

# Solution and Solid State Nuclear Magnetic Resonance Investigation of Poly(methylmethacrylate)/Poly(ethylene oxide) Blends

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**ABSTRACT:** It is well known that nuclear magnetic resonance spectroscopy (NMR) is a powerful method to characterize blends compatibility at the molecular level. In this work binary blends formed by poly(methylmethacrylate)/poly(ethylene oxide), PMMA/PEO, were investigated by different solution and solid state NMR techniques to obtain information on blends homogeneity and compatibility. It was characterized that the values of  $T_1^H\rho$  obtained by vari-

able contact time and delayed contact time experiments, for each composition, were distinct and this fact suggests that regions with different molecular mobilities exist, as a consequence of blending interaction. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2955–2958, 2003

**Key words:** poly(methylmethacrylate); poly(ethylene oxide); nuclear magnetic resonance; blends compatibility

## INTRODUCTION

Knowing that the chemistry of ternary blends are an important field to obtain new polymers with determined application, it is necessary to start investigating the binary blends pair to understand their behavior. The main purpose of this work is to obtain enough information from binary blends to study later the ternary blends formed by poly(methylmethacrylate)/polyvinylpyrrolidone (PVP)/poly(ethylene oxide) (PMMA/PVP/PEO). Thus, to accomplish this it was necessary to prepare the PMMA/PEO blends and to evaluate the influence of the PEO added to PMMA with respect to microstructure and molecular mobility. Nuclear magnetic resonance (NMR) spectroscopy was chosen due to the fact that solution and solid state data, when correlated, can allow us to evaluate the dynamic behavior of binary blends.<sup>1,2</sup> It is known that the stereoregularity of polymer chains influence polymer–polymer miscibility.<sup>1,3–5</sup> PMMA is an atactic polymer and PEO is a semicrystalline polymer. In the NMR spectrum the changes in the lineshapes and/or frequency of the resonance signals of the pure polymers in comparison to those of blend components have been used as an evidence of interaction between both blend components. Besides, the proton spin–lattice relaxation time in the rotating frame ( $T_1^H\rho$ ) permits to estimate the scale of miscibility of a polymer

pair.<sup>4–15</sup> These studies focus the determination of blend microstructure and correlate them with relaxation data. Based on this aim we decide to measure the  $T_1^H\rho$  for two experiments variable contact time and delayed contact time, because the  $T_1^H\rho$  determined by variable contact time (VCT) depends on proton spatial proximity, and the interaction process can influence the values of this parameter. The measurement of  $T_1^H\rho$  by delayed contact time will give to us the behavior of the chains homogeneity along the macromolecular chains.<sup>3–10</sup>

## EXPERIMENTAL

### Blends preparation

A commercial PMMA ( $M_n = 28,000$  and polydispersity 2.96), supplied by ICI Acrylic, Inc., New York, and PEO ( $M_n = 4,000.000$  and supplied by Aldrich Chemical Company, Inc., St. Louis) were blended at different proportions (80/20, 70/30, and 50/50) by casting the solution onto plates. The solvent used was chloroform, and the blends were kept for one week on a dissector and after that were put on vacuum oven for 3 days, to complete 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 Varian Inova 300 spectrometer, operating at 75.4 MHz for  $^{13}\text{C}$ . The solution  $^{13}\text{C}$  spectra were obtained in quantitative con-

