

Carbon-13 Assignments of EPDM/PP Atactic Blends by DEPT and HETCOR

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SYNOPSIS

The structure of the elastomeric ethylene-propylene-diene terpolymer/atactic polypropylene (EPDM/PPA) blends were assigned by NMR using DEPT (distortionless enhancement by polarization transfer) and HETCOR (heteronuclear correlation) sequences. These methods were carried out to elucidate solid-state ¹³C-NMR assignments of polymeric blends.

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INTRODUCTION

A knowledge of the structure and dynamics at the molecular level of polymers is of great importance to understand their physical properties. The complex nature of most systems is not easy to unravel. This is true even for homopolymers due to the existence of crystalline and amorphous phases and also because of the molecular weight distribution. Further complications may occur for systems such as polymer blends or copolymers. The difficulty is in accurately assigning the polymeric blends in the solid state.¹⁻³

Polymeric science is one of the many areas in which nuclear magnetic resonance (NMR) spectroscopy can be successfully applied. It is well known that NMR in conventional solution (¹H and ¹³C) in most cases, cannot be used alone to predict precise ¹³C assignments of a complex polymeric mixture. Advanced NMR techniques such as two-dimensional (2-D-NMR) and spectral editing features have been used to solve problems that were previously not well established.⁴⁻⁶ The present work was based on two distinct problems that may occur in systems such as ethylene-propylene-diene terpolymer/atactic polypropylene (EPDM/PPA). The first one comes from the chemical nature of the two polymers. Both present highly aliphatic chains and this fact can promote

signal overlapping when these kind of compounds are analyzed by NMR spectrometry. Interpreting the values of proton spin lattice relaxation time in the rotating frame for individual carbons can be a great problem. Second, the microstructure of PPA splits the NMR lines into several peaks that absorb at distinct points near the NMR frequency, due to the sequence distribution, or at least make them larger than the normal signal.

In this work distortionless enhancement by polarization transfer (DEPT) and heteronuclear correlation (HETCOR) experiments were used to show the overlapped NMR signals in the blends at solid state. The resonance located at 27.8 ppm was assigned as the CH group from PPA and CH₂ group from EPDM.

EXPERIMENTAL

All samples were analyzed on a Varian Gemini 300 spectrometer at 299.9 MHz for ¹H and at 75.4 MHz for ¹³C. All measurements used 5-mm tubes, 20% for ¹³C and 5% for hydrogen solutions in 1,2,4-trichlorobenzene with addition of benzene-*d*₆ as a field lock at ambient probe temperature. This solvent was carefully chosen to avoid any disparity between the chemical shifts detected in solution and the solid state, probably due to the type of polymer solvent interaction. 1-D proton spectra were recorded with a spectral width of 20,000 Hz, pulse width of 45°, recycle time of 1 s, and 16 transients. 1-D ¹³C spectra

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were recorded with a spectral width of 50,000 Hz, pulse width of 90° , recycle time of 2 s, and 500 repetitions. DEPT spectra were acquired with a spectral width of 3,125 Hz, pulse width of 90° , recycle time of 1 s, and 512 transients. Hydrogen (HETCOR) was registered with a spectral width of 1,579.8 Hz, pulse width of 90° , recycle time of 0.5 s, and 32 repetitions. ^{13}C (HETCOR) was registered with a spectral width of 7077.1 Hz, pulse width of 90° , recycle time of 0.5 s, and 3,000 transients.

RESULTS AND DISCUSSION

In a previous work⁷ the NMR study of EPDM/PPA blends at solid state were investigated by a variable contact time experiment (VCT). A change in chemical shift of the methyl region associated with the PPA was observed. In this study the methyl resonance showed differences in frequency absorption for distinct contact times when a series of spectra were recorded (see Fig. 1). This fact suggested the existence of a correlation between sequence types related to PPA through the methyl region and the type of mobility domains of the polymer blends. So, the precision of the ^{13}C assignments were only possible using NMR in solution employing DEPT and HETCOR sequences.

