

# Study of Nylon 6 and Poly(propylene Oxide) Blends by Thermal Measurements and Carbon-13 NMR High Resolution Solid-State

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## SYNOPSIS

Samples of Nylon 6/poly(propylene oxide), with poly(propylene oxide) (PPO) content varying up to 35%, have been examined using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and nuclear magnetic resonance (NMR) carbon-13 at solid-state. Carbon-13 spectra were measured by cross-polarization (CP), magic angle spinning (MAS), and high-power hydrogen decoupling (HPHD). The variation contact time experiment and MAS technique were also determined. The data are discussed in terms of compatibility and plasticization of the samples. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Polymeric blends can be defined as polymer mixtures exhibiting homogeneity at molecular level.<sup>1</sup> The nature of intermolecular forces in blends is specific. They can be linked by Van der Waals forces, dipole-dipole interaction, or hydrogen bond.<sup>2</sup> The polymers involved must present sufficient thermodynamic compatibility to avoid phase separation during the mixing process.<sup>3</sup>

In terms of compatibility, blends are described as miscible, semi-miscible, or immiscible. Generally speaking, compatible mixtures present strong interaction between polymers. Just one phase and a single sharp glass transition ( $T_g$ ) are found. For semi-compatible blends, two values of  $T_g$  are detected. Incompatible blends are biphasic systems in which the continuous phase is formed by the polymer that is present in high quantity. These systems have two values of  $T_g$  that are similar to the two homopolymers.<sup>2,4</sup>

There are several criteria for evaluating polymeric blends<sup>1</sup> compatibility, such as: the thermodynamic parameter ( $\chi$ )<sup>3</sup>; solubility parameter ( $\delta$ )<sup>2</sup>; glass transition temperature<sup>4</sup>; and others. Thermogravimetric analysis (TGA) is a technique that gives information

about thermal stability. The changes in bulk can be associated to the decompositions of materials, which are related to sample homogeneity.<sup>5</sup> The  $T_g$  behavior can be the first indication of compatibility for a polymeric blend. Therefore, the calorimetric techniques do not give information about mixing on the molecular scale. NMR spectroscopy in solids is a good way to characterize the sample compatibility at different molecular levels. In most cases, proton and carbon-13 NMR relaxation times, both in the rotating frame<sup>6</sup> and the laboratory, are used to analyze polymeric blend compatibility.<sup>7</sup> However, the high-resolution NMR carbon-13 spectra of solids can provide the homogeneity blends at molecular level.<sup>8</sup> Variation contact time experiments together with MAS technique can establish the behavior of polymers' compatibility.<sup>9-11</sup>

In this work the main purpose is to analyze the compatibility range of Nylon 6/PPO blends using TGA and  $T_g$  behavior as well as the NMR response.

## EXPERIMENTAL

### Samples

The samples were prepared from Nylon 6 (Nitrocarbonyl) and poly(propylene oxide) (Dow Química). The number average molecular weight of Nylon 6 was found to be 15.200 by using vapor pressure os-

mometry (VPO). The number average molecular weight of PPO was found to be 900. The glass transition temperature for Nylon 6 was measured as 55°C; the melting temperature and crystalline temperature were found to be 233° and 183°C, respectively, by using differential scanning calorimetry (Perkin-Elmer DSC-2) in the temperature range 25–250°C, using a heating rate of 10°C/min with indium as a calibration standard. The decomposition temperature was determined as 425.5°C by thermogravimetric analysis (TGA Perkin-Elmer 7 series), in the temperature range 30–600°C, using a heating rate of 10°C/min, at N<sub>2</sub> atmosphere. The crystallinity degree for Nylon 6 was found to be 48.5% by X-ray diffraction.

Thick films of Nylon 6 and Nylon 6/PPO were prepared by dissolving mixtures with different PPO contents in formic acid. The solutions were cast onto glass plates, which were placed in an oven at 65°C for 90 minutes. After that, the films were removed from the support, dried, and stored in a desiccator with a vacuum for three days at room temperature.

