Solution and Solid-State NMR Investigation of Poly(methyl methacrylate)/Poly(vinyl pyrrolidone) Blends

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ABSTRACT: The development of polymer blends has become very important for the polymer industry because these blends have shown to be a successful and versatile alternative way to obtain a new polymer. In this study, binary blends formed by poly(methyl methacrylate) (PMMA) and poly(vinyl pyrrolidone) were prepared by solution casting and evaluated by solution and solid-state NMR. Variations in the microstructure of PMMA were analyzed by ^{13}C solution NMR. Solid-state NMR promotes responses on physical interaction, homogeneity, and compatibility to use these blends to understand the behavior of the ternary blends. The NMR results led-us to acquire information on the polymer blend microstructure and molecular dynamic behavior. From the NMR solution, it was possible to evaluate the microstructure of both polymer blend components; they were atactic. From the solid state, good compatibility between both polymer components was characterized. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 372–377, 2004

Key words: NMR; polymer blends; characterization

INTRODUCTION

Temary blends are gaining an important share in the field of polymer property diversification, and their chemistry is one of the most common methods used to improve polymer properties. To understand temary blend behavior, it is necessary to investigate the binary blend pair to obtain some information on compatibility and miscibility. The general purpose of this study was to elucidate the temary blend behavior of poly(methyl methacrylate) (PMMA)/poly(ethyleneoxide) (PEO)/poly(vinyl pyrrdidone) (PVP). First, it was necessary to investigate the binary blend pair formed by PMMA and PVP to obtain responses of the blend behavior. The first investigation was done by the evaluation of the influence of the PVP in the PMMA/PVP blend microstructure, and we correlated these data with the molecular mobility of the binary blends in different component proportions. On the basis of a previous NMR investigation of PMMA/PVP done by Silva and Tavares,[1] we started using-solution NMR measurements and continued the investigating with solid-state NMR techniques.[1–9] NMR spectroscopy was used as an absolute method of analysis because it is composed of several techniques. In NMR spectra, the changes in the lineshapes and frequency of the resonance signals of the pure polymers in comparison to those of blend components can be used as evidence of interaction between the blend components.[6] Also, the proton spin-lattice relaxation times in the rotating frame ($T_1^H\rho$) allows one to estimate the scale of miscibility of a polymer pair.[7–9] The first solid-state study of PMMA/PVP[1] gave us some information on the blend range homogeneity and compatibility. This second study focused on the determination of blend microstructure and correlated it with relaxation data. With this aim, we decided to measure the $T_1^H\rho$ applying two techniques, variable contact time (VCT) and delayed contact time (DCT). $T_1^H\rho$ determined by VCT depends on proton spatial proximity (due to the polarization transfer), and the interaction process can influence the values of this parameter. The measurement of $T_1^H\rho$ reveals the behavior of the chain homogeneity along the macromolecular chains due to intermolecular interaction.

EXPERIMENTAL

Blends

Binary blends formed by PMMA and PVP were prepared by chloroform solution casting at different proportions: 80/20, 70/30, and 50/50. The solutions were cast onto plates, and they were kept in a dissector for at least 2 weeks. To obtain drying films, these films were put in a vacuum oven for about 260 h at 50°C. Then, the obtained films were analyzed by IR spec-

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troscopy to accompany the complete residual solvent elimination.

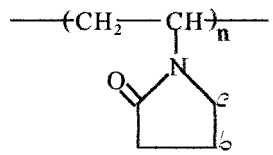
NMR

All solution NMR spectra were obtained on a Varian Mercury 300, and the solid spectra were obtained on a Varian Inova 300 spectrometer operating at 75.4 MHz for ^{13}C. The solution ^{13}C spectra were obtained in quantitative conditions. All solid NMR experiments were obtained at ambient probe temperature and were performed with gated high decoupling. A zirconium oxide rotor 7 mm in diameter was used to acquire the NMR spectra at spinning rates of 5.8 kHz. The ^{13}C-NMR spectra were obtained with magic-angle spinning (MAS), cross-polarizationmagic-angle spinning (CP-MAS), and VCT. A range of contact time was established from 0.2 to 8 ms. $T_1^H\rho$ values were determined from the intensity decay of ^{13}C peaks with increasing contact times. This relaxation parameter was also measured by a DCT experiment with a spin-locking range from 0.2 to 8 ms.

