5724 *Macromolecules* **2002,** *35,* 5724−5726

# NMR Characterization of Sodium Poly(α-L-glutamate)/Poly(ethylene oxide) Blends

**D. J. Harris,[†] T. J. Bonagamba,[†,‡,§] and K. Schmidt-Rohr*[,†,§]**

*Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003; Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos, São Paulo, Brazil, Caixa Postal 369, 13560-970; and Chemistry Department and Ames Laboratory, Iowa State University, Ames, Iowa 50011*

*Received March 29, 2001*
*Revised Manuscript Received September 10, 2001*

## Introduction

Poly(ethylene oxide), PEO, forms complexes or miscible blends with many small molecules and polymers including *p*-dihalogenobenzene,[1,2] hydroxybenzenes,[3,4] urea,[5] thiourea,[6] $HgCl_2$,[7] and poly(vinylphenol).[8,9] Recently, mixtures of sodium poly(α-L-glutamate) (PGNa) and PEO have been studied.[10] A crystal structure, inferred from differential scanning calorimetry (DSC), circular dichroism (CD), and wide-angle X-ray diffraction (WAXD) peak intensities, was reported. The PEO crystallite blocks were thought to be anchored to the PGNa helical core via sodium ion−dipole interactions.[10] The conformation of the PEO was reported to change due to the complexation: some of the OC−CO bonds were expected to have trans torsion angles.[10] However, the experimental data of Pemawansa et al.[10] do not offer strong support to the broad conclusions presented in that article.

We have performed solid-state nuclear magnetic resonance (NMR) studies of PEO conformations and packing in a variety of environments[4,11] and now apply the same methods to PEO−PGNa blends. The conformation and packing of PEO in the crystalline phase of the blend is compared with that of pure PEO based on the fine structure in the $^{13}$C cross-polarization/magic-angle spinning (CP-MAS) spectrum. The OC−CO conformation is specifically determined using double-quantum NMR spectroscopy (DOQSY),[11,12] which can easily distinguish gauche and trans conformations. $^1$H spin diffusion experiments are employed to estimate chain mixing in the amorphous regions of the blend. We also repeated some of the previously described experiments,[10] including DSC, WAXD, and $^{23}$Na NMR.

## Experimental Section

**Synthesis of (−$^{13}$C−$^{13}$C−O−) PEO**. Doubly $^{13}$C-labeled PEO was synthesized by anionic polymerization of labeled ethylene oxide gas in THF as described previously.[11] Gel permeation chromatography determined $M_n = 27$ kg/mol and $M_w = 30$ kg/mol (PDI = 1.10). A $^1$H NMR spectrum showed that 13% of the ethylene oxide units are −$^{13}$C−$^{13}$C−O−.

Unlabeled PEO of $M_w = 10$ kg/mol was purchased from Aldrich.

**Preparation of Blends**. Blends were prepared by separately dissolving a 5:1 wt:wt ratio of unlabeled PEO and PGNa in 4:1 vol:vol of methanol and water. After stirring for 24 h, the solvent was evaporated. The resulting film was dried under vacuum at 40 °C for 48 h. Samples containing $^{13}$C−$^{13}$C-labeled PEO were prepared in an analogous fashion.

**Wide-Angle X-ray Diffraction (WAXD)**. WAXD was performed using a Siemens D500 instrument with Ni-filtered Cu K radiation source in transmission mode.

**Differential Scanning Calorimetry (DSC)**. DSC measurements were performed with 10 mg samples loaded in Al pans on a DuPont Instruments DSC 2910. Samples were heated at 10 °C/min from 25 to 130 °C.

**$^{13}$C CP-MAS NMR**. The CP-MAS spectra of a 5:1 PEO:PGNa blend and of pure PEO (both unlabeled) were measured at −70 °C on a Bruker DSX-300 spectrometer. Samples were packed in 7 mm $ZrO_2$ rotors and spun at 5 kHz. The 90° pulse lengths were 4.2 $\mu$s for $^{13}$C and 4.6 $\mu$s for $^1$H. The $^1$H decoupling field strength was 80 kHz. The experiments used recycle delays of 5 s, and each spectrum is the sum of 128 scans.

