

# A High-Resolution Solid-State NMR Investigation of Molecular Mobility of Poly(methyl methacrylate)/Poly(vinyl pyrrolidone)/Poly(ethylene oxide) Ternary Blends

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**ABSTRACT:** The ternary blends of poly(methyl methacrylate)/poly(vinyl pyrrolidone)/poly(ethylene oxide), PMMA/PVP/PEO, were prepared by melting process, using a Haake plastograph, and nuclear magnetic resonance spectroscopy (NMR) was used as a methodology to characterize the molecular mobility of blend components, because NMR has several techniques that allow us to evaluate polymeric materials in different time scales. The NMR results showed that the blends were miscible on a molecular level. The values of proton lattice relaxation

time in the rotating frame ( $T_{1\rho H}$ ) indicate that the ternary blend interaction did not reduce the intermolecular distance, because it is dipole–dipole. The molecular motion of each component, even in the miscible amorphous phase and the addition of PEO, has a definitive effect on the PMMA molecular mobility. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1492–1495, 2006

**Key words:** compatibility; NMR; ternary blends

## INTRODUCTION

Polymeric ternary blends can be prepared by at least two ways, using solution cast; and melting mix. Focusing on the preparation of a new material, two questions arise: one is related how to prepare it? and the other is how it will be characterized? The response for the first question is related to the best way and the appropriated conditions to blend the polymers. For the second one, the employment of a methodology that uses spectroscopic measurements, which will give information on blend components behavior, and is noninvasive. For that reason, we prepared the PMMA/PVP/PEO ternary blend by melting process and used NMR as a methodology to characterize the blend components miscibility and interaction, because NMR has several techniques that allow us to evaluate polymeric materials in different time scales. MAS  $^{13}\text{C}$  technique permits to obtain information about part or whole sample, by varying acquisition conditions, which can be choice to detect only mobile carbons. This generates information on sample molecular mobility in a certain time scale. The routine CPMAS  $^{13}\text{C}$

technique informs on changes in sample environment, as it depends on the extent of the interaction and the molecular motions, since CP rates depends on the exchange of protons directly attached or of neighboring protons.<sup>1,2</sup> It is known that mobile carbons atoms take longer time to cross polarize than less mobile. Solid-state NMR also offers a great variety of relaxation times and they are informative on molecular mobility, in distinct time scales.<sup>1–10</sup> The spin-lattice relaxation process is generally dominant in solid state giving direct information on molecular motion. The proton spin-lattice relaxation time in the rotating frame is highly important and it is used to study the dynamic of samples, because it is sensitive to molecular motions in a frequency of tens of kilohertz.<sup>1–10</sup> In summary, the focus of this work is to understand the molecular mobility behavior of the PMMA/PVP/PEO ternary blends, to evaluate the blend components miscibility and interaction.

## EXPERIMENTAL

### Blends preparation

A commercial PMMA ( $M_n = 28,000$  and polydispersity 2.96, supplied by ICI Acrylic), PVP (supplied by BASF as luviskol K 30), and PEO ( $M_n = 4000.000$  and supplied by Aldrich Chemical Company) were blended at different proportions (90/5/5, 80/10/10,

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70/15/15, and 70/20/10), by casting the solution onto plates and by melting, using a HAKKE plastograph, at 200°C. For casting the solution, the solvent used was chloroform, and the blends were kept for 1 week on a dissector and after that were put on vacuum oven for 3 days, to completely remove the solvent. The solvent elimination was accompanied by infrared spectroscopy.

### NMR measurements

The solution NMR spectra were obtained on VARIAN MERCURY 300 and the solid spectra on a VARIANINOVA 300 spectrometer, operating at 75.4 MHz for  $^{13}\text{C}$ . The solution  $^{13}\text{C}$  spectra in deuterated chloroform ( $\text{CDCl}_3$ ) were obtained in quantitative conditions. All solid NMR experiments were obtained at ambient probe temperature and were performed using gated high decoupling. A zirconium oxide rotor of 7 mm diameter was used to acquire the NMR spectra at a spinning rate of 5.8 kHz. The  $^{13}\text{C}$ -NMR spectra were carried out in the magic angle spinning (MAS) with a short delay between 90 pulses; cross-polarization magic angle spinning (CPMAS) with 2 s of recycle delay and variable contact-time (VCT), using the same CPMAS conditions with a range of contact time established from 0.2 to 8 ms. The proton spin-lattice relaxation time in the rotating frame was measured by delayed contact-time (DCT) experiment, using a spin-locking range from 0.2 to 8 ms.