From the ^{13}C -NMR spectra of EPDM/PPA blends in solution with PPA content above 20%, it was observed that the methyl and methylene resonances showed splittings [Fig. 2(a,b)] that was only detected in the spectrum of pure PPA (Fig. 3). The splitting found at the methyl carbon resonance region occurs due to the nonstereoregularity structure of PPA. From this region it was assigned pentad and heptad sequences referred to as isotactic, het-

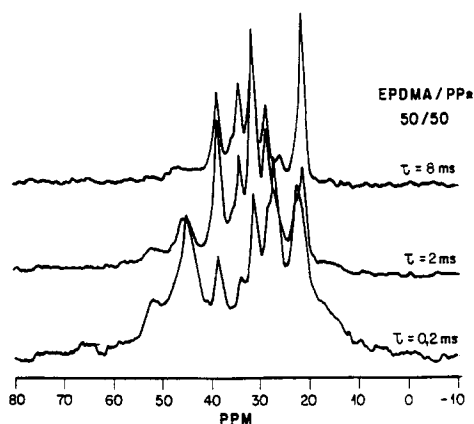


Figure 1 ^{13}C -NMR spectra of EPDM/PPA blends at different contact times at solid state.

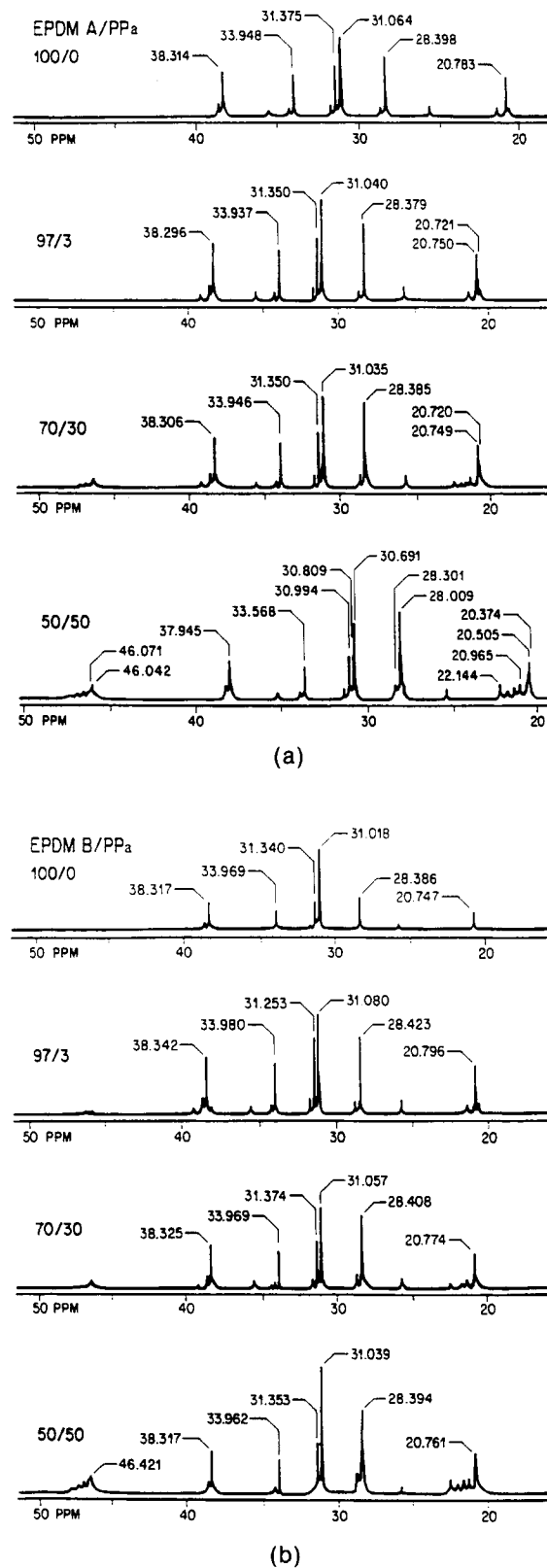


Figure 2 (a) ^{13}C -NMR spectra of EPDM A/PPA blends in solution and (b) ^{13}C -NMR spectra of EPDM B/PPA blends solution in 1,2,4-trichlorobenzene with benzene- d_6 .