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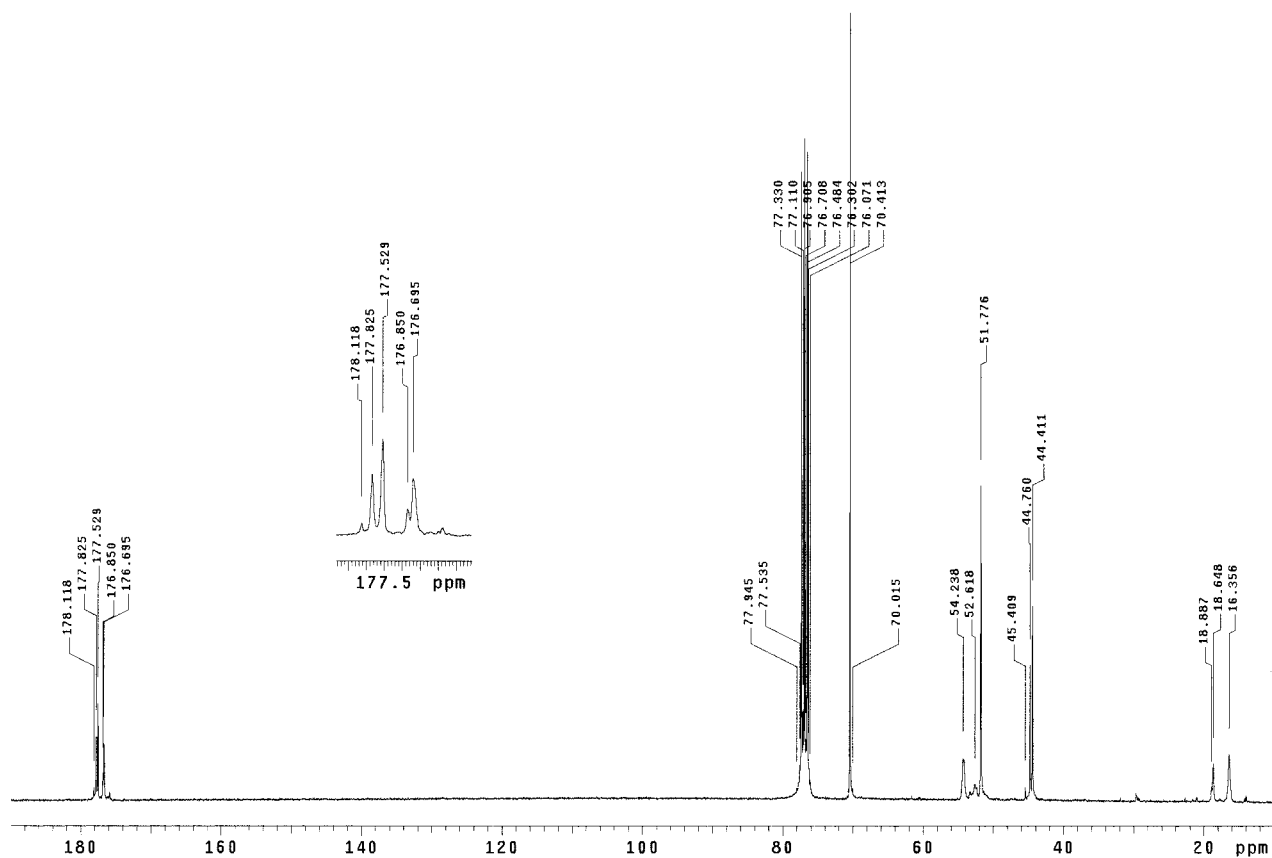


Figure 1  $^{13}\text{C}$ -NMR solution spectrum of the binary blend PMMA/PEO (80/20).

ditions,  $90^\circ$  pulse, gated decoupler and 20 s of time delay. 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 rates of 5.8 kHz. The  $^{13}\text{C}$ -NMR spectra were carried out in the magic angle spinning (MAS), cross-polarization magic angle spinning (CPMAS) and VCT. A range of contact time was established from 0.2 to 8 ms.  $T_1^{\text{H}\rho}$  values were determined from the intensity decay of  $^{13}\text{C}$  peaks with increasing contact times. This relaxation parameter was also measured by delayed con-

tact time (DCT) experiment using a spin-locking range from 0.2 to 8 ms.

## RESULTS AND DISCUSSION

### Solution NMR

The  $^{13}\text{C}$ -NMR solution spectrum of the PMMA/PEO 80/20 (w/w) proportion is presented in Figure 1. Both polymer signals were detected and no change in the chemical shift of all detected carbons in related to the homopolymers, were observed.