RESULTS AND DISCUSSION

Solution NMR

To understand the microstructure of the commercial PVP (Luviskol K 30; see structure), it was used in ^{13}C solution NMR in different solvents, including deutered chloroform ($CDCl_3$), deuterium oxide (D_2O), and deutered sulfoxide [dimethyl sulfoxide/DMSO].[5] The solution of PVP in D_2O and DMSO showed a split in the carbonyl group, CH_2, and CH of the chain. Therefore, in $CDCl_3$ the carbonyl group was wide and presented a shoulder at lower frequency, but the CH_2 and CH showed the microstructure. In all solvents, the PVP was atactic (Fig. 1). Another interesting point was related to the detection of the two signals located at 29.7 ppm (CH_2-c) and 20.7 ppm (CH_2-b) from the heterocycle (Fig. 2). We investigated these signals considering first some polymer impurities, focusing on the idea the polymer was soluble in chloroform and precipitated with acetone. After that, the polymer were resoluble in chloroform, the ^{13}C solution NMR was also recorded at the same conditions, and the two signals were detected in the same chemical shifts. The second supposition was related to the polymer configuration to confirm that two other techniques were used. A proton attached test keeps the CH_2 nonhydrogenated carbon up and CH and CH_3 inverted; in this experiment, both signals were still up, confirming that they could have been the CH_2 or nonhydrogenated carbon. To identify the carbon, we recorded a heteronuclear correlation (HETCOR) (^{13}C—^{1}H), and those signals were correlated to hydrogen, confirming the CH_2. After all analyses, we attributed those signals to the isotactic configuration sequence. As expected, the solvent (chloroform) did not influence the microstructure, but the polymerization process for obtaining PVP did.



From the ^{13}C-NMR solution spectra of the PMMA/PVP blends, all NMR signals from both polymers were detected, and no influence of PVP on the chemical shift signals or overlapping signals were observed. When the form of carbonyl signals for the samples in deutered chloroform (Fig. 3) were analyzed, no change in the signals was detected with the variation in the polymer component proportions.

Solid-state NMR

PVP was investigated by basic MAS ^{13}C-NMR; a short delay between 90° pulses was applied to observe the mobile region. Routine CP-MAS ^{13}C-NMR and $P_1^H\rho$ were also used.[1] The MAS and CPMAS ^{13}C-NMR spectra showed wide signals that are common for amorphous materials blends, corroborating the signals observed by solution NMR, which showed split signals due to the microstructure. $T_1^H\rho$ for the carbonyl group was 2.3 ms, a typical value for an amorphous rigid material.

PMMA was also investigated by the same techniques, and the chemical behavior was different, although both polymers were amorphous. Therefore, the value of $T_1^H\rho$ for the carbonyl group was 2.3 ms, too.

Analyzing the MAS ^{13}C-NMR spectra of the binary blends, focusing on the mobile region, we observed only signals from PVP in these spectra, which indicated that PVP may have constituted the mobile domain.

Compared to the CP-MAS ^{13}C-NMR spectra of the blends, signals from both polymers were detected, which permitted us to assign the chemical structures of the blends.

The investigation of the molecular dynamic mobility of the blends in this study was centered on the influence of PVP on the PMMA matrix, and it was done with a VCT experiment, from which a series of CP-MAS ^{13}C-NMR spectra showed the ^{13}C decay with increasing contact time and informed on the blend homogeneity. From the VCT blend decay, the $T_1^H\rho$ value for the carbonyl group of the PMMA matrix in all of blends was determined. To evaluate and confirm the behavior of this parameter, we also measure $T_1^H\rho$

