Natural Abundance ^{15}N Solid-State NMR Study of Nylon-6 in Blends

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Received 24 September 2002; accepted 10 April 2003

ABSTRACT: Natural abundance solid-state nuclear magnetic resonance spectroscopy (NMR) of nitrogen-15 (^{15}N) was applied to investigate the films of nylon-6 and their blends with poly(propylene oxide) (PPO). The NMR ^{15}N results allowed us to identify the crystalline forms present in these blends and also confirmed the previous NMR results obtained by ^{13}C-NMR study. From all NMR data the antiplasticization phenomena and plasticization effects caused by PPO content, in the blends were characterized. The polyoxide action is a function of its proportion. However, because the samples were prepared by solution casting, the residual solvent action cannot be ignored. The ^{15}N chemical shift changes were influenced by both PPO and residual solvent. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3872–3875, 2003

Key words: natural abundance ^{15}N; solid-state NMR; nylon-6; films; blends

INTRODUCTION

Solid-state NMR provides a great deal more information on sample properties than does solution NMR because of the physical interaction; it also has discriminating pulse sequences that provide the components present in different domains[1–5] because they present distinct mobilities. ^{13}C and ^{15}N solid-state spectra permit us to evaluate the difference in the domains and the conformation ordination chains attributed to crystallinity formation, respectively.[1–10]

To improve the mechanical properties of nylon-6, blends with poly(propylene oxide) (PPO)[11,12] and polycarbonate[12] were investigated and characterized by solid-state NMR by Tavares et al.[11,12] Three different ranges of blends were investigated using cross-polarization/magic angle spinning (CP/MAS) ^{13}C-NMR techniques. In the first NMR studies we discovered that low PPO content (1–5%) in the blends does not act as a plasticizer for this polymer, as would be expected, but rather acts as an antiplasticizer. Concerning the structural forms of nylon-6/PPO blends, these results led us to consider whether the structural changes originate from a function of PPO amount. To better understand the behavior of these blends, we chose to study the ^{15}N nuclei by solid-state NMR. The solid-state NMR characterization of ^{15}N was previously reported by Powell and Mathias.[7–9] Analysis by CP/MAS allows us to obtain a solid-state spectrum in natural abundance of ^{15}N with good sensitivity. In nylon-6 the CP/MAS ^{15}N peaks were shown to correlate with two predominant crystalline forms, that is, the alpha (α) and gamma (γ) structural crystal forms.[9] Others resonances were also observed that can be attributed to the amorphous phase and the noncrystalline interphase forms.[10,13,14]

The main purpose of this work was to obtain new and better information on the miscibility, compatibility, and chain conformation of blends, using for the first time ^{15}N solid-state data.

EXPERIMENTAL

Preparation of blends

Thick films of nylon-6 and nylon-6/PPO blends were prepared by dissolving mixtures with different PPO contents (up to 20%) in formic acid. The solutions were cast onto glass plates that were then placed in an oven at 65°C for 90 min. After that, the films were removed from the support, dried, and stored in a dissector with a vacuum for 3 days at room temperature. Solvent elimination were carried out by infrared spectroscopy until the OH solvent band was completely eliminated.

NMR measurements

All NMR solid-state spectra were obtained on a Varian Unity Inova 300 spectrometer (Varian Associates, Palo Alto, CA) operating at 299.9 and 30.3 MHz for ^{1}H and ^{15}N, respectively. All experiments were performed at

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Contract grant sponsor: Conselho Nacional de Desenvolvimento Cientifico e Tecnológico (CNPq).