## RESULTS AND DISCUSSION

The microstructure of the ternary PMMA/PVP/PEO at different proportions, analyzed by  $^{13}\text{C}$  solution NMR in  $\text{CDCl}_3$ , showed that the carbonyl carbons were split (Fig. 1), due to the nontactic order in the blends. No difference in the chemical shift was found comparing to PMMA itself.

Figure 2 shows the  $^{13}\text{C}$  MAS spectrum of ternary blends (80/10/10). A short delay between 90° pulses were applied to observe the mobile region, and as it can be seen, only signals derived from PEO, located at approximately 70 ppm, and from PMMA, at 16 ppm ( $\text{CH}_3$ ), 45 ppm ( $\text{C}_{\text{quaternary}}$ ), and 51 ppm ( $\text{CH}_3\text{—O}$ ), were detected, indicating that PEO is acting as a plasticizer for PMMA, because these polymers have affinity.

Figure 3 exhibits the  $^{13}\text{C}$  CPMAS spectrum of ternary blend at 80/10/10 proportion. The NMR spectrum shows signals from all blend components, and the pattern of it is a typical behavior of miscible blend at the molecular level.

The VCT experiment for the 80/10/10 proportion (Fig. 4) showed the behavior of the  $^{13}\text{C}$  decays with

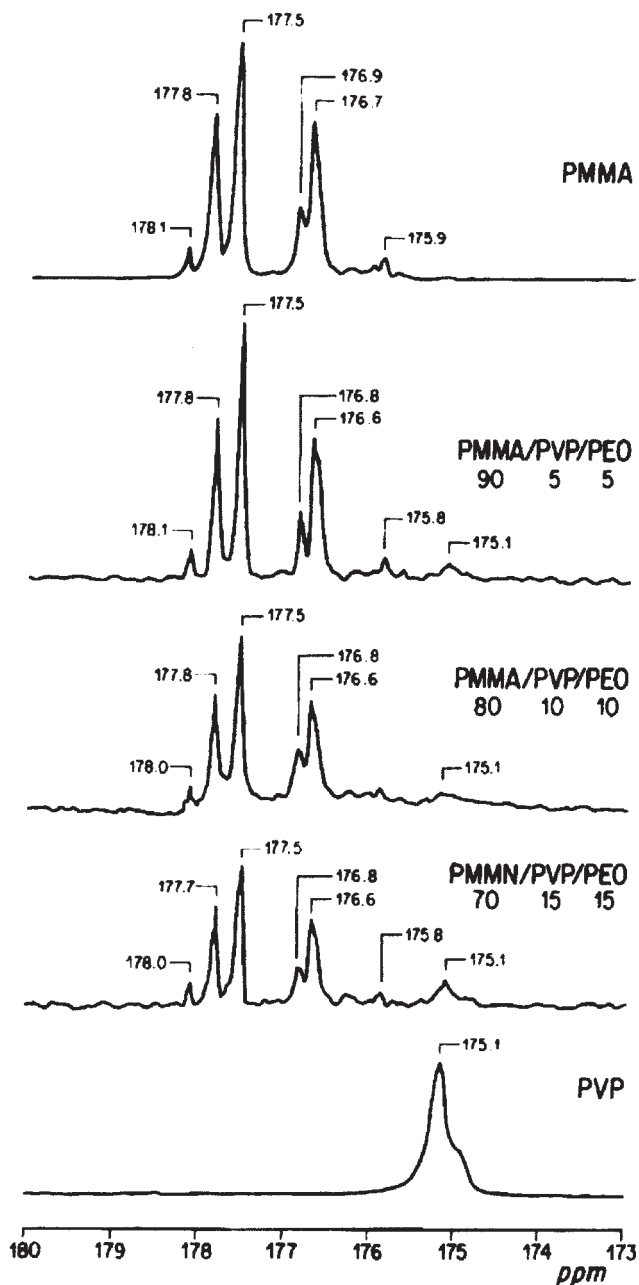


Figure 1  $^{13}\text{C}$  solution NMR spectra of the carbonyl region of PMMA/PVP/PEO blends at different proportions.

the increasing of contact-time for the blend. The decay presents a typical pattern of amorphous sample.