**Static Double-Quantum NMR**. Static 2D DOQSY NMR spectra of the $^{13}$C-labeled PEO were recorded on a Bruker MSL-300 spectrometer at a $^{13}$C resonance frequency of 75.5 MHz in a 4.5 mm diameter coil of a static variable-temperature probe. The proton 90° pulse length was ca. 3.1 $\mu$s, corresponding to a radio-frequency (rf) field strength of $\gamma B_1/2\pi = 80$ kHz during cross-polarization. For decoupling, the $^1$H rf field strength was increased to ~100 kHz. Typical carbon 90° pulse lengths were 2.6 $\mu$s. A cross-polarization time of 500 $\mu$s and a signal-acquisition time of 2.6 ms were used. The double-quantum excitation and reconversion delays were $2\tau = 280$ $\mu$s each. The pulse sequence did not decouple $^{13}$C−$^{13}$C dipolar interactions; thus, all spectra have dipolar splittings in the $\omega_2$ direction. A combination of phase cycling and 5.5 kHz off-resonance evolution was used to reduce artifacts in the spectra.[13] The recycle delay was 7 s, and the spectrum was obtained at −40 °C under a flow of dry nitrogen gas. The measuring time for each 2D double-quantum spectrum was ca. 20 h. The simulated 2D spectra were calculated directly in the frequency domain by summing up signals for an isotropic distribution of $\mathbf{B_0}$ orientations.[14,15]

**Proton Spin Diffusion NMR Experiments**. The $^1$H spin diffusion data were measured on the Bruker MSL-300 spectrometer in a 7 mm $ZrO_2$ rotor using the Goldman−Shen pulse sequence[16] with a 40 $\mu$s $T_2$ filter to initially destroy the magnetization in the rigid domains. The spinning rate was 5 kHz, and the 90° pulse lengths were 4 $\mu$s for $^{13}$C and 4.4 $\mu$s for $^1$H. The recycle delay was 5 s, and each spectrum is the sum of 2048 scans. Six values of spin diffusion mixing times were used: 0.5, 2, 5, 10, 20, and 50 ms.

**$^{23}$Na NMR**. $^{23}$Na spectra of the neat PGNa, of the unlabeled PEO−PGNa blend, and of a 5 wt % solution of 5:1 PEO:PGNa dissolved in benzene were recorded in a 5 mm horizontal coil in the DSX-300 spectrometer. The typical number of scans was 128. Background signal from the glass tube was subtracted from the experimental spectra.

**$^{13}$C Solution NMR**. The $^{13}$C spectra were obtained at ambient temperature in a Bruker DPX-300 at a frequency of 75.5 MHz. 1 wt % of 10K PEO was dissolved in a 1:1 mixture of $D_2O$ and methanol. An aliquot of a $D_2O$ solution containing 1 wt % PEO and 10 wt % PGNa was injected into the 5 mm NMR tube before each measurement. The recycle delay used for each experiment was 6 s, and the number of scans was typically 1024. $^1$H NMR was used to quantify the ratio of PEO:PGNa for each concentration.

## Results and Discussion

**DSC.** The 5:1 PEO 10K−PGNa 1.5−3K blend showed a broad melting transition (see Figure 1) with an almost identical melting temperature as neat PEO. Our thermograms are consistent with those previously published,[10] which also showed almost identical melting

---

[†] University of Massachusetts.
[‡] Universidade de São Paulo.
[§] Iowa State University.
* To whom the correspondence should be addressed: Tel (515) 294-6105, Fax (515) 294-0105, e-mail srohr@iastate.edu.

