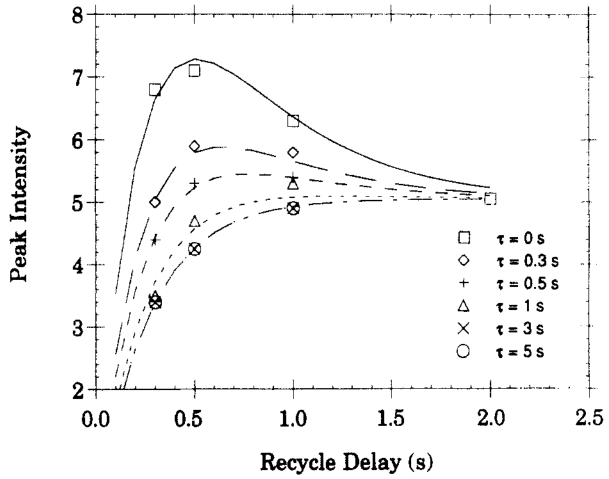

Figure 3. ^{13}C T_1 saturation–recovery data for the PTMO soft-segment methylene carbon in solution-grade Biomer as a function of recycle delay and NOE delay (τ) acquired with the pulse sequence shown in Figure 2. Lines show the fit to the model at the same τ values.

librium. This is a transient nuclear Overhauser enhancement, caused by saturation of the protons by decoupling during the 34-ms acquisition period and the several hundred milliseconds that the protons take to relax.

To demonstrate the cause of and cure for this behavior, we have modified the saturation–recovery sequence to allow for an NOE delay, τ, after the acquisition and decoupling period (Figure 2). At this time, a 90° ^{13}C pulse eliminates any carbon magnetization that has accumulated. In effect, this is a "reset" pulse for restarting ^{13}C relaxation without NOE effects.

Saturation–recovery data for the PTMO soft-segment methylene carbon in the solution-grade Biomer with this new pulse sequence are shown in Figure 3. If simple spin–lattice relaxation were occurring in this system, then the partial saturation–recovery curves would be independent of the "reset" pulse time τ and depend only on the recycle delay. The dependence of the peak intensity on τ indicates that cross-relaxation with protons is occurring.

Solving the modified Bloch equations (1) and (2) for the transient nuclear Overhauser enhancement during this experiment (assuming that abundant H spins are not influenced by dilute C spins and C spins are saturated at time τ and are affected by residual saturation of H spins) we obtain

$$\frac{I_z}{I_{eq}} = 1 - e^{-(\tau+t)/T_{1H}} \qquad (4)$$

$$\frac{S_z}{S_{eq}} = 1 - e^{-t/T_{1C}} + \frac{\epsilon\gamma_I}{2\gamma_S}\frac{T_{1H}}{T_{1H} - T_{1C}}\, e^{-\tau/T_{1H}}\,[e^{-t/T_{1C}} - e^{-t/T_{1H}}] \qquad (5)$$

where t is the recycle delay and ϵ is an effectiveness factor ($0 \leq \epsilon \leq 1$) to characterize the maximum fractional NOE obtained (relative to eq 3). While we would expect $\epsilon = 1$ in solution, it may be less in a rubbery solid where only some of the motions are fast compared to ω_L.

A simultaneous fit of eq 5 to the data in Figure 3 gives $S_{eq} = 5.05 \pm 0.13$, $T_{1C} = 0.269 \pm 0.017$ s, $T_{1H} = 0.441 \pm 0.053$ s, and $\epsilon = 0.70 \pm 0.07$ (uncertainty limits are 2σ or 95% confidence intervals). Typical values of T_{1H} are 0.5–1 s and values of T_{1C} for soft-segment carbons are 100 ms to several seconds for polyurethanes,[13] so the fitted parameters are reasonable. The effectiveness value of 0.70 indicates that there is indeed significant liquid-like motion in the rubbery domain. This transient NOE model predicts ^{13}C signal intensity well for the full range of τ and t values, as seen from the lines in Figure 3. No explicit time constant T_{SI} is obtained, since this rate is coupled to $T_{SS} = T_{1C}$ by motion (through eq 3 and ϵ).