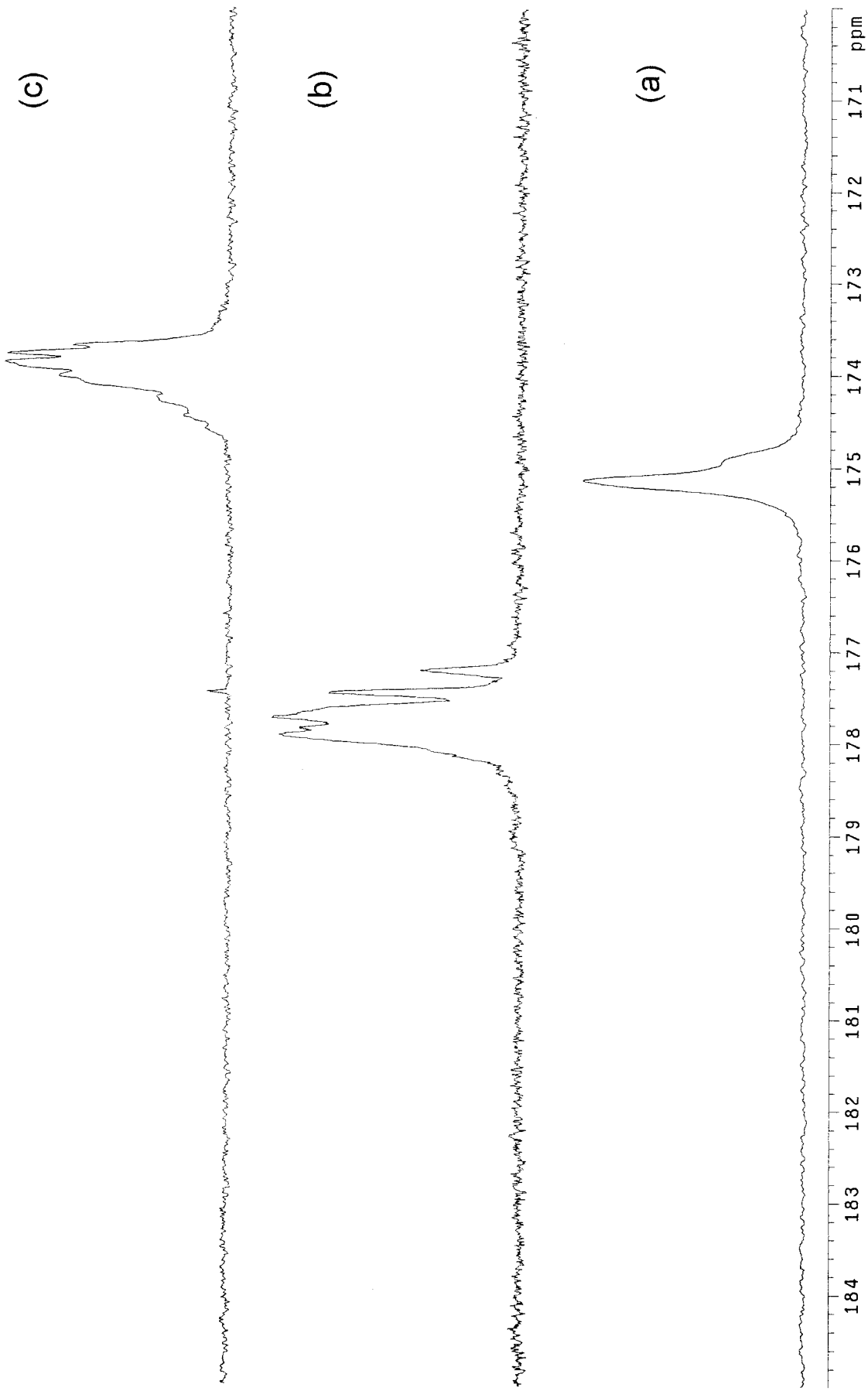


Figure 1 ^{13}C solution NMR of the carbonyl region of PVC in different solvents: (a) deutered chloroform ($CDCl_3$), (b) deuterium oxide (D_2O), and (c) deutered sulfoxide (DMSO).