#### TGA Measurements

The mixtures were analyzed in TGA Perkin-Elmer 7 Series, in the temperature range 30–600°C, using a heating rate of 10°C/min, at N<sub>2</sub> atmosphere.

#### DSC Measurements

The blends of Nylon 6/PPO were analyzed by a DSC-2 (Perkin-Elmer) in the temperature range 25–250°C, using a heating rate of 10°C/min, with indium as a calibration standard.

#### NMR Measurements

All measurements were carried out using a Varian VXR 300 spectrometer operating at 75.4 MHz. The analyses were done by cross-polarization/magic angle spinning/high-power hydrogen decoupling (CP/MAS/HPHD); variation contact time experiment (range of contact time ( $\tau$ ) varied from 0.05 to 8 ms); and without cross-polarization (MAS/HPHD), in 7 mm o.d. rotors at 5 KHz.

## RESULTS AND DISCUSSION

The results obtained by TGA are listed in Table I. The table shows that low quantities of PPO (from 1–5%) added to Nylon 6 cause an increase in thermal stability. This fact can be explained in terms of better organization of the amorphous phase. This order

**Table I TGA Results for Pure Nylon 6 and Nylon 6/PPO Blends**

	PPO Content (%)	TG Value (°C)
	—	425.5
	1	435.3
	2	432.8
	3	436.6
	5	444.9
Nylon 6	10	421.0
	15	416.2
	20	413.0
	25	365.0–397.0
	35	297.0–390.0

was attributed to polymer high crystallization through the increase of momentary freedom in relation to molecular motion of chains, so that PPO acts as a nucleation agent and is considered an antiplasticizer.<sup>12,13</sup> Therefore, when PPO contents vary from 10 to 20% a slight decrease can be observed in the thermal stability. It happens because the high quantity of PPO promotes a sufficient decrease in the crystallites; thus the plasticization phenomena can be detected. Above 20% PPO, two decomposition temperatures were found and incompatible blends were formed.

The carbon-13 NMR spectrum in solid-state for Nylon 6 film shows that this polymer presents an  $\alpha$  crystalline form (Fig. 1), as assigned by the literature.<sup>14</sup> Analysis of the carbon-13, CP/MAS/HPHD spectra of Nylon 6/PPO blends clearly shows that all compositions present the same assignments as for pure polymer (see Fig. 2). Another interesting finding from the CP/MAS spectra is that all compositions are compatible at molecular level, in spite of the antiplasticization process.

From the variation contact time experiment (VCT) (Fig. 3), it can be seen that the behavior of carbon-13 peak decays are completely distinct. Figure 3(a) confirms that low PPO content in the mixtures is responsible for the antiplasticization process; that the total concentrations of carbon-13 signals are located at short contact times (the best contact time for a blend with 1% PPO is 50  $\mu$ s, while from 2% to 5% is 100  $\mu$ s); and that no signal at all was detected at long contact time, considering that the flexible domains are usually found in this region, due to the long time necessary to cross-polarize ( $\tau$  = 8 ms). Thus, this range of compositions may not be interpreted as incompatible blends. Figure 3(b) illustrates another set of mixtures; in these cases