10.1021/ma010545t CCC: $22.00

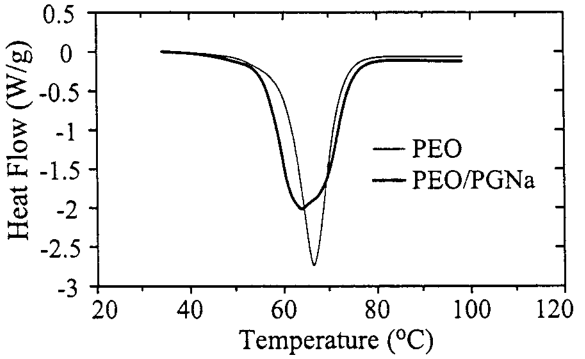

**Figure 1.** DSC thermograms of pure PEO and of a 5:1 PEO 10K−PGNa 1.5−3K blend.

peaks for the blend and neat PEO. The nearly identical melting temperature suggests that ordinary PEO crystallites are present in the blend and gives no support for a new structure. Broadening of the PEO melting endotherm is simply a dilution effect due to the presence of PGNa. There is no melting point depression or a new $T_m$ associated with a crystalline complex.

**WAXD.** The presence of undistorted $7_2$ helical PEO crystallites in the 5:1 PEO−PGNa blend is also confirmed by WAXD. The X-ray diffractograms are not shown here but are similar to those presented previously.[10] In both this and the previous study, the peaks in the blend have identical *d* spacings as those observed in neat PEO. The previously published results had observed *d* spacings of 6.58 and 6.63 Å for the blend, not significantly different from the peak at 6.52 Å in pure PEO. The relative intensities of the 4.61 and 6.52 Å peaks vary by 10−20% from the ratio found in PEO, but this is insufficient evidence to base claims of a different crystal structure. Because of partial mixing of PEO and PGNa in the amorphous regions, small changes in the WAXD intensity pattern are to be expected.

**$^{13}$C CP-MAS and 2D DOQSY NMR.** Solid-state NMR provides additional compelling evidence that PEO in the PEO−PGNa blend does not adopt novel conformations or chain packing as previously reported.[10] The $^{13}$C isotropic chemical shift observed in the CP-MAS NMR spectrum is highly sensitive to the conformation and packing of crystalline polymers. In complexes of PEO with hydroxybenzenes, clear changes in the position and fine structure of the PEO resonance are observed.[3,4] Even for helices in which all the C−C bonds are gauche, variations in the detailed conformation and/or packing lead to detectable spectral changes.[3,4]

The $^{13}$C CP-MAS NMR spectrum of a 5:1 PEO 10K/PGNa 1.5−3K blend was measured at −70 °C (Figure 2a) and compared with that of pure PEO (Figure 2b). There are several peaks and shoulders in the PEO spectrum[17] due to inequivalent carbons in the distorted crystalline helix. The similarity of the spectra for the PEO−PGNa blend and pure PEO indicates that the crystalline peaks previously observed in WAXD arise from the $7_2$ helix of PEO, packed as in ordinary PEO crystallites. Small differences, e.g. around 70 ppm, can be attributed to changes in the amorphous regions of PEO, whose mobility is reduced by mixing with PGNa.

A specific probe of the PEO OC−CO bond conformation in the crystalline state is provided by static 2D DOQSY NMR. DOQSY NMR spectra of a 5:1 $^{13}$C−$^{13}$C−PEO/PGNa blend (Figure 3a) and of the neat 13% $^{13}$C−$^{13}$C-labeled PEO (Figure 3b) were recorded at −40 °C. At this temperature, the amorphous regions still possess so much mobility that their spin relaxation times are short and thus contribute little intensity to the DOQSY spectra. The spectral patterns for the blend and for neat PEO are almost identical. A simulation with a mean torsion angle of $y = 74°$ and a Gaussian distribution width of 5° is shown in Figure 3c; it matches both experimental spectra. A similar deviation of the gauche OC−CO bond conformation from 60° has been shown in PEO/hydroxybenzene[11] complexes, and the 74° value is needed in these simulations to match the experimental spectra. The slightly broader features in the PEO−PGNa blend are likely due to a lower $^{1}$H decoupling power level during acquisition. There is no evidence of trans OC−CO bonds, which would produce two long diagonal ridges with slopes of two,[4,11,18] as shown in Figure 3d. The minimum amount of trans conformers safely detectable in this experiment is 20% of all crystalline OC−CO bonds.[19]