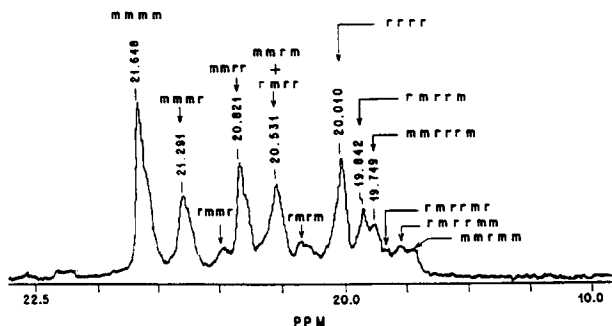


Figure 3 ¹³C-NMR spectra of the methyl region of PPA in solution with 1,2,4-trichlorobenzene with benzene-*d*₆.

erotactic, and syndiotactic configurations according to the literature.⁵ Otherwise, the EPDMs did not show any splitting at all.

DEPT Assignments

The EPDMs and their blends, EPDM B/PPA 97/3 and EPDM A/PPA 50/50, were analyzed by ¹³C-NMR using the DEPT sequence (Figs. 4–6). From Figure 4 it can be seen that there is no splitting at the methyl region for pure EPDM.⁸ According to this response the EPDM chains were assigned (based on the literature) as shown in structure I.

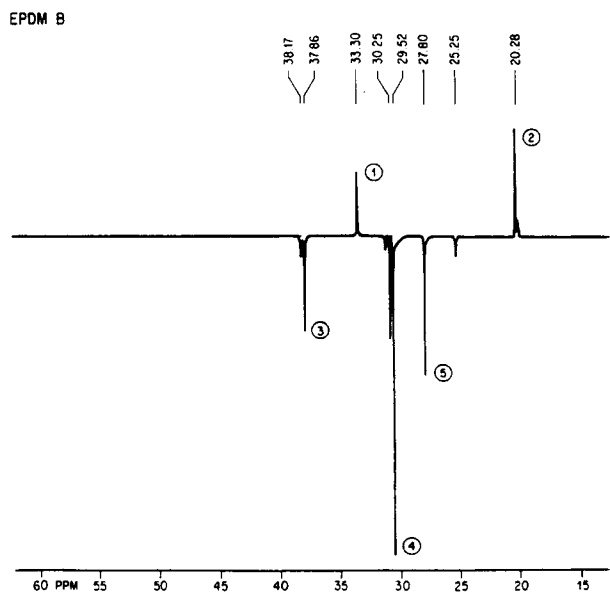
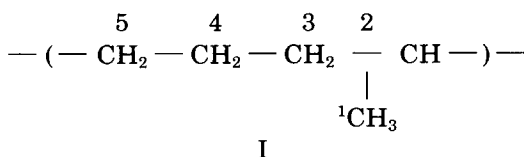


Figure 4 ¹³C-DEPT spectrum of pure EPDM.

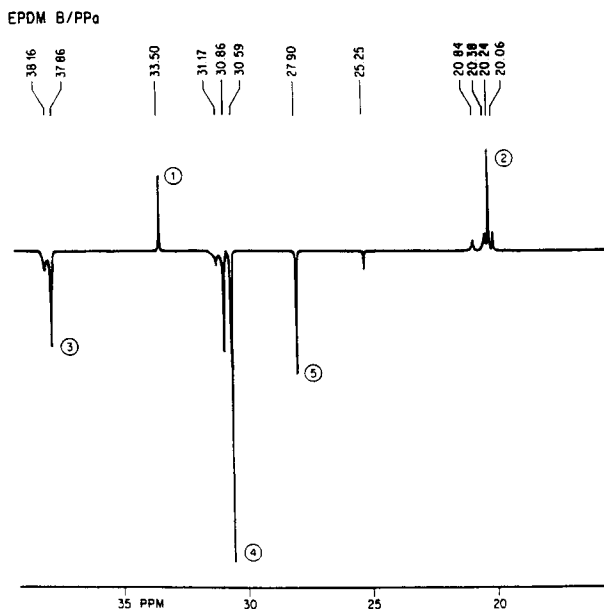


Figure 5 ¹³C-DEPT spectrum of EPDM B/PPA 97/3.

