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The Determination of an Alternating Monomer Sequence Distribution in Propylene–Butadiene Copolymers Using Carbon-13 Nuclear Magnetic Resonance

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ABSTRACT: Pulsed Fourier transformed carbon-13 nuclear magnetic resonance spectra were used to determine that two copolymers of propylene and butadiene made with different catalysts both had a perfectly alternating monomer sequence distribution. The two copolymers were also hydrogenated and the ^{13}C nmr spectra of the resulting polyalkanes were compared to past ^{13}C nmr spectra for branched alkanes and ethylene propylene copolymers. The ^{13}C data are shown to be more sensitive to structure than proton nmr data and clearly exclude the presence of structures with adjacent identical monomers. The ^{13}C nmr spectra of the original copolymers show that a vandium catalyst system produced alternating copolymers with all of the butadiene in a trans configuration. The copolymer made with a titanium catalyst system is also shown to have an alternating structure but with 89% of the butadiene in a trans configuration and 11% in a cis configuration. Low concentrations of polybutadiene homopolymer are detected and quantitatively measured in both polymer systems. The ^{13}C nmr spectra are not useful for determining tacticity in this polymer system.

The synthesis of copolymers of propylene and butadiene with alternating monomer sequence distribution has been reported.[1-5] The strongest evidence for the alternating structure is a 1:1 monomer composition in the copolymer, irrespective of varied composition in the monomer feed. Both infrared (ir) analysis and proton nuclear magnetic resonance (pmr) analysis can be used to determine composition in the polymer. However, unambiguous spectroscopic observation of an alternating monomer sequence structure has not been entirely satisfying. Previous investigators[3] found that it was necessary to use 220 MHz proton nmr spectra to assign an alternating structure to the copolymers. Even so, those data and earlier infrared data[1,2] could only be used to infer an alternating structure. They could not be used to unambiguously exclude the presence of nonalternating structure.

We have found that carbon-13 nuclear magnetic resonance (^{13}C nmr) is a sensitive method for determining the monomer sequence distribution in ethylene propylene copolymers.[6,7] If one would hydrogenate a propylene–butadiene copolymer, the resulting polyalkane would be analogous to a copolymer of ethylene and propylene. If in fact the propylene and butadiene monomers were alternating, the resulting polyalkane would be composed of regular, repeating sequences of five methylene carbons bounded by tertiary carbons each bearing a methyl group. Because of the sensitivity of ^{13}C nmr chemical shifts to methylene sequence lengths in branched alkanes,[8-10] it would be a straightforward task to determine the presence and concentration of sequences coming from nonalternating structures. Furthermore, by combining the chemical shifts for the polyalkane with approximate alkene substituent effects derived from the literature,[13] one could expect to be able to interpret the ^{13}C nmr spectra of the original (nonhydrogenated) copolymers in terms of sequence distribution, as well as be able to determine the cis and trans structure around the olefin bond.

This report demonstrates how ^{13}C nmr can be used to determine the alternating monomer structure for two propylene butadiene copolymers made with different catalysts but both of which are reported to produce an alternating copolymer. The data show how ^{13}C nmr can be used to unambiguously preclude the presence of any nonalternating structure in these copolymers.

Experimental Section

The random-noise, proton decoupled, natural abundance ^{13}C nmr spectra were obtained from the Fourier transform of the free induction decay using a Varian XL-100-15 pulsed nmr spectrometer. All the spectra were obtained at the Major Analytical Instrument Facility at Case Western Reserve University.

Spectra were obtained at ambient probe temperature using 12-mm tubes. The polymers were examined as approximately 20% (w/v) solutions in a 1:1 $CCl_4/CDCl_3$ mixed solvent. The $CDCl_3$ was used for the internal deuterium lock. Internal tetramethylsilane was present in all samples as an internal chemical shift reference. The spectra were obtained using a spectral width of 5000 Hz, 8192 data points, and 0.8 sec acquisition time. The spectra of the propylene–butadiene copolymers were obtained using a 60° pulse. This was achieved using a 35-μsec pulse width for the spectrum shown in Figure 1. (The power amplifier was used to obtain the spectrum shown in Figure 5, consequently the 60° pulse was achieved using an 8-μsec pulse width.) A 30° pulse using a 15-μsec pulse width was used to obtain the spectra of the hydrogenated copolymers. The number of transients accumulated for the spectra shown are as follows: 2500 for Figures 1 and 2; 15,436 for Figure 3; 25,961 for Figure 4; and 2,060 for Figures 5 and 6.