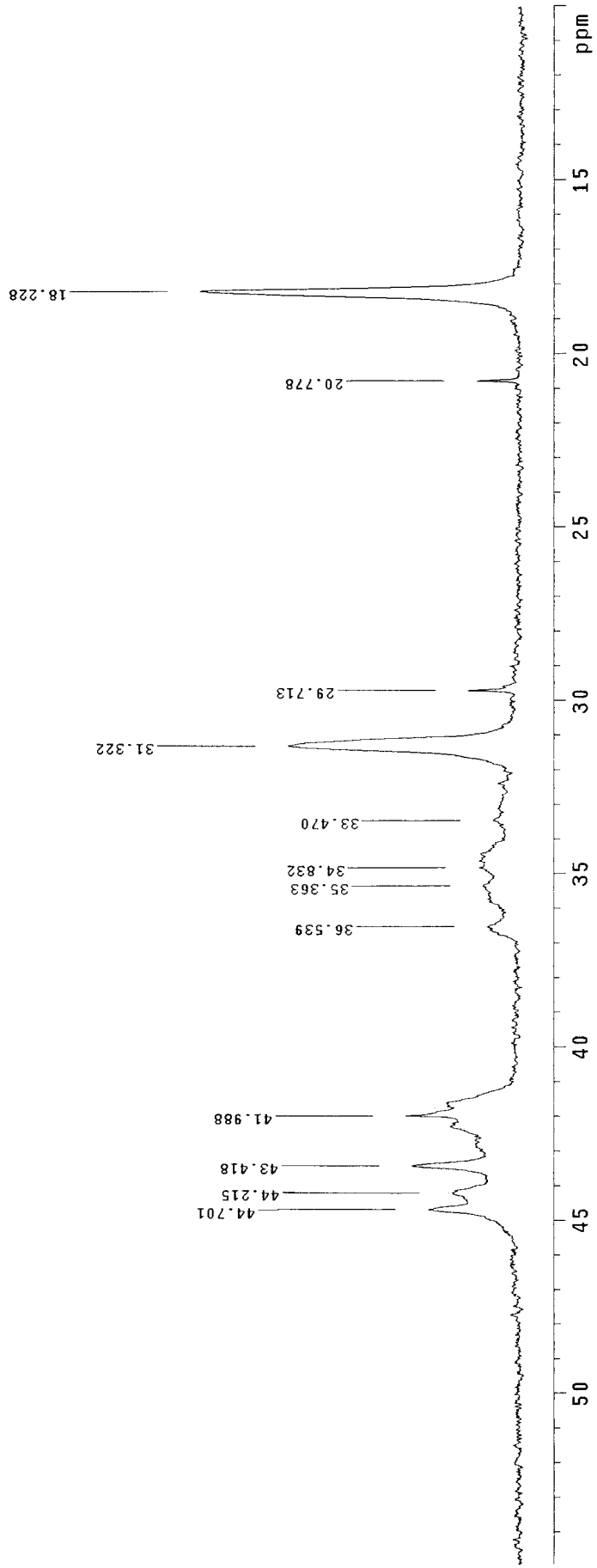


Figure 2 ^{13}C solution NMR of signals located at 29.7 ppm (CH_2-c) and 20.7 ppm (CH_2-b) from the heterocycle of the PVP structure.