Figure 5 shows a similar DEPT spectrum explained by the low PPA content in the blend. A split was detected in the methyl and methylene regions attributed to different configuration sequences presented in the PPA microstructure in Figure 6.

Because the blend is formed by two polymers that have similar chemical natures, it was found that the DEPT experiment was unable to distinguish the overlapped resonances, although the HETCOR experiment provided a good source for the assignment of blend spectra at solid state.

HETCOR Assignments

This technique elucidated the presence of overlap signals of CH₂ groups (5) (ethylene-EPDM) and CH groups (6) of PPA. Figures 7–9 show the HETCOR spectra.

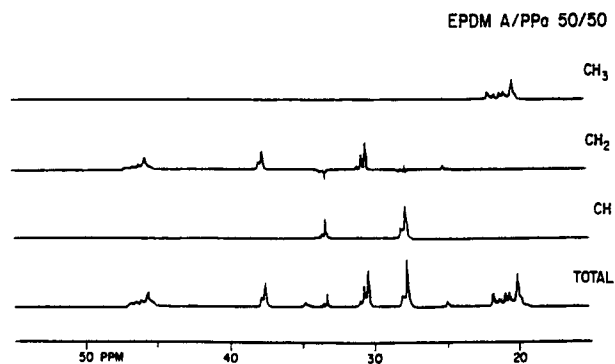


Figure 6 ¹³C-DEPT spectrum of EPDM A/PPA 50/50.