Journal of Applied Polymer Science, Vol. 90, 3872–3875 (2003)

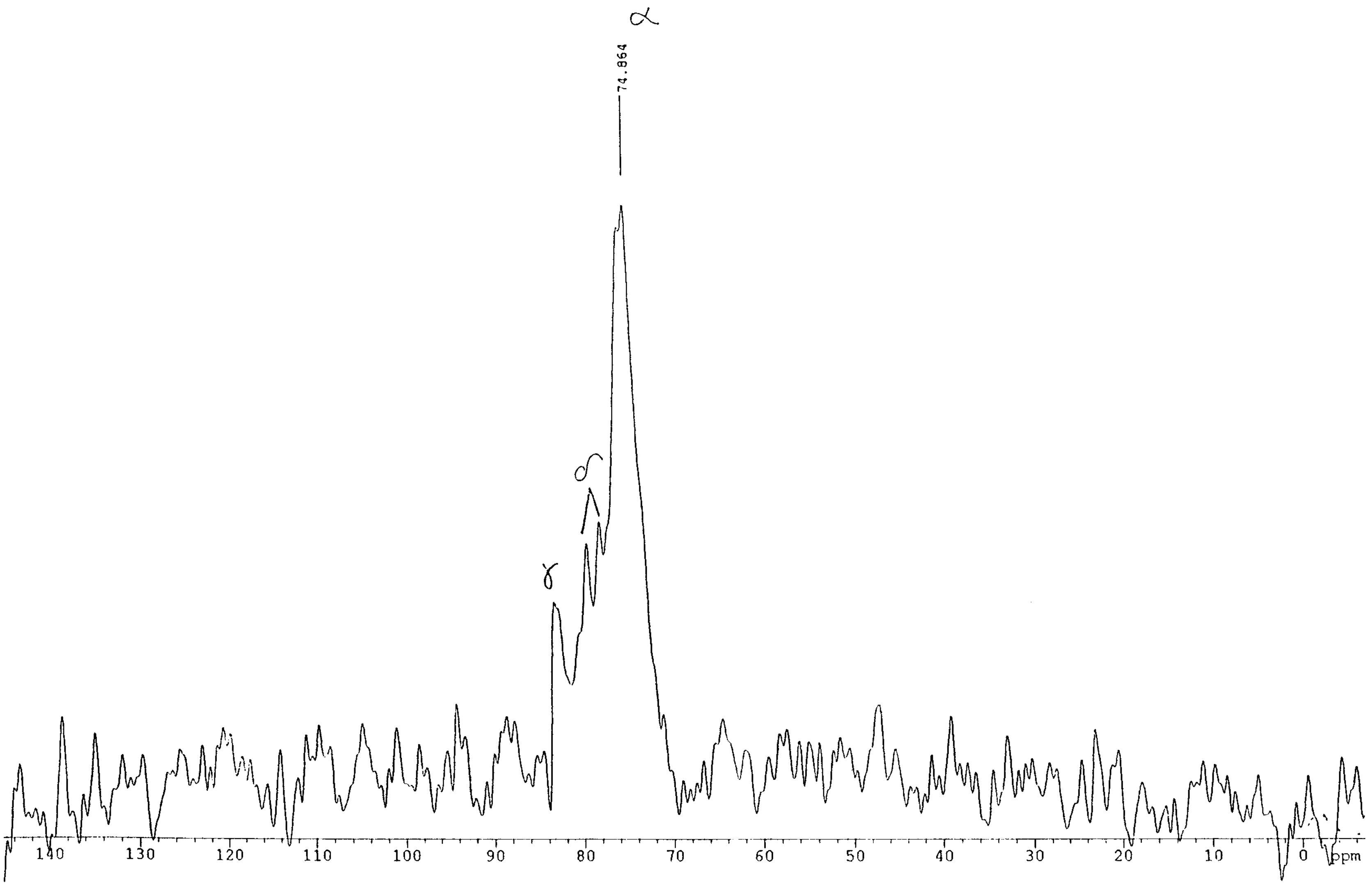

Figure 1 Natural abundance CP/MAS ^{15}N-NMR spectrum of nylon-6 film.