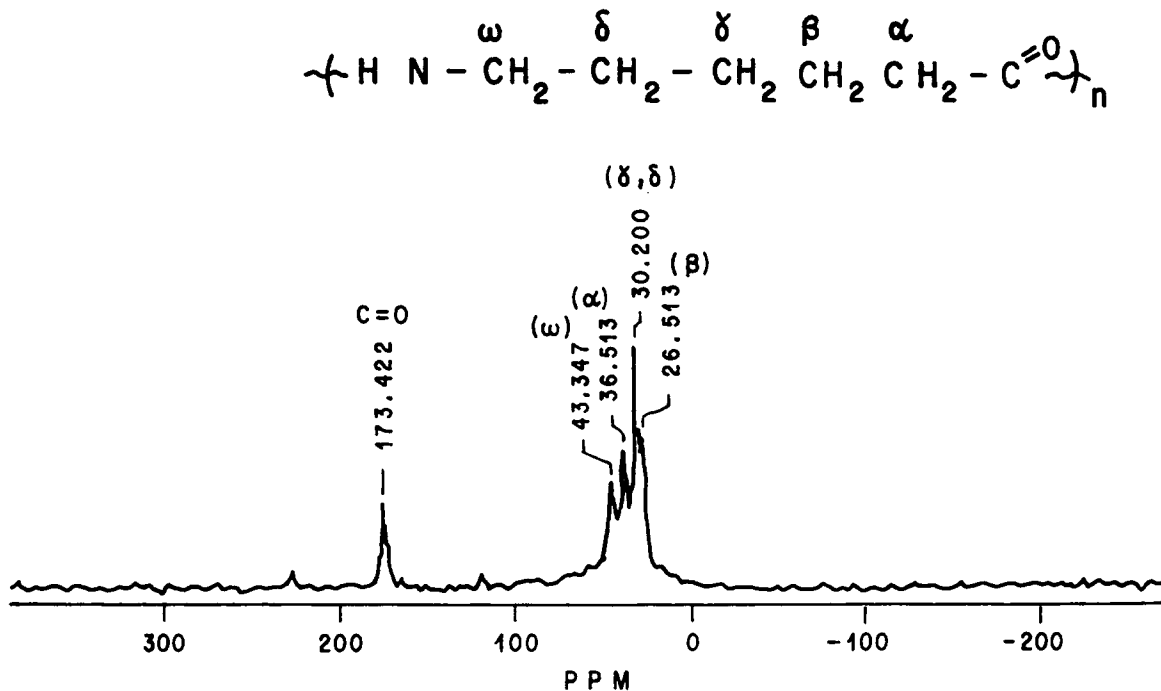


Figure 1 CP/MAS carbon-13 NMR spectrum of Nylon 6 film.

intermediate amounts of PPO added to Nylon 6 promote homogeneous blends. For 20% of PPO the distribution of attenuations signals intensity of carbon-13 presents a perfect homogeneity decay (the best contact time was found to be 1 ms). The behavior of this distribution can be attributed to compatible blends. The third set (Fig. 3[c]) represents samples from 25–35% of PPO incorporated into Nylon 6; the attenuations intensities of carbon-13 resonance lines are dislocated to short contact times, but not so abrupt as those caused by small quantities of PPO. For blend with 25% of poly(propylene oxide), two domains with distinct mobilities are found (one located at 100  $\mu\text{s}$ —rigid domain—and the other one concentrated at 4 ms—flexible domain). In this case the samples behave differently than observed for other PPO quantities added to polymer. Looking at the Nylon 6/PPO blend (65/35), at long contact time only carbon-13 resonance lines of PPO were registered. So the existence of two different domains may be interpreted as an incompatible blend.

The proton spin-lattice relaxation time in the rotating frame ( $T_{1\rho}$ ) for the highest peak ( $\delta = 30.25$  ppm), was measured from the carbon-13 peak intensities determined by VCT (See Table II). The values of proton spin-lattice relaxation time in the rotating frame corroborated with the analysis done from VCT decay. The value found for pure Nylon 6 film was the base. When small quantities of PPO

(from 1% to 5%) were incorporated to polymer, a great reduction of proton  $T_{1\rho}$  was detected (the polymer became more rigid—antiplasticization process). Therefore, when the amount of PPO increases from 10–20%, the value of this parameter increases, although these values are smaller than the value found for the pure Nylon 6 (plasticization phenomena). The proton  $T_{1\rho}$  value for blends with PPO content up to 20% was found to be higher than the value measured for pure Nylon 6, which can be translated as incompatibility range.