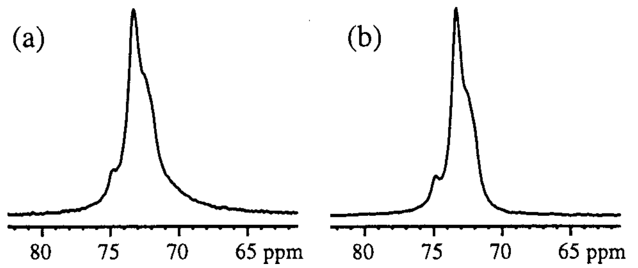

**Figure 2.** CP/MAS $^{13}$C NMR spectra, at −70 °C and 5 kHz spinning rate, of (a) PEO−PGNa (5:1) and (b) pure PEO (processed with 20 Hz Lorentzian line broadening). The fine structure in the lines is due to packing effects of the crystalline $7_2$ PEO helices in the crystal lattice.[17]

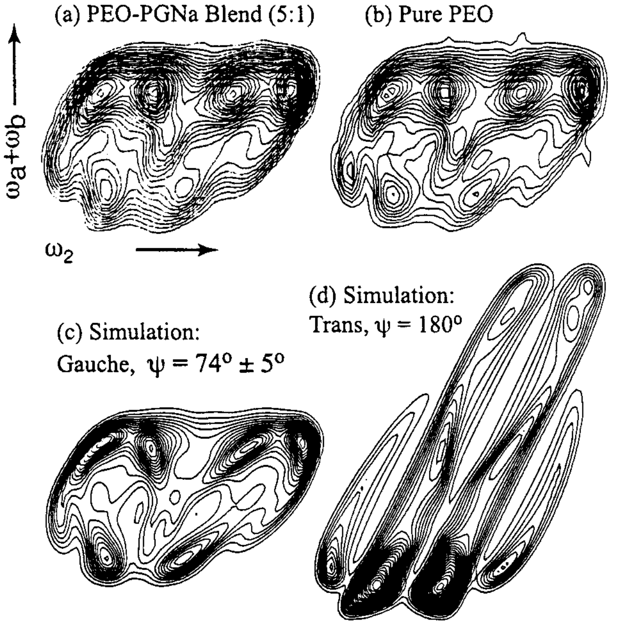

**Figure 3.** Comparison between DOQSY NMR spectra, at −40 °C, of the crystallites in (a) a 5:1 $^{13}$C−$^{13}$C−PEO/PGNa blend and (b) neat 13% $^{13}$C−$^{13}$C-labeled PEO. The lower decoupling power in the experiment on PGNa−PEO may have caused greater broadening in the lower part of the spectrum. (c) Simulated DOQSY spectrum based exclusively on gauche O−C−C−O conformations, which is consistent with both experimental spectra. (d) Simulation for trans OC−CO torsion angles. No evidence of this conformer is observed in the experimental spectra (a) and (b).