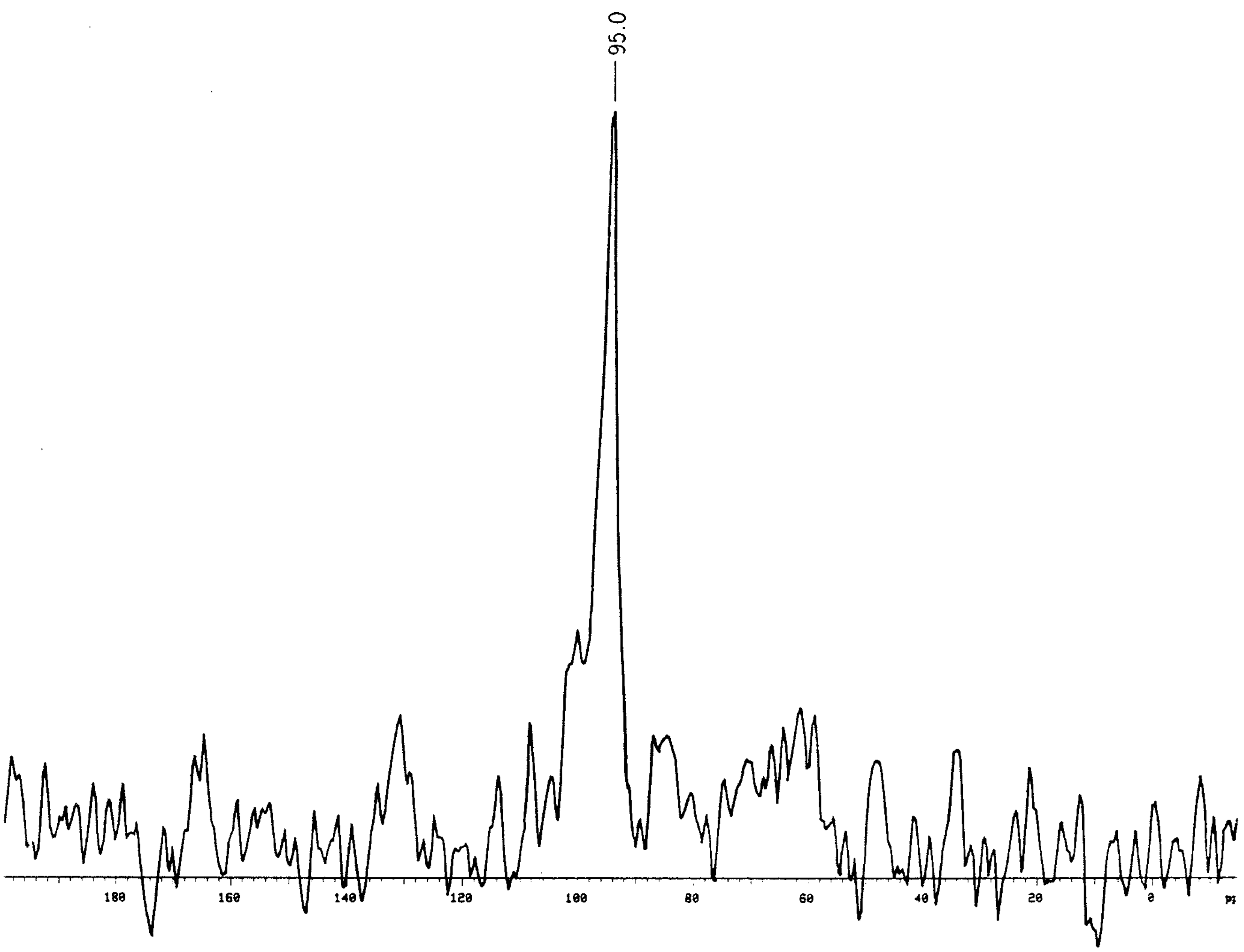

Figure 2 Natural abundance CP/MAS ^{15}N-NMR spectrum of nylon-6/PPO blends with 5 wt % of PPO.

probe ambient temperature by use of gated high-power decoupling. A zirconium oxide rotor of 7 mm diameter was used to acquire the NMR spectra at rates of 4.5 kHz. ^{15}N spectra were referenced to the chemical shift of glycine (0 ppm). The ^{15}N spectra were carried out in the cross-polarization mode with magic-angle spinning (CP/MAS) with 3 s of delay and 1 ms of contact time.