The  $T_g$  behavior found for the Nylon 6/PPO blends is in agreement with the proton spin-lattice relaxation time in the rotating frame. In our laboratory a linear behavior was detected for these two parameters.

The MAS technique was carried out in order to obtain information about the mobile region of the systems. For pure Nylon 6, only the  $\text{CH}_2$  group was detected. The same peak was found for samples with PPO content varying up to 5%. However the line peaks of  $\text{CH}_2$  groups are broader than those observed for Nylon 6 spectra. The broadening signals are related to mobility; in this case the samples became more rigid. This fact may be associated with the effect caused by PPO as an antiplasticizing agent. In this sense the samples may crystallize, induced by the small PPO content incorporated. Concerning blends with 10–20% of PPO, two resonance lines of

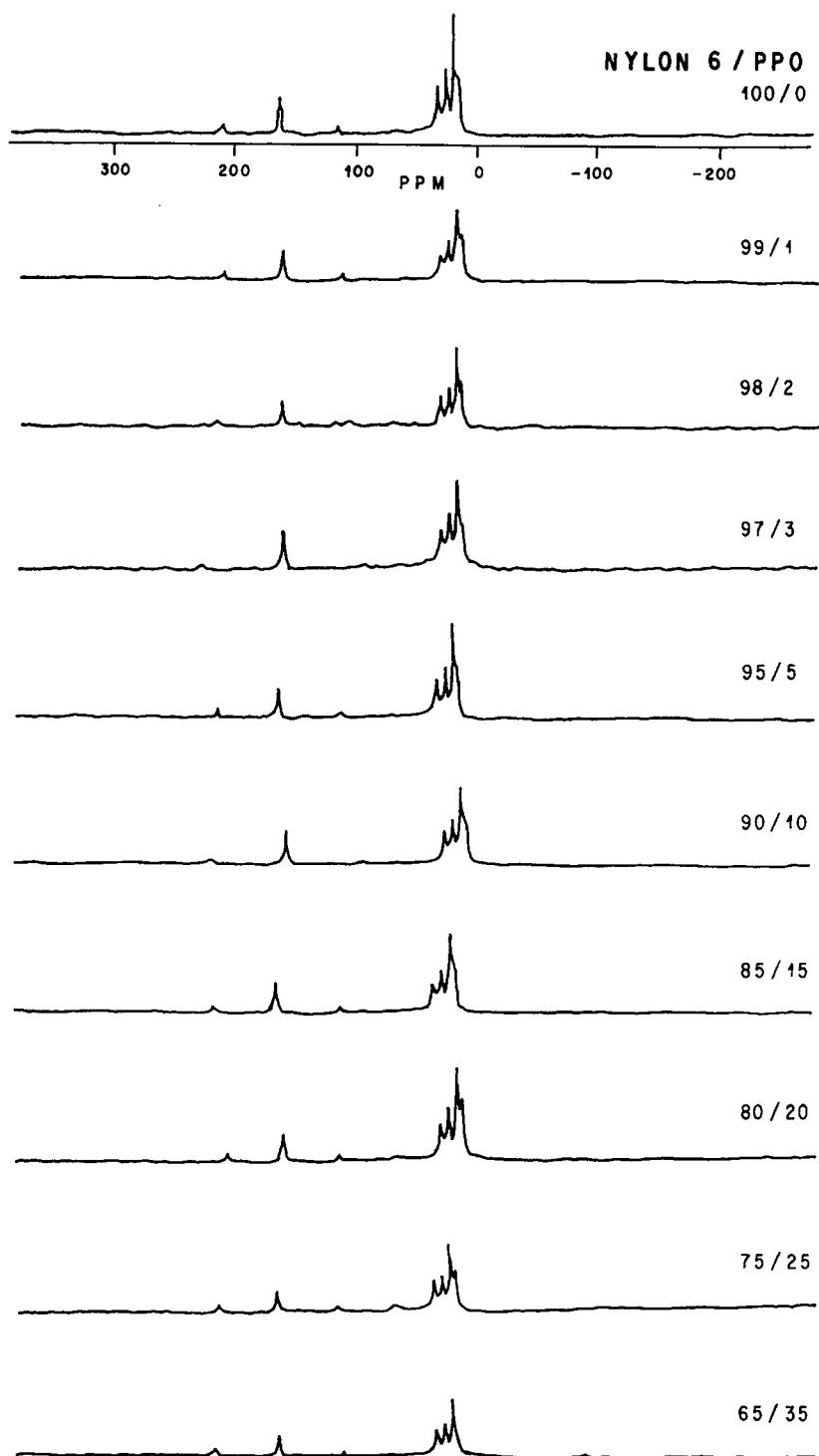
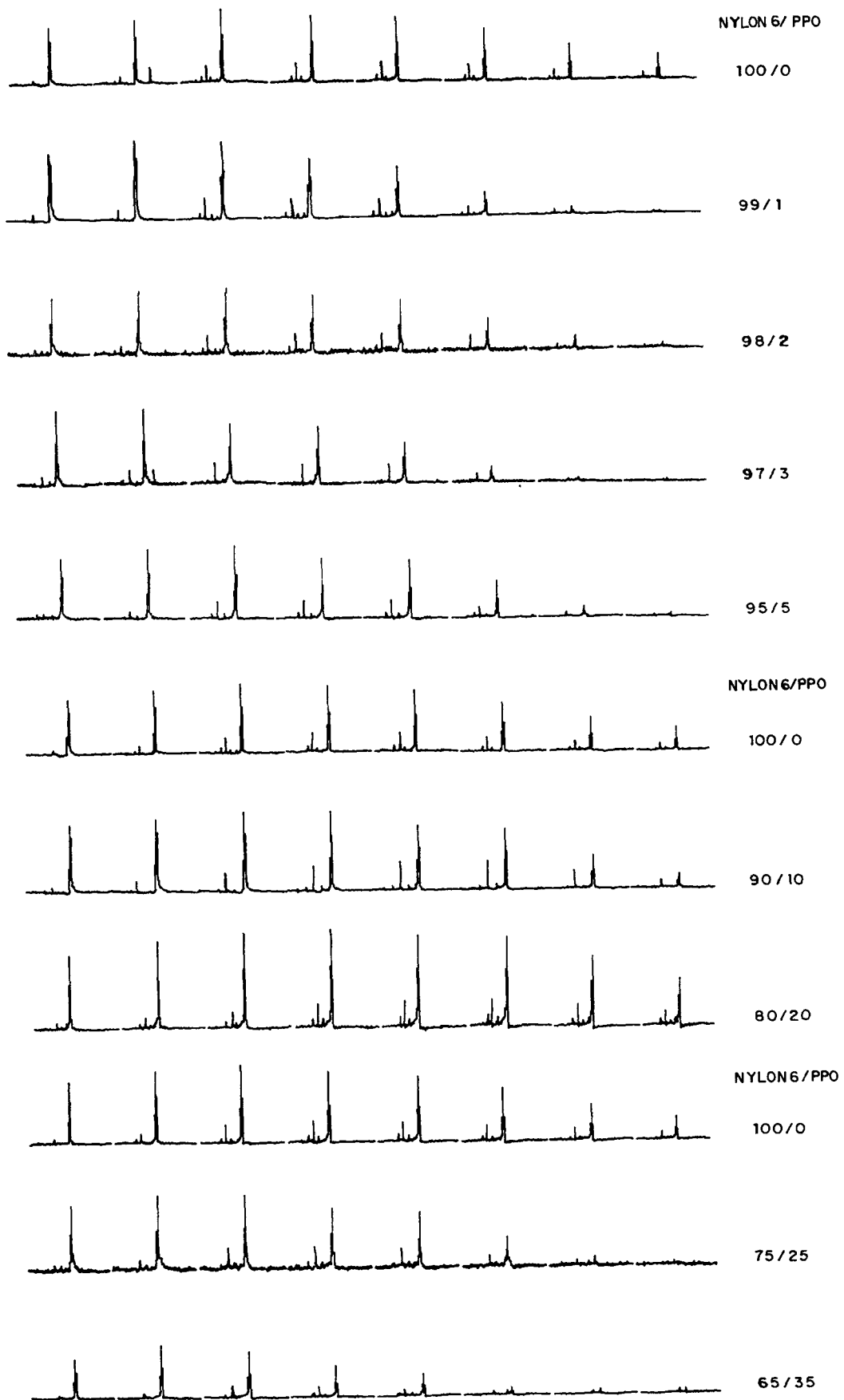