**$^{1}$H Spin Diffusion.** In the Goldman−Shen experiment, the $^{1}$H magnetization in the crystalline PEO and rigid PGNa phases is initially destroyed, resulting in signal only from the amorphous PEO regions. Through

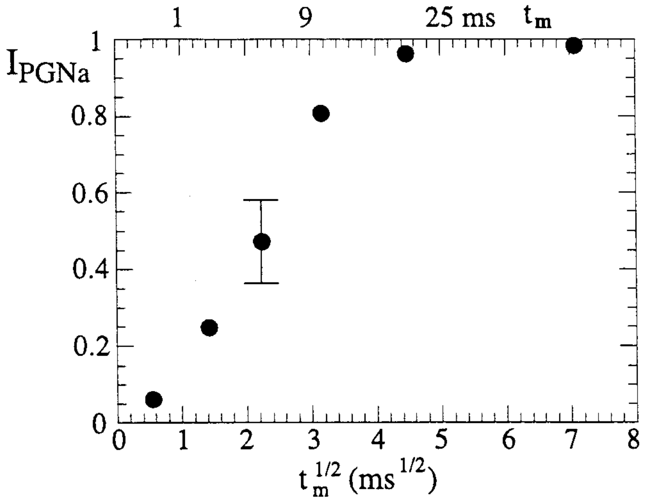

**Figure 4.** Goldman−Shen $^1H$ spin diffusion experiment with $^{13}C$ detection, recording spin diffusion from the mobile amorphous PEO to the PGNa. The PGNa signal intensity is plotted as a function of the square root of the spin diffusion mixing time, $t_m$.

$^1H$ spin diffusion during the mixing time $t_m$, the magnetization transfers from amorphous PEO to PGNa, whose $^{13}C$ signals are detected after 0.5 ms cross-polarization from $^1H$. As seen in Figure 4, the magnetization equilibrates within 20 ms of spin diffusion time. This shows that in the amorphous regions PEO and PGNa are mixed on a 10 nm scale.[14] At the same time, the difference in PEO and PGNa mobility suggests the presence of small domains rich in PGNa, rather than mixing of individual PEO and PGNa chains.

**$^{23}$Na NMR Results.** The dynamics of the sodium counterion was examined with $^{23}Na$ NMR line width measurements. At room temperature, the line widths of the $^{23}Na$ counterion of the PGNa are identically 1.4 kHz in neat PGNa and in a 5:1 PEO 10K/PGNa 3K blend. The identical line width suggests that the $Na^+$ ions are bound to the PGNa chains and not solvated by the mobile PEO chains.

The $^{23}Na$ line width of 5:1 PEO 10K/PGNa 3K dissolved in benzene was also determined. While the previous article reported no detectable signal,[10] a strong signal was observed with a 0.9 kHz line width. This broad line width indicates that nonpolar benzene does not lead to large increases in PGNa mobility. Pemawansa et al.[10] suggested that the $T_1$ relaxation time of the $^{23}Na$ ions in benzene must be extremely long; however, a value of less than 1 s was experimentally measured in this work.

**$^{13}$C Solution NMR Results.** Evidence for complexation was not seen in the $^{13}C$ solution NMR spectra, summarized by the graph in Figure 5. Only a small chemical shift change, of less than 0.03 ppm, was observed with the addition of PGNa to the PEO solution. If the interactions between PEO and the surfactant were strong, the expected change of the chemical shift would be on the order of 0.2 ppm, as seen in a PEO−sodium dodecyl sulfate system.[20]

## Conclusions

The similarity between the solid-state NMR results for PEO:PGNa blends and neat PEO clearly indicates that the PEO crystallites are undisturbed, and there is no significant crystalline complex with different PEO conformation or packing. The DOQSY NMR, $^{23}Na$, and $^{13}C$ CP-MAS spectra all support this conclusion. Furthermore, there is no evidence of strong complexation in the $^{13}C$ solution NMR spectra. The results of the WAXD and DSC data for the PEO:PGNa blends are similar to the information presented by Pemawansa et al.[10] However, the results are now shown to contradict the previous claim that an unusual PEO conformation or packing in the crystallites exists in the blends. Spin diffusion experiments indicate proximity of amorphous PEO and PGNa on a 10 nm scale.

