

# <sup>13</sup>C-NMR Characterization of Poly(1,5-hexadiene)\*

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## Synopsis

Poly(1,5-hexadiene) was prepared and its structure characterized by high-field <sup>13</sup>C nuclear magnetic resonance. The polymer was shown to contain repeating five-membered rings separated by methylene bridges, with both *cis* and *trans* placements present in a 54:46 ratio. The result is compatible with the Marvel-Garrison two-step reaction mechanism.

## INTRODUCTION

Poly(1,5-hexadiene) was first prepared by Marvel and Stille<sup>1</sup> using a triisobutylaluminum/titanium tetrachloride catalyst system. The reaction is of interest because it is the simplest and the most clear-cut case where cycloaddition is favored over 1,2-addition. Over the years this polymeric system has been re-examined,<sup>2-6</sup> and mechanisms proposed for the polymerization.<sup>2,6</sup>

We have prepared poly(1,5-hexadiene) and studied the polymer with high-field <sup>13</sup>C nuclear magnetic resonance (NMR). By this means, detailed information is available on both its structure and the polymerization mechanism.

## EXPERIMENTAL

The monomer, 1,5-hexadiene, was obtained from Aldrich Chemical Co (Metuchen, NJ). The catalyst system contained 1:0.5 molar ratio of diethylaluminum chloride (DEAC) from Texas Alkyl (Deer Park, TX) and  $\delta$ -titanium trichloride (TiCl<sub>3</sub>).

Polymerization was carried out in a 1-gallon reactor equipped with an air-driven stirrer. The monomer (100 g) was charged into the reactor containing 2.0 L hexane. The system was sparged with argon for 1 h, and the reactor temperature maintained at 65°C. At this time 8 mL DEAC and 4 mL TiCl<sub>3</sub> were added to initiate the polymerization. The polymerization was carried out for 4 h, and the reaction mixture was transferred to a quench pot containing 600 mL isopropanol. The resulting polymer was washed several times and dried in an oven (80°C) overnight.

<sup>13</sup>C NMR spectra were obtained on a Nicolet NT 360 spectrometer operating at 90.56 MHz. Three samples from the same polymerization were analyzed,

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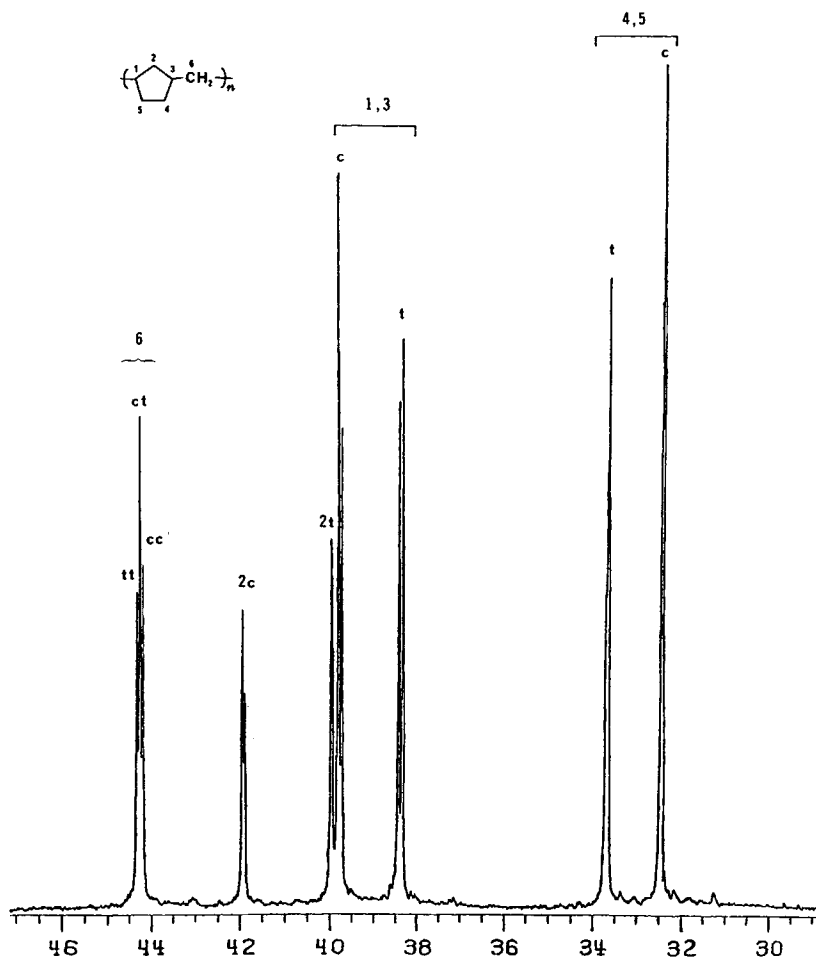
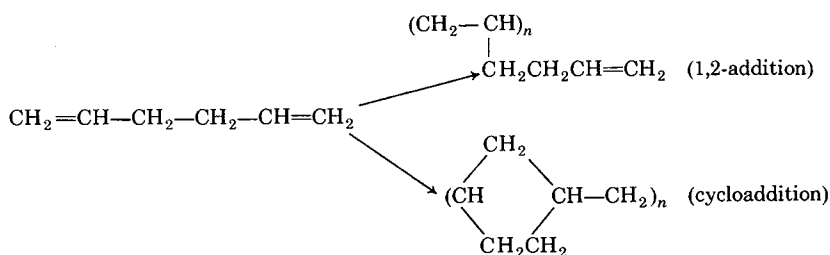


Fig. 1.  $^{13}\text{C}$  NMR at 90 MHz of poly(1,5-hexadiene). The APT spectrum (not shown) gives positive assignments for carbons 2c and 2t.

and gave similar results. Two samples were dissolved in 1,2,4-trichlorobenzene with  $d_6$ -benzene added as field/frequency lock. The third sample was dissolved in  $d_2$ -1,1,2,2-tetrachloroethane in order to expose any olefinic carbons. The probe temperature ranged from  $75^\circ$  to  $115^\circ\text{C}$ . Other instrumental parameters included: 70 degree pulse, 4 s repetition rate, 16K data points with zero-filling for data processing, and broadband  $^1\text{H}$  decoupling. All shifts were referenced to tetramethylsilane at 0 ppm. Spectral intensities were obtained by electronic integration of areas.