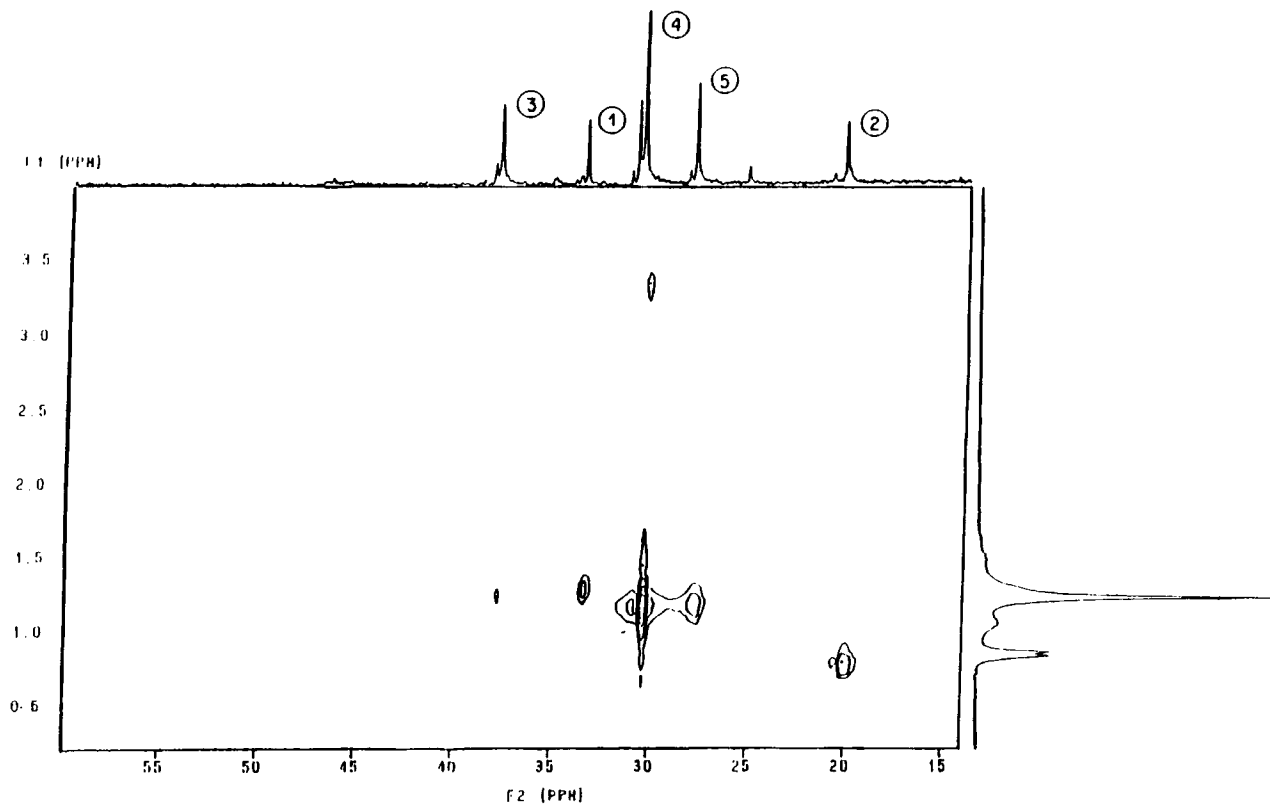


Figure 7 HETCOR of EPDM B.