TABLE I  
Microstructure (%) of Quaternary Carbon and Carbonyl Group of PMMA and Their Blends with PEO

PMMA/PEO (weight/weight)	Microstructure (%)		
	mm	mr	rr
100/0 <sup>b</sup>	4.3	36.9	58.8
100/0 <sup>c</sup>	4.0	34.4	61.6
90/10	3.5	37.0	59.5
80/20	3.3	37.3	59.4
70/30	4.0	38.3	57.7
50/50	3.5	36.7	59.9

<sup>a</sup> PMMA pellet.

<sup>b</sup> PMMA film.

TABLE II  
Assignment of the Microstructure of Quaternary Carbon from PMMA and Their Blends with PEO

PMMA/PEO (weight/weight)	Assignment (ppm)		
	mm	mr	rr
100/0 <sup>a</sup>	45.2	44.6	44.2
100/0 <sup>b</sup>	45.2	44.6	44.2
90/10	45.4	44.7	44.4
80/20	45.4	44.7	44.4
70/30	45.3	44.6	44.3
50/50	45.3	44.7	44.3

<sup>a</sup> PMMA pellet.

<sup>b</sup> PMMA film.

**TABLE III**  
Assignment of the Microstructure of Carbonyl Group  
from PMMA and Their Blends with PEO

PMMA/PEO (weight/weight)	Assignment (ppm)		
	mm	mr	rr
100/0 <sup>a</sup>	175.9	176.7	177.6
100/0 <sup>b</sup>	175.8	176.7	177.6
90/10	175.7	176.5	177.4
80/20	175.9	176.7	177.5
70/30	175.8	176.6	177.4
50/50	175.8	176.6	177.4

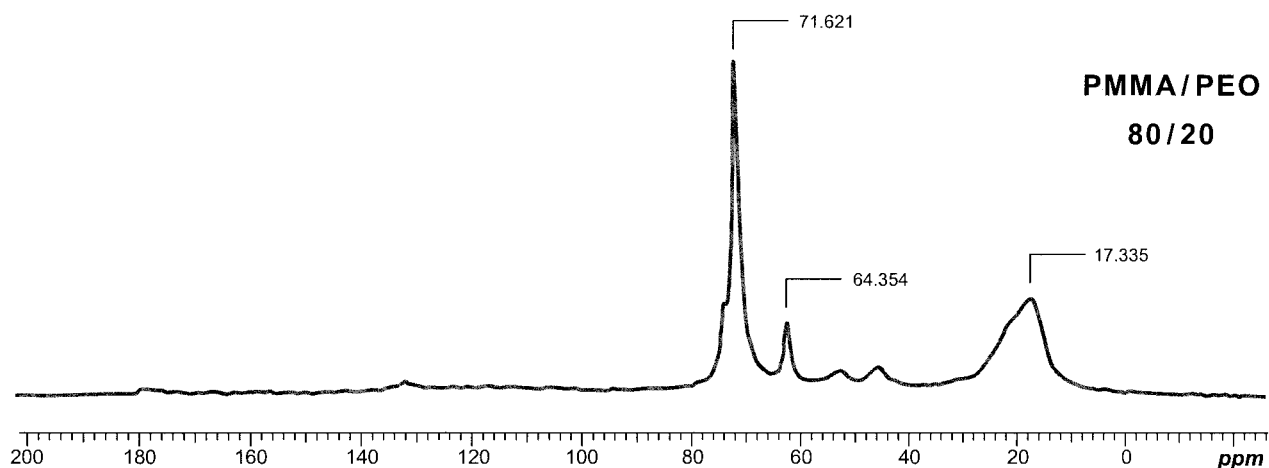
<sup>a</sup> PMMA pellet.

<sup>b</sup> PMMA film.