The high molecular weight copolymers of propylene and butadiene were obtained from the Maruzen Petrochemical Co., Ltd. Copolymer A was made with a vanadium catalyst system and copolymer B was made with a titanium catalyst system. The copolymers were hydrogenated using a Raney nickel catalyst, and also using *p*-toluenesulfonylhydrazide.[14] Both methods produce a polyalkane having the same ^{13}C nmr spectra.

Results and Discussion

The ^{13}C nmr spectrum is shown in Figure 1 for a propylene–butadiene copolymer made with a vanadium catalyst that is reported to produce a copolymer with an alternating monomer sequence distribution. The seven resonances were assigned to the structure shown in Figure 1 after comparing the ^{13}C chemical shifts to those found for this co-

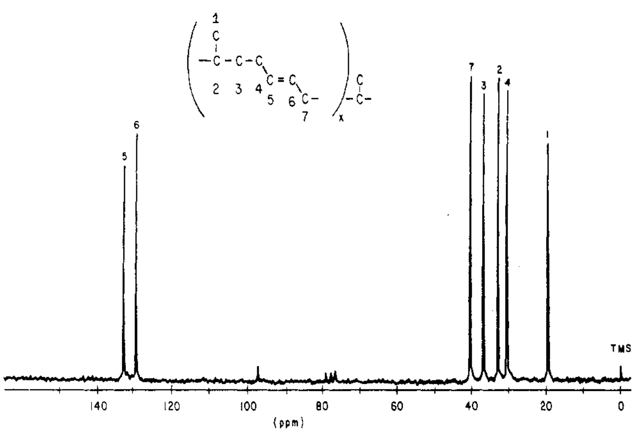


Figure 1. Pulsed (FT) ^{13}C nmr spectrum of an alternating propylene–butadiene copolymer made with a vanadium catalyst, copolymer A. The spectrum was obtained at ambient temperature from a 20% (w/v) solution in 1:1 CCl_4:$CDCl_3$.

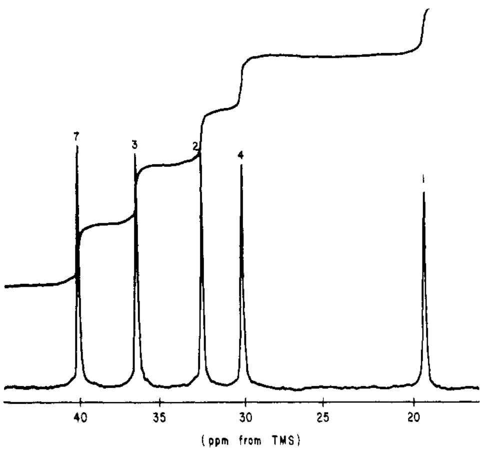


Figure 2. Horizontal expansion and integration of the aliphatic portion of the ^{13}C nmr spectrum shown in Figure 1.

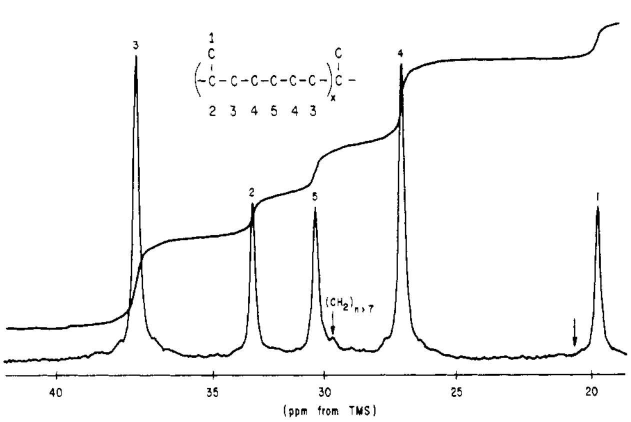


Figure 3. Pulsed (FT) ^{13}C nmr spectrum of the polyalkane obtained by hydrogenating an alternating propylene–butadiene copolymer made with a vanadium catalyst, copolymer A. The spectrum was obtained at ambient temperatures from a 20% (w/v) solution in 1:1 CCl_4:$CDCl_3$.