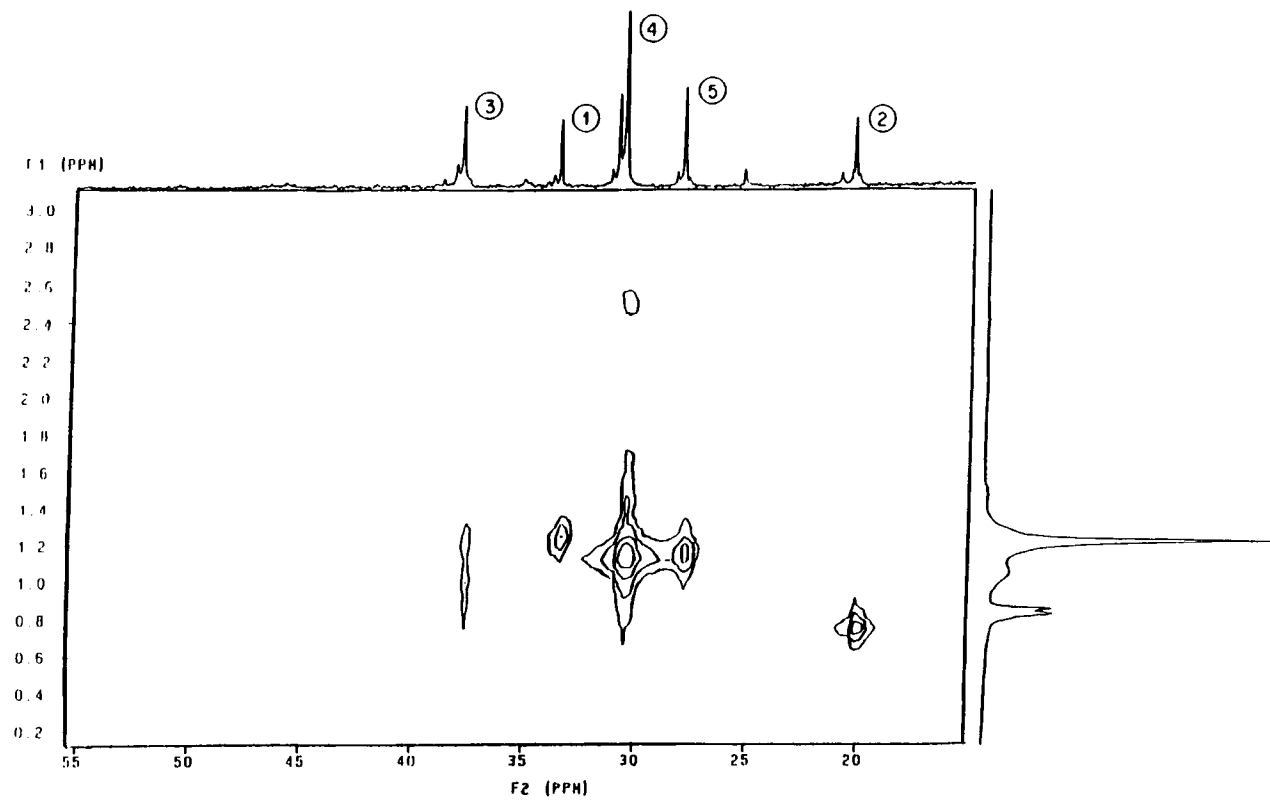


Figure 8 HETCOR of EPDM B/PPA 97/3.

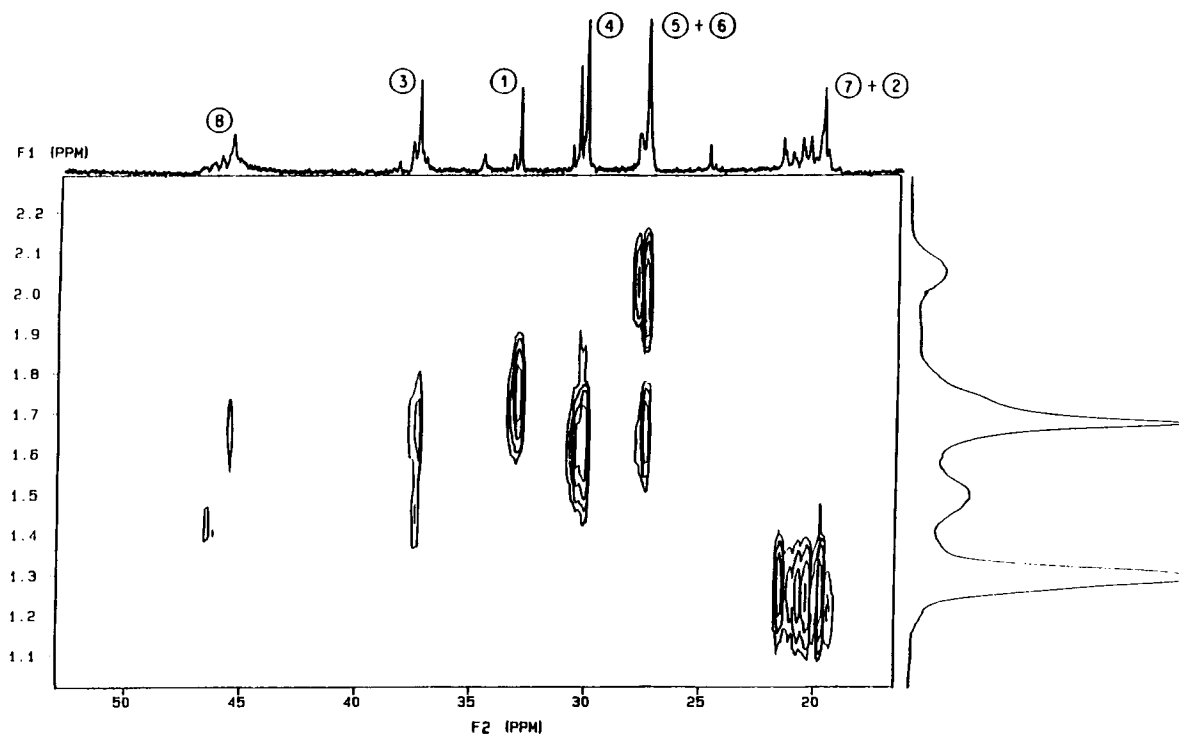


Figure 9 HETCOR of EPDM A/PPA 50/50.