From the delayed contact-time experiment, the values of solid-state proton spin-lattice relaxation data in the rotating frame, for the carbonyl group, were measured by DCT, and the values are listed in Table I.

From the relaxation data exhibited in Table I, it is clear that, as the proportion of both PEO and PVP

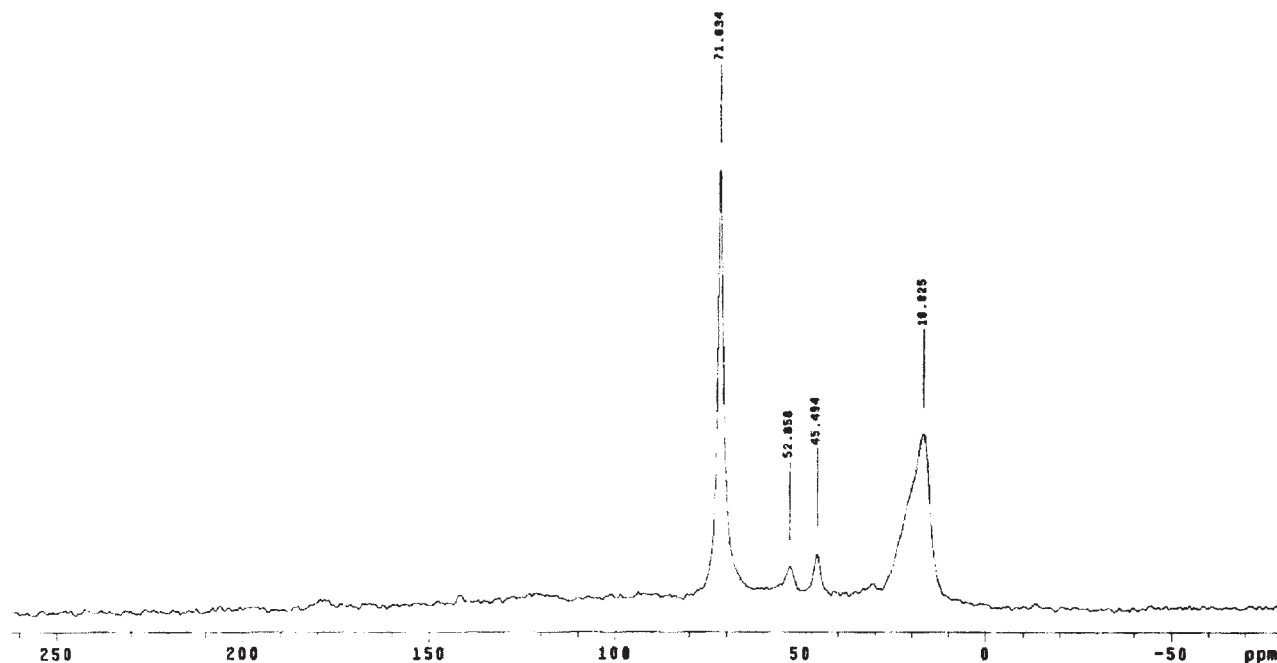


Figure 2  $^{13}\text{C}$  MAS NMR spectrum of the ternary blend PMMA/PVP/PEO 80/10/10, with short recycle delay between 90 pulses.

increases, the relaxation parameter also increases comparing to both polymers. Increase in this parameter shows that the chains are more mobile, which confirms that PEO and PVP are acting as plasticizers for PMMA matrix. And, as just one value of this parameter was found, it can indicate that these compositions are miscible in the molecular level.