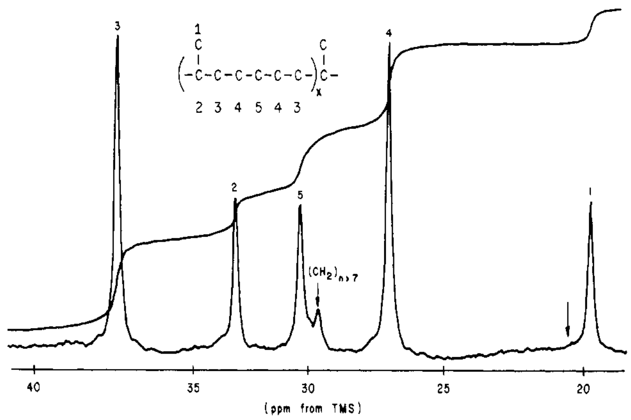


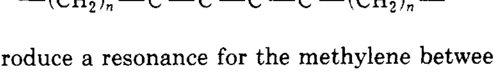
Figure 4. Pulsed (FT) ^{13}C nmr spectrum of the polyalkane obtained by hydrogenating an alternating propylene butadiene copolymer made with a titanium catalyst, copolymer B. The spectrum was obtained at ambient temperature from a 20% (w/v) solution in 1:1 CCl_4:$CDCl_3$.

polymer after it was hydrogenated and then considering the expected shift effects of an olefin bond. Figure 2 shows the expanded high-field portion of Figure 1 and its integrated areas. The methyl resonance is slightly attenuated because the pulse repetition rate is slightly too fast for the methyl spin–lattice relaxation time. However, the areas are equal, within experimental error.

The interpretation of the spectrum in Figure 1 is simplified if one first considers the ^{13}C nmr spectrum of the hydrogenated copolymer. This spectrum is composed of only alkane carbons, which are shown as the expanded spectrum in Figure 3. If the original copolymer was perfectly alternating, the resulting polyalkane, after hydrogenation, would have a structure with regular, repeating runs of five methylene carbons bounded by tertiary carbons bearing methyl groups. The ^{13}C nmr spectrum of this structure can be calculated using revised parameters[8] for the Grant and Paul equation[9] for empirically predicting alkane ^{13}C chemical shifts. Furthermore, the ^{13}C nmr chemical shifts have been reported[8] for 2,8,14,20-tetramethylheneicosane, a compound with three repeating runs of five methylenes. This compound thus serves as a specific model compound for chemical shift assignments. These data plus those reported for ^{13}C nmr studies of ethylene propylene [6,7,10–12] copolymers provide a solid basis for determining if the alternating structure suggested for the copolymer is valid.

The ^{13}C nmr spectrum of sample A shown in Figure 3 unequivocally shows that the hydrogenated copolymer of propylene and butadiene has a structure of regular, repeating runs of five methylene carbons. The ^{13}C chemical shifts and the relative intensities of these resonances are given in Table I. There are five major resonances in the ratio of 2:1: 1:2:1. The agreement between the observed chemical shifts and those predicted using the empirical parameters based on the Grant and Paul equation for branched alkanes supports the structure $(CHCH_3CH_2CH_2CH_2CH_2CH_2)_x$. This simple ^{13}C nmr spectrum easily shows that the original copolymer had alternating propylene and butadiene monomers.

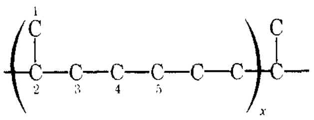
If the original copolymer was not entirely alternating, the polymer would contain segments of adjacent propylene monomers and adjacent butadiene monomers. The hydrogenated copolymer would then contain several types of distinct resonances that are found in the ^{13}C nmr spectra of ethylene–propylene copolymers and terpolymers.[6,7] The sequence of adjacent propylene monomers



$$—(CH_2)_n—\overset{\overset{\displaystyle C}{|}}{C}—C—\overset{\overset{\displaystyle C}{|}}{C}—C—(CH_2)_n—$$

would produce a resonance for the methylene between the tertiary carbons at approximately 46.1 ppm, a tertiary carbon resonance approximately 2.3 ppm upfield from the observed tertiary resonance (peak 2 in Figure 3), and a methyl carbon resonance for a PPE sequence[6,7] approximately 0.7 ppm downfield from the observed methyl resonance.[7] In addition, if there are adjacent propylene monomers,