The NOE effect is eliminated when τ is several times T_{1H}. The enhancement reported here is a transient effect, as cross-relaxation is occurring while both carbon and proton spins are undergoing spin–lattice relaxation during the saturation–recovery experiment. This is in contrast to traditional liquid-state NOE experiments, where protons are continuously irradiated to maintain saturation and maximize the NOE effect. Under such steady-state conditions[14] or with prolonged saturation in the solid,[10,11] larger NOE effects may be obtained. The above model predicts an enhancement of $2\epsilon = 1.4$ could be obtained for the Biomer sample if proton saturation was maintained.

Carbon sites in the rubbery region with substantial motion will have both the shortest T_{1C}s and the largest NOE effects, and only these sites are discussed in this note. In experiments where an unusual maximum in the signal intensity with recycle delay is observed, such as for the soft-segment carbons in this polyurethane, detecting the presence of cross-relaxation is simple. However, for samples with weaker enhancements, a saturation–recovery curve such as that shown for $\tau = 0.5$ s may be seen. This fractional enhancement will cause the spin–lattice relaxation time to appear spuriously short. In cases where a biexponential model for relaxation is employed, the enhancement will affect both the time constants and the relative fractions determined for the two spin populations. Thus, T_1 saturation–recovery experiments designed to survey the relaxation behavior of multiphase systems may be misleading, and NOE–spoil experiments with delays of several times T_{1H} should be performed in conjunction with the saturation–recovery experiments to determine the magnitude of this effect.

Future studies involving steady-state saturation–recovery T_1 experiments on softer, more mobile phase-separated polymers are likely to encounter inadvertent NOE effects. This modified NOE–spoiler saturation–recovery sequence can be used to avoid this complication and will have a clear time advantage over the inversion–recovery sequence for relaxation studies of such samples, because of the disparate T_1 values for sites in different phases.

Acknowledgment. The solid-state NMR spectrometer employed in this work was obtained with financial support from the Shell Oil Foundation. Support for this research was provided by NSF Grants CBT-8657496 and DMR-8603839, NIH Grants HL-21001 and HL-24046, and by the Shell Oil Foundation.

References and Notes

(1) Noggle, J. H.; Schirmer, R. E. *The Nuclear Overhauser Effect*; Academic Press: New York, 1971.
(2) Kessler, H.; Gehrhe, M.; Griesinger, C. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 490.
(3) Neuhaus, E.; Williamson, M. *The Nuclear Overhauser Effect in Structural and Conformational Analysis*; VCH Publishers: New York, 1989.
(4) Schaefer, J. *Macromolecules* **1972**, *5*, 427.
(5) Komoroski, R. A.; Maxfield, J.; Mandelkern, L. *Macromolecules* **1977**, *10*, 545.
(6) Schaefer, J. *Macromolecules* **1973**, *6*, 882.
(7) Axelson, D. E.; Mandelkern, L.; Levy, G. C. *Macromolecules* **1977**, *10*, 557.
(8) Komoroski, R. A.; Maxfield, J.; Sakaguchi, F.; Mandelkern, L. *Macromolecules* **1977**, *10*, 550.
(9) Gibby, M. G.; Pines, A.; Waugh, J. S. *Chem. Phys. Lett.* **1972**, *16*, 296.
(10) White, J. L.; Haw, J. F. *J. Am. Chem. Soc.* **1990**, *112*, 5896.
(11) Findlay, A.; Harris, R. K. *J. Magn. Reson.* **1990**, *87*, 605.
(12) Fukushima, E.; Roeder, S. B. W. *Experimental Pulse NMR: A Nuts and Bolts Approach*; Addison-Wesley Publishing Company: Reading, 1981.
(13) Okamoto, D. T. Ph.D. Thesis, University of Wisconsin-Madison, 1991. Okamoto, D. T.; Cooper, S. L.; Root, T. W. *Macromolecules* **1992**, *25*, 1068.
(14) Schaefer, J.; Natusch, D. F. S. *Macromolecules* **1972**, *5*, 416.

Registry No. MDI/BD/PTMO (block copolymer), 107678-92-2; ED/MDI/PTMO (block copolymer), 107375-35-9.