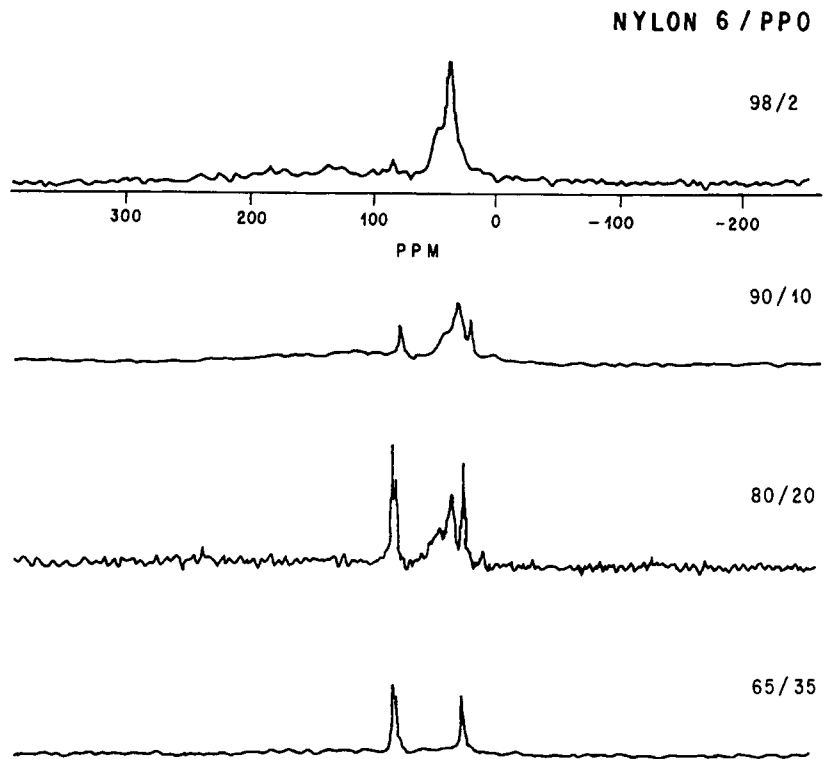
Figure 2 CP/MAS carbon-13 NMR spectra of pure Nylon 6 and Nylon 6/PPO blends.

Nylon 6 ( $\text{CH}_2$ ) as well as the methyl and CH group of PPO were detected. Analyzing mixtures with PPO content up to 20%, the blend with 25% PPO still shows resonance lines for both polymers, while at 35% PPO only signals belonging to PPO were ob-