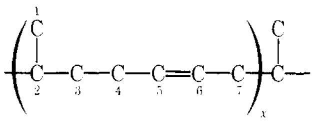
Table I
Observed[a] and Calculated[b] ^{13}C Chemical Shifts for Hydrogenated Alternating Propylene – Butadiene Copolymer



Position	^{13}C chemical shift Obsd	^{13}C chemical shift Calcd	Rel intensities Obsd	Rel intensities Calcd
1	19.74	19.89	0.80	1
2	32.79	32.47	0.96	1
3	37.15	37.10	2.00	2
4	27.15	27.39	1.81	2
5	30.41	30.26	1.05	1
Polyethylene	29.74	29.70		

[a] The observed chemical shifts are an average for samples A and B and are ±0.03 ppm. [b] The calculated chemical shifts were calculated using the revised alkane parameters,[8] a constant of 2.96 for TMS reference, and the Grant and Paul equation.[9]

Table II
Carbon-13 Chemical Shifts[a] Observed for an Alternating Copolymer of *trans*-1,4-Butadiene and Propylene



	Carbon position 1	2	3	4	5	6	7
δ_c	19.33	32.50	36.47	30.18	131.68	128.41	39.95
				(24.18)[b]	(130.63)[b]	(129.47)[b]	(34.38)[b]

[a] ppm relative to internal tetramethylsilane; δ_c are averages found for copolymer A made with a vanadium catalyst and for copolymer B made with a titanium catalyst. [b] δ_c for this position for a cis olefin configuration observed in copolymer B made with a Ti catalyst.

there would of necessity be adjacent butadiene monomers. After hydrogenation this would result in a polyethylene-like peak near 29.7 ppm from TMS.[8,10]

No resonance was detected in the ^{13}C nmr spectrum of the saturated or unsaturated polymer near 46.1 ppm to indicate the presence of a single methylene carbon between tertiary carbons. A tertiary carbon resonance for a tertiary carbon in a PPE sequence would be difficult to detect, if present in low concentration, as it would lie almost under the resonance at 30.41 (peak 5, Figure 3). However, one can conclude that this sequence is not present, as the associated methyl resonance should be approximately 0.7 ppm downfield from the EPE type methyl[7] identified as peak 1 in Figure 3. The absence of such a peak, indicated at the position with the arrow, gives credence to the conclusion that there are no measureable adjacent propylene monomers present.

There is a small resonance seen at 29.74 ppm. This chemical shift is associated with a chain of at least seven methylene units. This is a polyethylene-like resonance. Since there are no detectable adjacent propylene monomers, one must conclude that the polyethylene-like resonance in the hydrogenated polymer indicates the presence of adjacent butadienes from polybutadiene homopolymers present as a slight impurity in original copolymer. The relative area suggests <2% homopolymer is present.

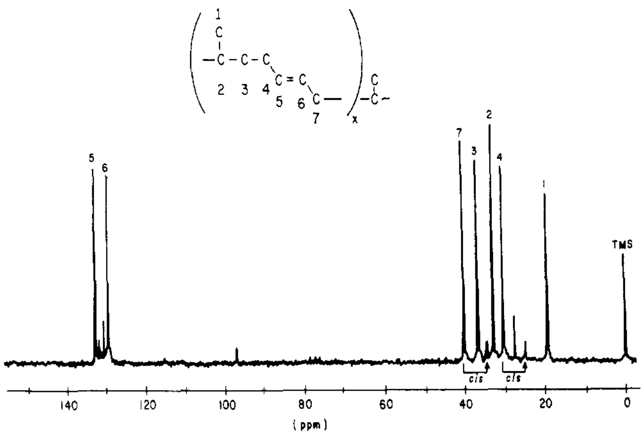


Figure 5. Pulsed (FT) ^{13}C nmr spectrum of an alternating propylene–butadiene copolymer made with a titanium catalyst, copolymer B. The spectrum was obtained at ambient temperature from a 20% (w/v) solution in 1:1 CCl_4:$CDCl_3$.