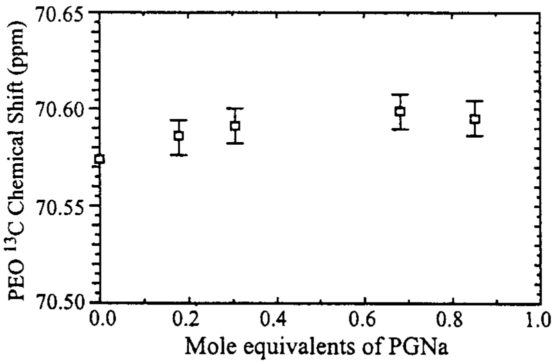

**Figure 5.** Effect of added PGNa on the chemical shift of the $^{13}C$ line of PEO in 1:1 $D_2O$:methanol. The PEO concentration was maintained at 1 wt %. Strong complexation would be expected to change the chemical shift by ~0.2 ppm.

**Acknowledgment.** T.J.B. thanks the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP)—Brazil for a fellowship. We thank A. J. Waddon for help with WAXD and J. Morin for help with DSC analyses. Support for the NMR facility was provided by NSF/MRSEC at UMass Amherst.

## References and Notes

(1) Point, J. J.; Coutelier, C. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 231−239.
(2) Point, J. J.; Jasse, B.; Dosière, M. J. *J. Phys. Chem.* **1986**, *90*, 3273−3277.
(3) Spevacek, J.; Paternostre, L.; Damman, P.; Draye, A. C.; Dosière, M. *Macromolecules* **1998**, *31*, 3612−3616.
(4) Harris, D. J.; Bonagamba, T. J.; Hong, M.; Schmidt-Rohr, K. *Macromolecules* **2000**, *33*, 3375−3381.
(5) Tadokoro, H.; Chatani, Y.; Kobayashi, M.; Yoshihara, T.; Murahashi, S.; Imada, K. *Rep. Prog. Polym. Phys. Jpn.* **1963**, *6*, 303.
(6) Tadokoro, H. *Macromol. Rev.* **1966**, *1*, 119.
(7) Iwamoto, R.; Saito, Y.; Ishihara, H.; Tadokoro, H. *J. Polym. Sci., Part A-2* **1968**, *6*, 1509−1525.
(8) Zhang, X. Q.; Takegoshi, K.; Hikichi, K. *Macromolecules* **1993**, *26*, 2198−2201.
(9) Qin, C.; Pires, A. T. N.; Belfiore, L. A. *Polym. Commun.* **1990**, *31*, 177−182.
(10) Pemawansa, K. P.; Thakur, A.; Karikari, E. K.; Khan, I. M. *Macromolecules* **1999**, *32*, 1910−1917.
(11) Harris, D. J.; Bonagamba, T. J.; Schmidt-Rohr, K. *Macromolecules* **1999**, *32*, 6718−6724.
(12) Schmidt-Rohr, K. *Macromolecules* **1996**, *29*, 3975−3981.
(13) Kaji, H.; Schmidt-Rohr, K. *Macromolecules* **2001**, *34*, 7368−7381.
(14) Schmidt-Rohr, K.; Spiess, H. W. *Multidimensional Solid-State NMR and Polymers*; Academic Press: San Diego, 1994.
(15) Schmidt-Rohr, K. *J. Am. Chem. Soc.* **1996**, *118*, 7601−7603.
(16) Goldman, M.; Shen, L. *Phys. Rev.* **1966**, *144*, 321−331.
(17) Schilling, F. C.; Tonelli, A. E.; Cholli, A. L. *J. Polym. Sci., Part B: Polym. Phys.* **1992**, *30*, 91−96.
(18) Schmidt-Rohr, K. *J. Magn. Reson.* **1998**, *131*, 209−217.
(19) Schmidt-Rohr, K.; Hu, W.; Zumbulyadis, N. *Science* **1998**, *280*, 714−717.
(20) Cabane, B. *J. Phys. Chem.* **1977**, *81*, 1639−1645.

MA010545T