RESULTS AND DISCUSSION

The nylon-6 film was first investigated by CP/MAS ^{13}C at solid state and by the proton spin–lattice relaxation time in the rotating frame ($T_1{}^H\rho$). The CP/MAS ^{13}C-NMR spectrum of nylon-6 film presented all resonance lines at the chemical shift of the α-crystalline form. The assignments were already described in a previous work[12] and are in agreement with the literature.

Figure 1 shows the CP/MAS ^{15}N-NMR spectrum of nylon-6 film. Four resonance lines were detected. The highest relatively sharp peak at 74.8 ppm with a line width at half-height of 70 Hz was assigned as the α-form, which is located in low frequency, most likely attributed to the solvent action. Three resonance lines at 77.8, 78.5, and 83.4 ppm with a line width at half-height of 28, 39, and 36 Hz, respectively, were detected. The peaks at 77.8 and 78.5 ppm were attributed to the amorphous phase or may have come from the noncrystalline interphase region with restricted mobility, and the NMR signal at 83.4 ppm was attributed to the γ-structural crystal form.

Figure 2 exhibits the natural abundance CP/MAS ^{15}N-NMR spectrum of nylon-6/PPO blends containing 5 wt % of PPO. Two NMR signals were detected: one sharp peak located at 95.0 ppm, which was attributed to the α-crystalline form. The change of 20 ppm in the chemical shift, for high frequency, was caused by the action of PPO resulting from the interaction process. The low PPO content in the blends showed that this polymer can act as an antiplasticizing agent[12]; in this case PPO can promote a localized crystallization process of an amorphous phase, or promote a

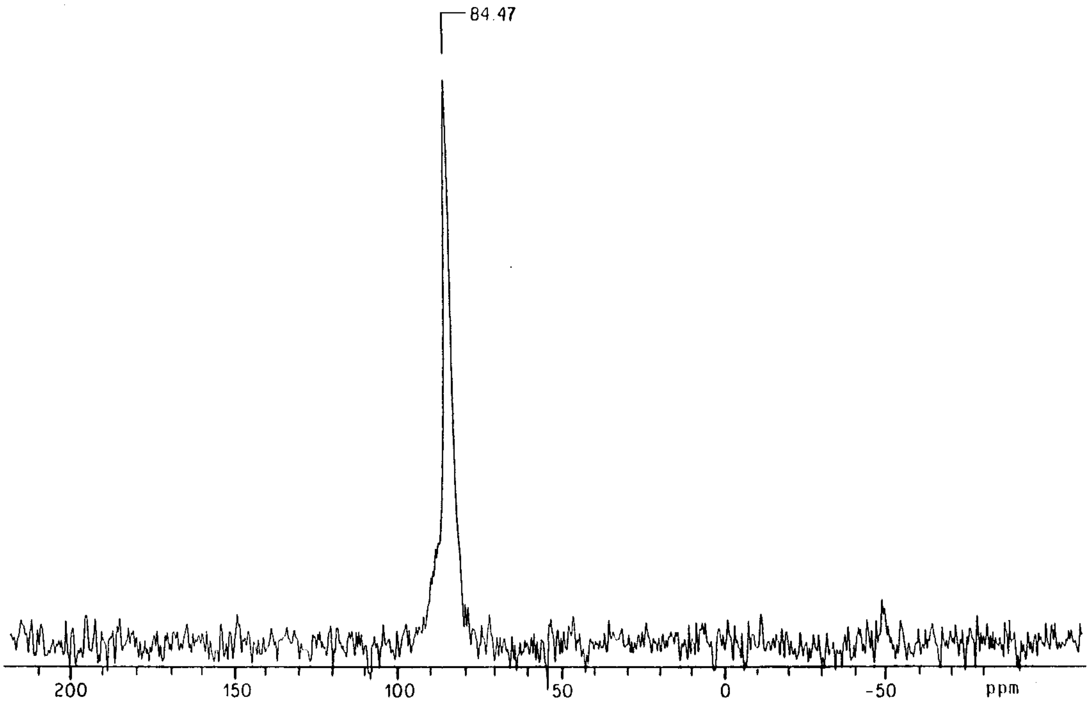

Figure 3 Natural abundance CP/MAS ^{15}N-NMR spectrum of nylon-6/PPO blends with 20 wt % of PPO.