## RESULTS AND DISCUSSION

The  $^{13}\text{C}$  NMR spectrum of poly(1,5-hexadiene) at 90 MHz is shown in Figure 1(a). The spectrum is relatively simple, with no indication of linear structure or olefinic moieties. Thus, cycloaddition has occurred exclusively.



The six-line pattern shown in Figure 1 also contains many fine structures, (e.g., at 44.3, 41.8, 39.7, and 38.4 ppm). The assignments of these resonances can be aided through the use of an APT experiment, which permits us to differentiate between methylene/quaternary carbons and methyl/methine carbons.<sup>7</sup> It turns out that the multiplet at 39.7 ppm contains separate methine and methylene resonances that are partially overlapped. A complete interpretation of the spectrum can be accomplished by referring to low-molecular-weight analogs<sup>8</sup> and using empirical additive rules for <sup>13</sup>C shifts.<sup>9,10</sup> The complete assignments are summarized in Table I.

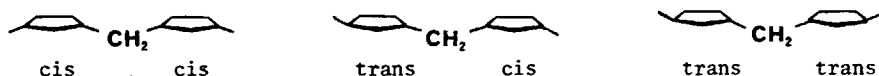
From the data in Table I, it appears that the <sup>13</sup>C shifts are sensitive of two stereochemical effects, both having the same origin. The larger effect (ca. 1.7 ppm) is due directly to the *cis-trans* placements of substituents at positions C<sub>1</sub> and C<sub>3</sub> across the cyclopentane ring.



TABLE I  
Poly(1,5-hexadiene)-Assignments of <sup>13</sup>C NMR Spectrum at 115°C in 1,2,4-Trichlorobenzene

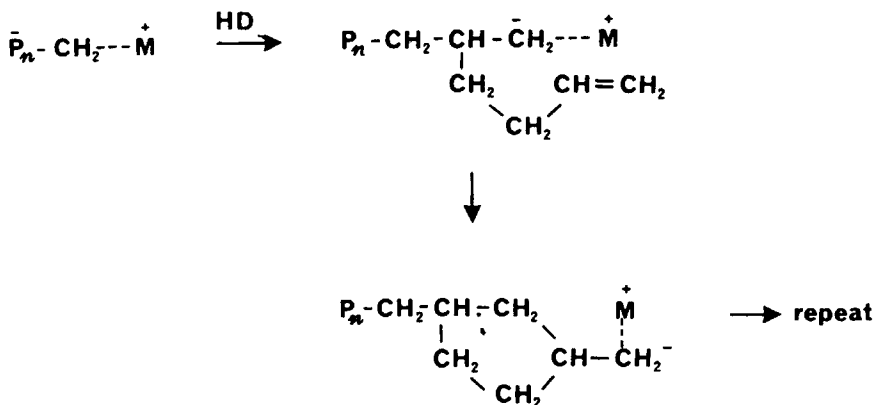
Carbon	Isomerism across ring	Isomerism across bridge	<sup>13</sup> C-Shift
6		<i>trans-trans</i>	44.30
		<i>cis-trans</i>	44.25
		<i>cis-cis</i>	44.20
2	<i>cis</i>	<i>cis, trans</i>	41.93, 41.88
	<i>trans</i>		39.90
1, 3	<i>cis</i>	<i>cis</i>	39.82
		<i>trans</i>	39.75
	<i>trans</i>	<i>trans</i>	38.45
		<i>cis</i>	38.40
4, 5	<i>trans</i>		33.72
	<i>cis</i>		32.50

The smaller effect (ca. 0.05 ppm) is due to the same isomerism across the methylene bridges:

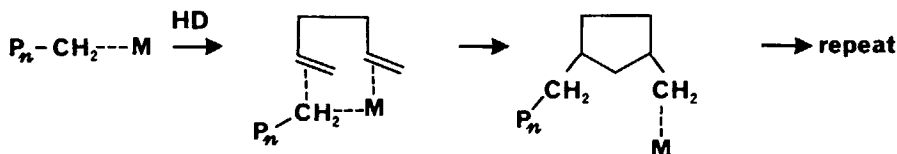


We believe this is the first report of the direct observation of *cis* and *trans* isomers in cycloaddition of nonconjugated dienes. From the spectral intensities, the *cis-trans* ratio is calculated to be 54 : 46.

In the original paper by Marvel and Stille,<sup>1</sup> some consideration was given to the reaction mechanism leading to cycloaddition. Marvel and Garrison<sup>2</sup> later proposed a two-step mechanism:



Later, in his comprehensive treatise on Ziegler-Natta polymerization,<sup>6</sup> Boor proposed a concerted one-step addition as an alternative mechanism:



A major difference in the two mechanisms is the structure of the resulting polymer. Boor's mechanism will lead to a preponderance of *cis-cis* cyclic structure, whereas Marvel and Garrison's mechanism is free of this stereochemical constraint. In view of the mixed *cis-trans* product found, it appears that Marvel and Garrison's mechanism (or variations thereof) is more consistent with the observed polymer structure.

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