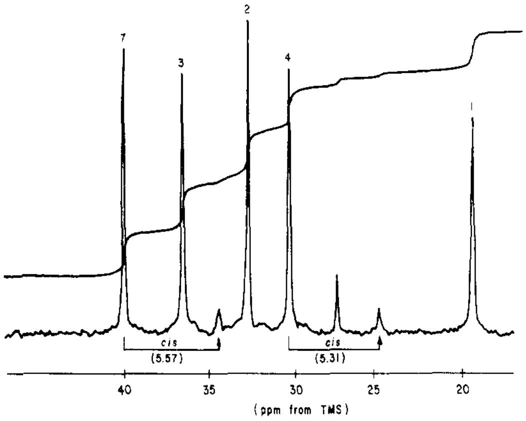


Figure 6. Horizontal expansion and integration of the aliphatic portion of the ^{13}C nmr spectrum shown in Figure 5.

Figure 4 shows the ^{13}C nmr spectrum for the polyalkane resulting from hydrogenating copolymer B. Copolymer B was polymerized with a titanium catalyst, also reported to produce an alternating copolymer of propylene and butadiene. The polyalkane resulting from hydrogenated copolymer B produces a ^{13}C nmr spectrum which indicates that the polymer has regular, repeating runs of five methylene carbons. Figure 4 differs from Figure 3 only in that there is a higher concentration of polymethylenes present. Therefore sample B must have a higher concentration of polybutadiene homopolymer than does sample A. This conclusion is verified by inspecting the ^{13}C nmr spectrum of the original copolymer shown in Figures 5 and 6.

There are more differences evident between the ^{13}C spectra of the original copolymers than is reflected in a comparison of the spectra of their respective hydrogenated analogs. I submit that the spectra for copolymer A, made with a vanadium catalyst, reflects a perfectly alternating copolymer where the butadiene olefin bond is all in a trans configuration. Whereas the spectra of copolymer B, made with a titanium catalyst, can be interpreted to reflect a perfectly alternating copolymer where in the copolymer 89% of the olefin bonds are in a trans configuration and 11% of the butadiene olefin bonds are in a cis configuration. Furthermore, the spectrum shows the presence of about 8 mol % *cis*-1,4-polybutadiene in copolymer B.

The assignments for the major resonances for copolymers A and B are summarized in Table II. These assign-

Table III
Relative ^{13}C Chemical Shifts for the Methylene Assignments for the Propylene–Butadiene Copolymer and Its Hydrogenated Analog

	Carbon position from Table II			
	7	3	2	4
Hydrogenated polymer	37.15 (3)[a]	37.15 (3)	32.79 (2)	27.15 (4)
Unsaturated polymer	39.95 (α)[b]	36.47 (β)	32.50 (β)	30.18 (α)
Δ(alkane − alkene)	−2.80	+0.68	+0.29	−3.03

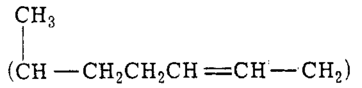
[a] Carbon position in the polyalkane shown in Table I. [b] The Greek letter designates the relative position to the olefin bond for the assignment shown in Table II.

Table IV
Structural Composition for an Alternating Propylene–Butadiene Copolymer Made with a Titanium Catalyst (Sample B)

A. Based on original copolymer (Figure 6)		B. Based on hydrogenated copolymer (Figure 4)	
Structure	Mol %	Structure	Mol %
cis-1,4-Polybutadiene homopolymer	8	Polybutadiene homopolymer[a]	7
Alternating propylene/ *trans*-1,4-polybutadiene	82	Alternating propylene/ butadiene[b]	93
Alternating propylene/ *cis*-1,4-polybutadiene	10		

[a] Calculated assuming the area of the polyethylene-like resonance at 29.74 ppm all comes from hydrogenated polybutadiene. [b] Calculated from the relative area of carbon 5 in the structure shown in Figure 4.

ments were made with the following interpretation. The ^{13}C nmr spectra of the hydrogenated copolymer has been shown to be evidence that the original copolymer must have the following repeating unit



$$\overset{\mathrm{CH_3}}{\overset{|}{(\mathrm{CH}}}-\mathrm{CH_2CH_2CH{=}CH-CH_2})$$