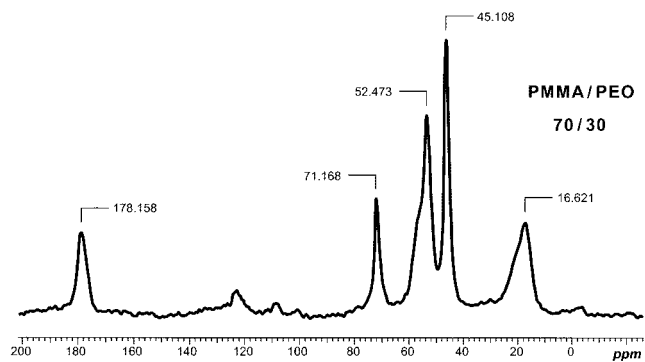
As the stereoregularity of polymer chains can influence the miscibility behavior of polymer blends, the determination of the microstructure of PMMA and their blends with PEO were necessary to be done. The microstructure was determined by <sup>13</sup>C solution NMR. From the analysis of <sup>13</sup>C solution spectra, it was observed that the percentage values for the microstructures, measured for quaternary carbons and carbonyl group (Table I), did not change for either type of carbons, as a consequence of the blending process. It was confirmed that even for different proportions no influence on the microstructure was observed, because the interaction process between both polymer blend components occurs with the same intensity with respect to the microstructure, and as was found for PMMA, a predominance of syndiotactic configuration was maintained.

Analyzing the chemical shift values for both carbonyl and quaternary carbons no influence in the assignments, for all studied proportion, were detected as expected (see Tables II and III), which confirms that the interaction process occurs indiscriminately for all carbons that take part of this process.

The <sup>13</sup>C-NMR spectrum obtained by MAS technique for PMMA/PEO (80/20) is presented in Figure 2, it



**Figure 2** <sup>13</sup>C-NMR spectrum obtained by MAS technique from PMMA/PEO (80/20).



**Figure 3** <sup>13</sup>C-NMR spectrum obtained by CPMAS technique from PMMA/PEO (80/20).

was detected that this blend presented a region with high mobility, which is constituted by PMMA/PEO interface chains. Signals located at 71.62 ppm for CH<sub>2</sub>-O from PEO and 17.39 ppm for methyl from PMMA were detected because those groups present high mobility in the binary blend. A small signal detected in 62 ppm was derived from to CH<sub>2</sub>-O group, and this NMR signal was attributed to a CH<sub>2</sub>-O that is probably plasticizing PMMA, indicating some interaction between both polymer blend components.

From the <sup>13</sup>C-NMR spectrum obtained by CPMAS technique (Figure 3), it can be seen that all polymers signals did not change their chemical shift values. Since this technique shows all type of carbons and according to the contact time used (1 ms), the carbons that belongs to the rigid region did not change their chemical shifts, they are not taking place of the interaction in the plasticizing process.

The values of solid state relaxation data, determined by proton spin-lattice relation time in the rotating frame, measured for VCT and DCT, for the carbonyl group (178.7 ppm) are listed in Table IV.

From the values of T<sub>1</sub><sup>H</sup>ρ, obtained by both VTC and DCT, it can be seen that there does not exists a strong

**TABLE IV**  
 $T_1^H\rho$  Relaxation Data Measured for the Carbonyl Group  
 (178.7 ppm) of the PMMA and Their Blends,  
 by VCT and DCT Experiments

Proportion (%) PMMA/PEO	$T_1^H\rho$ (ms)	
	VCT	DCT
100/0	2.3	2.5
80/20	9.0	7.2
70/30	8.9	4.5

dipolar coupling between proton of both polymers. Thus a nonefficient spin-diffusion occurs. The increase in the values of this parameter indicates the existence of heterogeneous phases in the blends. However, for the 80/20 proportion the proximity of  $T_1^H\rho$ , measured by both techniques, can indicate a existence of some plasticization effect. Therefore, for 70/30 proportion a phase separation process occurred.

### CONCLUSION

According to all NMR results, it was verified that the binary compositions are heterogeneous, but a plasticized interface between both blend components was detected.

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