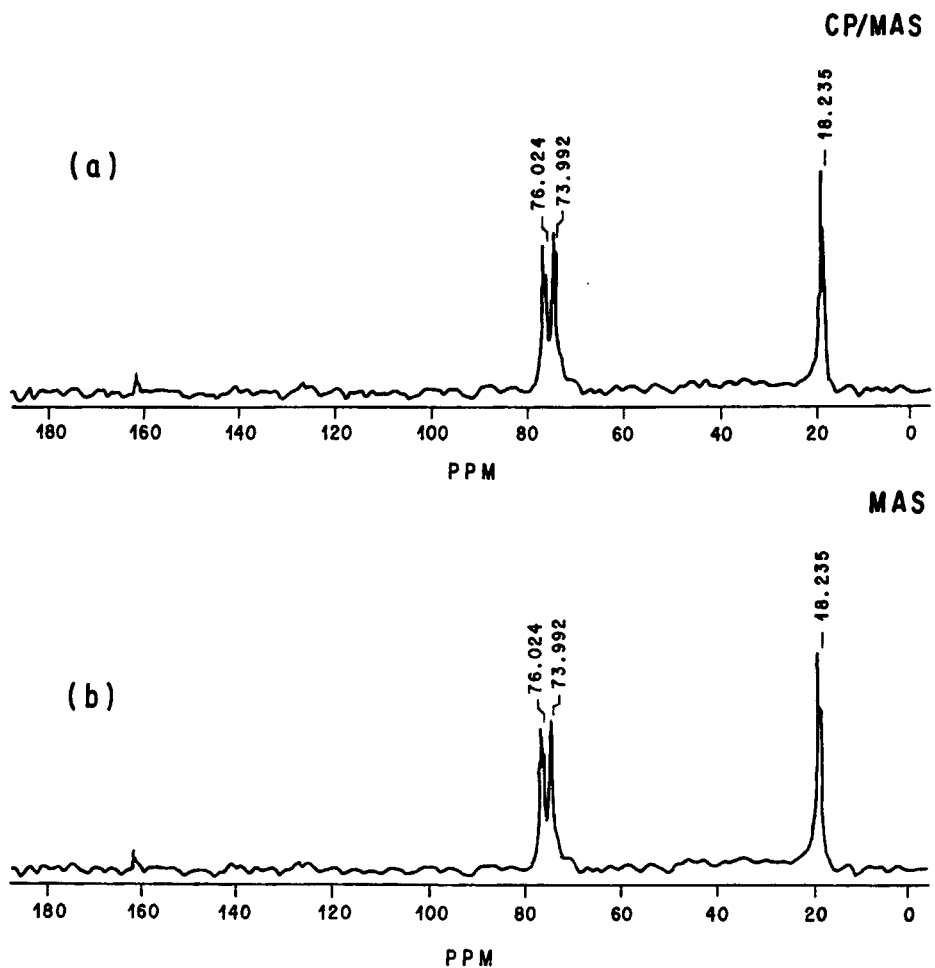
served. This is an indication that at least two domains with different mobilities were observed (Fig. 4). An interesting comparison can be made with the spectrum obtained from the variation contact time (the last contact time:  $\tau = 8$  ms); only signals from



**Figure 3** Variation contact time experiment: (a) pure Nylon 6/PPO blends with PPO content varying up to 5%; (b) pure Nylon 6/PPO blends with PPO range from 10–20%; and (c) pure Nylon 6/PPO blends with PPO content from 25–35%.



**Figure 4** MAS carbon-13 NMR spectra of pure Nylon 6 and Nylon 6/PPO blends.



**Figure 5** Carbon-13 NMR spectra of Nylon 6/PPO blends with 35% PPO: (a) CP/MAS technique; (b) MAS technique.

**Table II Proton Spin-Lattice Relaxation Time in the Rotating Frame for Pure Nylon 6 and Nylon 6/PPO Blends**

Sample (PPO%)	$T_{1\rho}$ (ms)
—	3.01
1	1.67
2	1.59
5	1.72
10	2.28
20	2.45
25	3.51
35	4.20

PPO were assigned, which confirms the presence of more than one phase with distinct mobility (see Fig. 5).

## CONCLUSION

In our conclusion it is clear that variation contact time experiments and MAS techniques, together with thermal analysis, are able to characterize the blend homogeneity at molecular level. For the systems investigated, the compatibility range was detected up to 20% of PPO. However, the best compatibility range is from 10% to 20% of poly(propylene oxide). This kind of study has been applied to other systems involving polymers with different natures and the compatibility was also analyzed.

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