reorganization in a more ordained phase, which makes the blend more rigid and probably causes changes in the ^{15}N spectrum resulting from changes in the chain conformations. These results are supported by the high values of $T_1{}^H\rho$ and also by the increase in the degradation temperature.[11] As previously observed the ^{15}N chemical shift was reported to be conformationally dependent.[8,13]

The natural abundance CP/MAS ^{15}N-NMR spectrum of the nylon-6/PPO blend that contains 20% of PPO is shown in Figure 3. An analysis of this spectrum shows two NMR signals, one highly sharp signal located at 84.5 ppm with a line width at half-height of 20 Hz and a wide shoulder located at 90 ppm with a line width at half-height of 120 Hz. The sharp resonance at 84.5 ppm was attributed to the α-crystalline form, whereas the shoulder located in the high-frequency region overlapping the NMR signals is attributed to the amorphous phase and the γ-crystalline form. Interestingly, an increase in the PPO content in the blend caused a plasticization effect, promoting high mobility to the sample, and the signals of the crystal forms do not change the chemical shift values in relation to pure nylon-6, although they are completely different from those of the sample that contains 5% of PPO.

The ^{15}N spectra of both polymer blends and the pure nylon-6 are different, revealing that the ^{15}N chemical environment in each sample can be reflected in this resonance peak, which can show the changes in mobility of the sample, as a result of the action of the second polymer component in the chain conformations.

The authors thank Varian Associates (Palo Alto, CA) for the ^{15}N-NMR spectra and Conselho Nacional de Desenvolvimento Cientifico e Tecnológico (CNPq) for the financial support.

References

1. Harris, R. K. In: Proceedings of the Fifth International Conference on Applications of Magnetic Resonance in Food Science, Aveiro, Portugal, 2000; Vol. I, pp 1–11.
2. Harris, R. K. In: NMR Studies of Solid Polymers; Fawcell, A. H., Ed.; Polymer Spectroscopy; Wiley: London, 1996.
3. Tavares, M. I. B.; Monteiro, E. E. C.; Harris, R. K.; Kenwright, A. Eur Polym J 1994, 30, 1089.
4. Bovey, F. A.; Mirau, P. A. NMR of Polymers; Academic Press: New York, 1996.
5. Silva, N. M.; Tavares, M. I. B.; Stejskal, E. O. Macromolecules 2000, 33, 115.
6. Powell, D. G.; Sikes, A. M.; Mathias, L. J. Macromolecules 1988, 21, 1533.
7. Mathias, L. J.; Powell, D. G.; Sikes, A. M. Polym Commun 1988, 29, 192.
8. Powell, D. G.; Mathias, L. J. J Am Chem Soc 1990, 112, 669.
9. Powell, D. G.; Sikes, A. M.; Mathias, L. J. Macromolecules 1989, 22, 3812.
10. Hatfield, G. R.; Glans, J. H.; Hammond, W. B. Macromolecules 1990, 23, 1654.
11. Tavares, M. I. B.; Castro, W. P.; Costa, D. A. J Appl Polym Sci 1995, 55, 1165.
12. Costa, D. A.; Pinto, E. S.; Oliveira, C. M. F.; Tavares, M. I. B. J Appl Polym Sci 1997, 64, 1635.
13. Weber, W. D.; Murphy, P. D. Polym Prepr (Am Chem Soc Div PMSE) 1987, 57, 341.
14. Shoji, A.; Ozaki, T.; Fujito, T.; Deguchi, K.; Ando, I. Macromolecules 1987, 20, 241.