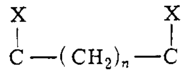
A comparison of the published ^{13}C chemical shifts of octane[9] with those[13] of *trans*-2-octene, *trans*-3-octene, *cis*-2-octene, and *trans*-2-octene indicates that a methylene carbon α to a trans olefin bond will be shifted 2.5 to 2.9 ppm downfield from the corresponding carbon in an alkane. Whereas a methylene carbon α to a cis olefin bond is about 3 ppm upfield from its analogous position in an alkane. A methylene carbon β to a trans olefin bond is shifted 0.3 to 0.5 ppm upfield from its corresponding position in an alkane. When an olefin bond is present at carbon five in the structure shown in Table II, there are two methylenes α to the olefin bond. If the olefin has a trans configuration, carbons 4 and 7 in Table II would lie about 3 ppm downfield from their chemical shifts in the alkane. Table III shows that there is a resonance (30.18) shifted 3.03 ppm downfield from the chemical shift (27.15) for carbon 4 in the polyalkane. Similarly the resonance at 39.95 ppm in the ^{13}C spectrum of the unsaturated polymer corresponds to a trans α shift as it is 2.80 ppm downfield from the corresponding carbon position in the polyalkane. The other two resonances in Figures 1 and 2 and 36.47 and 32.50 ppm show small upfield shifts from their position in their analogous alkane positions. This is consistent with the expected smaller β olefin shift effect.

If the olefin bond had a cis configuration, the alkane carbon shift for position 3 in Table I would be shifted about 3 ppm upfield to about 34 ppm. And correspondingly, the alkane carbon shift for position 4 would be shifted from 27.15 ppm to about 24 ppm. The ^{13}C nmr spectrum (see Figures 5 and 6) for the copolymer made with titanium shows these two chemical shifts, reflecting the presence of cis structure. The resonance at 34.38 and 24.18 ppm in Figure 6 shows a cis effect compared to their counterpart trans resonances, peaks 7 and 4. The difference between trans and cis methylenes of 5.31 and 5.57 ppm is similar to the 5.3–5.4 ppm difference reported for *cis*- and *trans*-1,4-polybutadiene.[15,16]

The resonance at 27.37 ppm seen in Figures 5 and 6 can be assigned to *cis*-1,4-polybutadiene homopolymer. The chemical shift corresponds to this assignment. Measuring the relative areas for the assignments in Figure 6 provides the compositional analysis for copolymer B shown in Table IV. Based on the composition shown in Table IV, part A, 89% of the alternating copolymer portion of sample B would have the double bond in a trans configuration and 11% of the double bonds would have a cis configuration. The relative area of the polymethylene peak in Figure 4 (at 29.74 ppm), when calculated as a C_4 (butadiene unit), gives a relative polybutadiene composition in agreement with the data for the nonhydrogenated, original sample. These analytical measurements were based on comparing the relative areas of similar carbons, *i.e.*, methylene carbons α to double bonds in one case and aliphatic methylene carbons in the second case. Consequently, errors coming from unequal nuclear Overhauser enhancement[17] or errors due to dissimilar spin–lattice relaxation times are negligible.[18] If one wants to accurately measure the relative areas of the methyl, methine, and olefin carbons, longer repetition between pulses should be employed.

The chemical shifts at 131.68 and 128.41 ppm in Table II were assigned to the trans olefin carbons. The most upfield resonance was assigned to position 6 in Table II, because this position would experience a γ substituent interaction with the methyl group that position 5 does not experience. The chemical shifts at 130.63 and 129.47 ppm in Table II correspond to the cis olefin carbons. Infrared analysis shows an absorption at 910 cm^{-1} indicating the presence of vinyl groups in the copolymer B. The concentration is below the detection limits for ^{13}C nmr. This conclusion comes about because one would see a ^{13}C resonance at 144 ppm due to vinyl carbon bearing one proton ($HC^{*}{=}CH_2$) and a resonance at 114 ppm due to the other vinyl carbon ($-HC{=}{}^{*}CH_2$).[16] It is estimated that the concentration is below 5%.[19] This is below the limit of detection for the manner in which the current spectra were obtained. The short-chain branches that would result after hydrogenation can also be shown to be distinct[8,10] and were not detectable in the polyalkane spectra.