## CONCLUSIONS

The NMR results showed that the blends of PMMA/PVP/PEO were miscible on a molecular level. The results of a spin-lattice relaxation time in the rotating frame indicate that the ternary blend interaction did not reduce the intermolecular distance and the molecular motion of each component, even in the

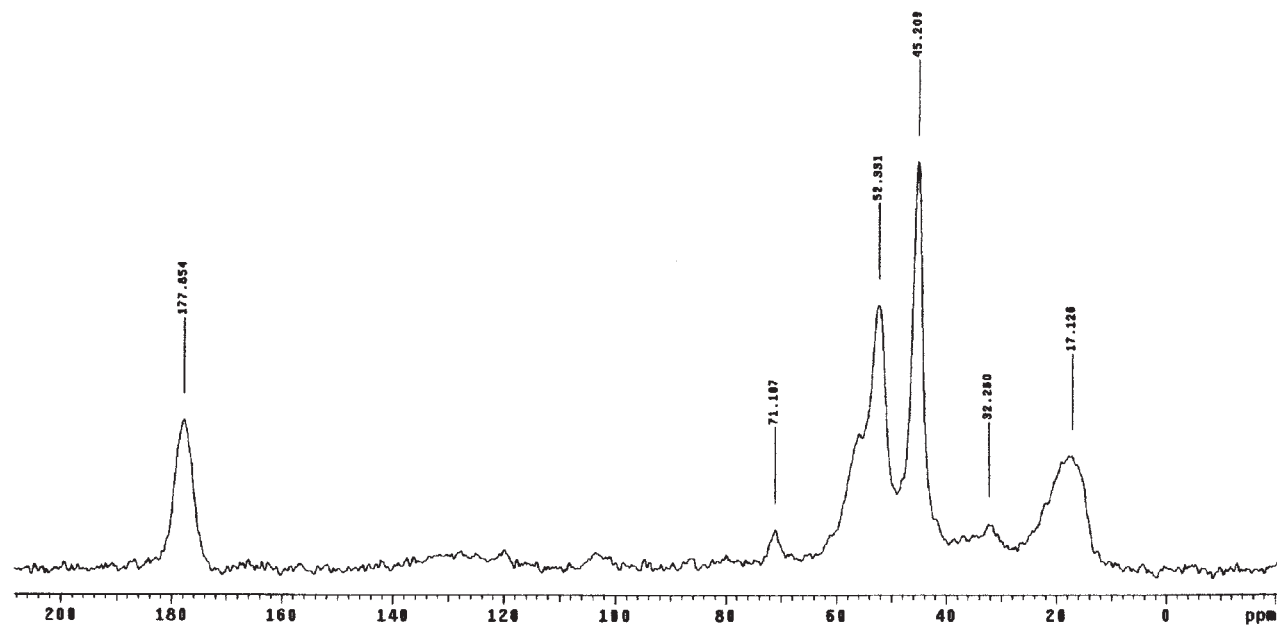


Figure 3  $^{13}\text{C}$  CPMAS spectrum of PMMA/PVP/PEO 80/10/10 at 1 ms of contact time.

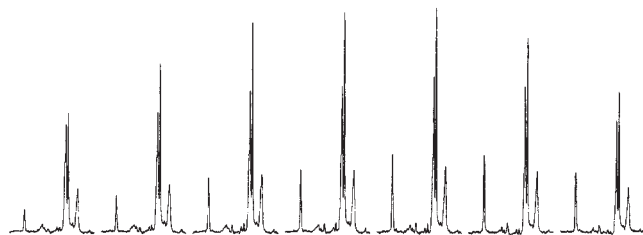


Figure 4 VCT experiment of PMMA/PVP/PEO 80/10/10.

TABLE I  
 $T_{1\rho H}$  Relaxation Data, Measured For DCT, for the  
 Carbonyl Group (178.2 ppm) of the  
 PMMA/PVP/PEO Blends

Proportion (%) PMMA/PVP/PEO	$T_{1\rho H}$ (ms) C=O
100/0/0	2.6
90/5/5	5.6
80/10/10	8.9
70/15/15	9.7
0/100/0	2.3

miscible amorphous phase, as well as the addition of PEO have a definitive effect on the PMMA molecular mobility.

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