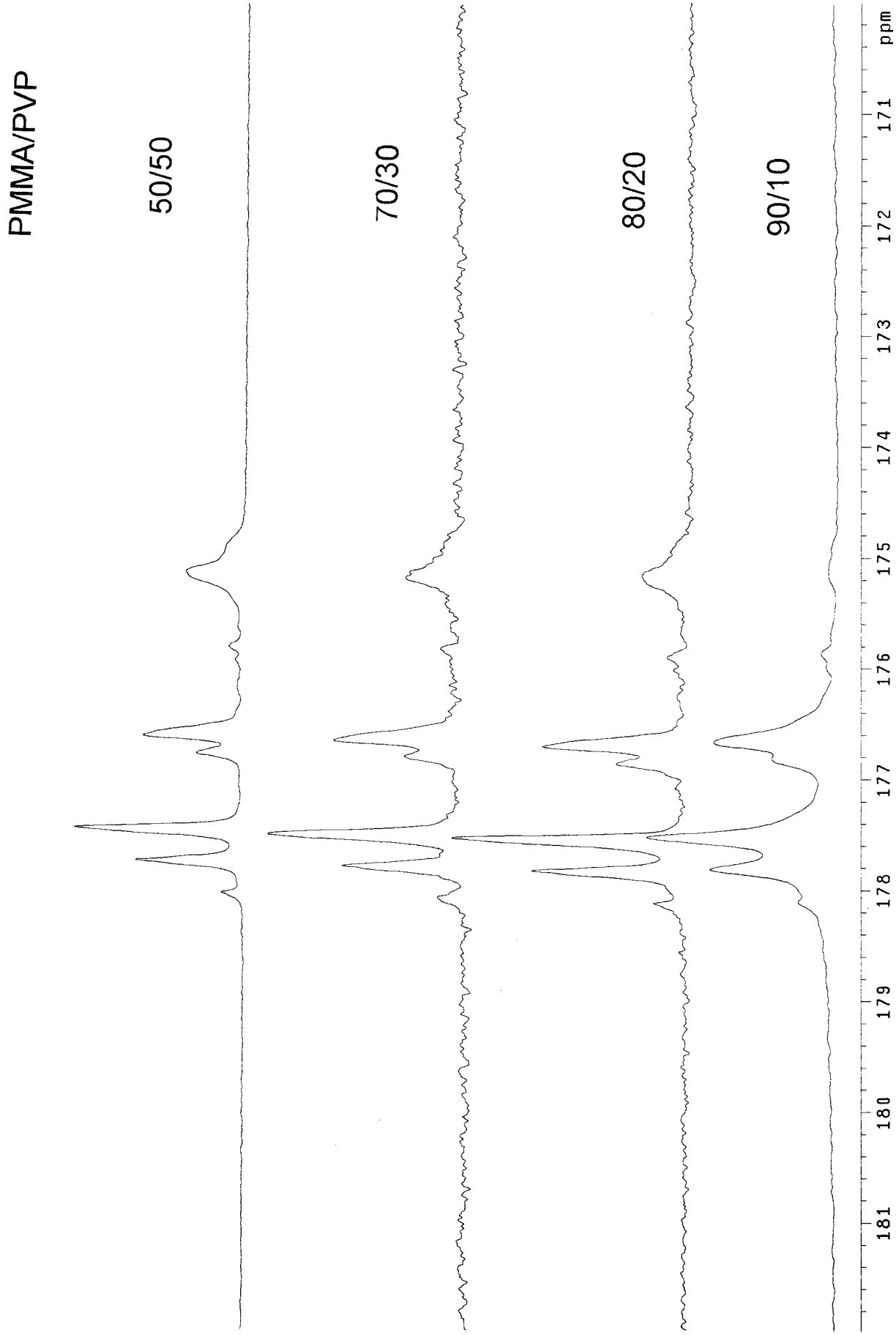


Figure 3 Carbonyl signals of PVP in different blend proportions.

TABLE I
Values of the Solid-State Relaxation Data Measured for VCT and DCT for the Carbonyl Group (178.7 ppm) of PMMA

PMMA/PVP (%)	$T_1^H\rho$ (ms) VCT	DCT
100/0	2.3	2.5
80/20	4.2	4.1
70/30	3.9	4.0
50/50	4.1	4.0

by DCT. The values of the relaxation parameter determined for both experiments are listed in Table I.

The carbon decays were single exponentials because intermolecular interactions between both blend components existed. Single values of $T_1^H\rho$ were found for each resolved carbon; an increase in the $T_1^H\rho$ values determined for the blends was detected. The PVP influenced the PMMA chain ordination, probably because it acted as a plasticizer, which corroborated with the MAS ^{13}C spectra, where only signals from PVP were registered for the blends because it was recorded with appropriate conditions to detect the mobile region.

CONCLUSIONS

The first results obtained by a PMMA/PVP binary blend pair made us keep this line as an analytical methodology to obtain more information about the temary PMMA/PVP/PEO system because the NMR measurements proved to be a good source for evaluating the blend behavior, which allowed a correlation between the solution and solid-state NMR data. On the basis of the purpose of this work, we conclude that there was an interaction between both polymer blend components in the proportion range investigated.

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