Carbon-13 nmr has been shown to be more sensitive than proton nmr for measuring tacticity in polypropylene[11,12,20] or poly(vinyl chloride).[21–23] However, the ^{13}C nmr spectra of alternating propylene–butadiene copolymers have no information enabling one to determine the stereoregularity of the propylene methyl groups. This is because there is too great a distance separating the stereointeracting groups. Consider the structure



$$\overset{X}{\overset{|}{C}}-(\mathrm{CH_2})_n-\overset{X}{\overset{|}{C}}$$

For polypropylene or poly(vinyl chloride), $n = 1$ and the ^{13}C chemical shifts are very sensitive to stereostructure. It has also been shown[8,24] for $n = 2$ that the ^{13}C chemical shifts can reflect configurational or conformational structure even though the magnitude of the effect is reduced. However, for the system under consideration $n = 5$ and the ^{13}C chemical shifts are not sensitive to stereostructure.

Past infrared analysis[1,2,4,5] of reported alternating propylene–butadiene copolymers certainly could be used to rule out the presence of long runs of butadiene or propylene. However, it was difficult to use those data to rule out the possibility of some random adjacent monomer and thus was not unequivocal. The 220-MHz proton nmr analyses[3] on the other hand were used to assign an alternating structure. However, the 220-MHz proton interpretation is based on deconvoluting badly overlapping multiplet patterns, calculating theoretical spectra, and simplifying the spectra by examining deuterated copolymers. The ^{13}C nmr method is more satisfying as direct observation of each copolymer can be made and the results appear unequivocal.

Conclusions

Pulsed Fourier transform ^{13}C nmr is shown to be an unambiguous method for determining an alternating monomer sequence distribution in copolymers of propylene and butadiene that were made with either a vanadium or a titanium catalyst. The two copolymers were hydrogenated and the ^{13}C nmr spectra of the resulting polyalkanes can be shown to reflect a regular repeating sequence of five methylene carbons bounded by tertiary carbons bearing methyl groups. This interpretation is based upon comparing the observed ^{13}C chemical shifts with expected values derived from empirical additivity relationships shown to hold for branched alkanes and by a comparison with analogous chemical shifts reported for ethylene–propylene copolymers. The determination of the structure for the hydrogenated copolymers provides a sound basis for interpreting the ^{13}C nmr spectra of the original propylene–butadiene copolymers. A trans or cis olefin bond substituent effect is shown to account for chemical shift differences between spectra of the hydrogenated and original copolymers. The spectra of the original copolymers show that the copolymer made with a vanadium catalyst is alternating with essentially all of the butadiene in a trans configuration. There appears to be less than 2% polybutadiene homopolymer present as an impurity. On the other hand the copolymer made with a titanium catalyst is an alternating copolymer with about 89% of the butadiene in a trans configuration and 11% of the butadiene in a cis configuration. This copolymer has about 7 to 8% *cis*-1,4-polybutadiene homopolymer present as an impurity. In the future, it should be possible to use the proposed interpretation of the ^{13}C nmr spectra of copolymers of propylene and butadiene to determine the extent of alternation without the necessity of also hydrogenating the copolymer and obtaining the ^{13}C nmr spectrum of the resulting polyalkane.

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The Nature of the Molecular Motions of Poly(L-proline) for the Cis ⇌ Trans Conformational Transitions

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ABSTRACT: Conformational analysis has been used to study the molecular motions in the cis ⇌ trans transitions of poly(L-proline) by assuming cooperative couplings between residues obey Gaussian functions. The results suggest that the free energy barriers to both the cis → trans and trans → cis transitions are minimum when three residues are involved in the cooperative motions. The cis → trans transition prefers to start at the N-terminal end of the chain and proceed inward, while the trans → cis transition nucleates, most probably, at the C-terminal end of the chain and proceeds inward. Only two stable conformations, corresponding to the observed cis and trans helices, have been found for every transition path tested. Also, a single energy barrier separates the cis and trans states.

This paper presents the results of an initial attempt, using conformational analysis, to describe the molecular motions taking place in poly(L-proline) as it undergoes an order-to-order conformational transition.[2-6] This transition is characterized by the cis ⇌ trans (C ⇌ T) torsional interconversion with respect to the imide bond of each resi-