Table I Structural Assignments of ¹³C Nuclei in EPDM A/PPA Blends

Sample EPDM A/PPA (phr)	δ (ppm)							
	EPDM					PPA		
	2 CH	1 CH ₃	3 CH ₂	4 CH ₂	5 ^a CH ₂	6 ^a CH	7 CH ₃	8 CH ₂
0/100						26.7	22.1	44.5
100/0	34.0	21.0	38.5	31.2	28.5	—	—	—
97/3	34.0	21.2	38.7	31.4	28.8	—	—	—
95/5	33.4	20.4	37.9	30.7	27.9	—	—	—
90/10	33.6	20.7	38.1	30.8	28.2	28.2	20.7	45.6
80/20	33.5	20.6	37.9	30.7	27.9	27.9	20.6	—
75/25	33.4	20.5	37.9	30.7	27.9	27.9	20.5	45.7
70/30	33.7	20.7	38.1	30.9	28.1	28.1	20.7	44.8
65/35	33.4	20.5	37.9	30.7	27.9	27.9	20.5	44.7
60/40	33.4	21.9	37.9	30.7	27.8	27.8	21.9	44.6
55/45	33.7	20.8	38.2	30.9	28.1	26.7	20.8	44.6
50/50	33.8	21.7	38.4	31.2	28.3	28.3	21.7	44.5
30/70	33.7	21.9	38.2	30.9	26.7	26.7	21.9	44.7

^a 5/6 are overlapped signals.

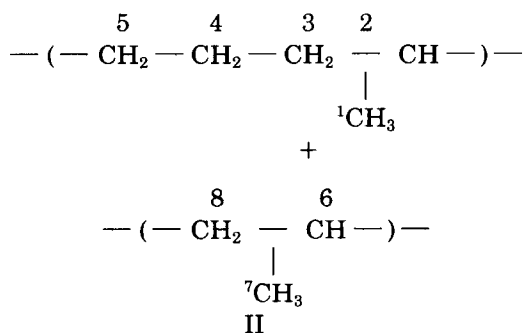
Table II Structural Assignments of ^{13}C Nuclei in EPDM B/PPA Blends

Sample EPDM B/PPA (phr)	δ (ppm)							
	EPDM					PPA		
	2 CH	1 CH ₃	3 CH ₂	4 CH ₂	5 ^a CH ₂	6 ^a CH	7 CH ₃	8 CH ₂
0/100						26.8	22.5	44.8
100/0	33.6	20.6	38.2	30.9	28.3	—	—	—
97/3	33.5	—	38.2	30.9	28.3	—	—	—
95/5	33.4	20.5	37.9	30.7	27.9	—	—	—
90/10	33.4	20.8	38.3	30.9	28.3	26.3	20.8	44.9
80/20	33.3	20.5	37.9	30.7	27.9	27.9	20.5	44.4
75/25	33.4	20.5	37.9	30.7	27.9	27.9	20.5	44.6
70/30	—	21.2	38.0	31.0	28.4	28.4	21.2	44.9
65/35	33.4	20.5	37.9	30.7	27.9	26.6	20.5	44.5
60/40	33.4	20.6	37.9	30.7	27.9	26.6	20.5	—
55/45	33.5	20.7	38.1	30.8	28.1	26.7	20.7	44.5
50/50	33.3	22.0	38.0	30.7	26.6	26.6	22.0	44.5
30/70	33.0	22.0	38.0	30.7	26.7	26.7	22.0	44.6

^a 5/6 are overlapped signals.

Figures 7 and 8 show the HETCOR spectra of pure and EPDM/PPA 97/3 blend, respectively, where no overlap peaks corresponding to CH₂ (5) and CH (6) were detected.

Based on NMR responses, the different ^{13}C nuclei belonging to EPDM/PPA blends were assigned as shown in structure II.



From structure II it is possible to more precisely assign the peaks detected in the solid-state spectra of EPDM/PPA blends. These assignments confirm that the interpretation of proton spin lattice relaxation time in the rotating frame parameter in the solid state, could be better obtained by the peak located at 30.9 ppm, due to no variation in the chemical shift because of the microstructure or the pres-

ence of any other overlapped signal. Therefore, this carbon was chosen to represent the molecular mobility of the blends and the compatibility of the systems. Tables I and II exhibit the chemical shifts of ^{13}C correlation of EPDM A/PPA and EPDM B/PPA blends, respectively.

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