

## The Infrared Identification of Short-Chain Branches in Polyolefins

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### INTRODUCTION

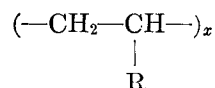
Recently, we determined the length of short branches in polymers prepared by the cationic polymerization of propylene.<sup>1</sup> Figure 1 is an infrared spectrum of a typical polymer in the methylene rocking region. There are two distinct absorption bands with centers at 769  $\text{cm.}^{-1}$  (13.00  $\mu$ ) and 739  $\text{cm.}^{-1}$  (13.43  $\mu$ ).

McMurray and Thornton,<sup>2</sup> and more recently Iogansen,<sup>3</sup> showed that the length of short branches in liquid hydrocarbons can be determined from the position of the methylene rocking vibration of the branch in the 790-720  $\text{cm.}^{-1}$  (12.6-13.9  $\mu$ ) region. Their hydrocarbon correlations are summarized in Table I. Willbourn<sup>4</sup> has questioned whether *n*-propyl, *n*-butyl, and *n*-pentyl branches in partially crystalline solid polymers would have infrared absorption bands at approximately the same frequencies as the liquid hydrocarbons. To resolve this question, we prepared a series of polymers that contained ethyl, *n*-propyl, *n*-butyl, *n*-pentyl, and *n*-hexyl branches and carefully determined the band centers of the methylene branch rocking vibrations.

### EXPERIMENTAL

The band positions reported in Tables II and III were determined on a Perkin-Elmer Model 112 Double-Pass Spectrometer with sodium chloride optics. The instrument was carefully calibrated in the 800-700  $\text{cm.}^{-1}$  region with acetylene,<sup>5</sup> ammonia,<sup>6</sup> and carbon dioxide.<sup>6</sup> The reported positions are believed to be accurate to better than 1  $\text{cm.}^{-1}$ . The half-band widths of the absorption bands are of the order of 15-20  $\text{cm.}^{-1}$ . Figure 1 was obtained on a Perkin-Elmer Model 221 Spectrophotometer with a sodium chloride prism-grating interchange.

All polymers and copolymers having structures of the type



were prepared by polymerizing the corresponding monomers with  $\text{TiCl}_3\text{-Al}(\text{C}_2\text{H}_5)_3$  catalyst systems. 2-Methyl-3-ethyl-1-pentene was polymerized with  $\text{AlCl}_3$  at  $-80^\circ\text{C}$ . Monomers were either NBS samples or were purified by distillation through a 50-cm. column. The low molecular weight polypropylene was an acetone-soluble extract from a Ziegler-Natta polypropylene.

### RESULTS AND DISCUSSION

The infrared rocking vibrations of the alkyl groups in the polyolefins prepared were assigned as shown in Tables II and III.

#### A. Ethyl Groups

The data in Table II show that the ethyl group in a variety of polymers has an infrared absorption band in the 785-760  $\text{cm.}^{-1}$  (12.74-13.18  $\mu$ ) region. This confirms the assignment by Rugg, Smith, and Waterman<sup>7</sup> of the weak 770  $\text{cm.}^{-1}$  (12.99  $\mu$ ) infrared

TABLE I  
Methylene Rocking Vibrations of Ethyl, *n*-Propyl, *n*-Butyl, *n*-Pentyl, and *n*-Hexyl Groups in Liquid Hydrocarbons

Group	Data of	
	McMurray and Thornton <sup>2</sup> $\text{cm.}^{-1}$ ( $\mu$ )	Data of Iogansen <sup>3</sup> $\text{cm.}^{-1}$ ( $\mu$ )
Ethyl	776-770 (12.88-12.98)	782 (12.79)
<i>n</i> -Propyl	743-734 (13.46-13.62)	739 (13.53)
<i>n</i> -Butyl	729-726 (13.71-13.81)	728 (13.74)
<i>n</i> -Pentyl	726-724 (13.78-13.81)	724.5 (13.80)
<i>n</i> -Hexyl	724-723 (13.82-13.84)	724.5 (13.80)
6 or more methylene sequences	724-722 (13.82-13.86)	721 (13.87)



TABLE III  
Infrared Rocking Vibrations of *n*-Propyl, *n*-Butyl, *n*-Pentyl, and *n*-Hexyl Groups in Solid Polymers

Polymer	Structure	Assignment	
		cm. <sup>-1</sup>	μ
Poly-1-pentene	$(-\text{CH}_2-\text{CH}-)_x$   C <sub>3</sub> H <sub>7</sub>	735	13.61
Low molecular weight polypropylene (terminal propyl group)	$(-\text{CH}_2-\text{CH}-)_x\text{CH}_2-\text{CH}_2-\text{CH}_3$   C <sub>3</sub> H <sub>7</sub>	740	13.51
Poly-1-hexene	$(-\text{CH}_2-\text{CH}-)_x$   CH <sub>3</sub>	724	13.81
Poly-1-heptene	$(-\text{CH}_2-\text{CH}-)_x$   C <sub>4</sub> H <sub>9</sub>	723	13.83
Poly-1-octene	$(-\text{CH}_2-\text{CH}-)_x$   C <sub>5</sub> H <sub>11</sub>	722	13.85
Noncrystalline ethylene-propylene copolymer	$(-\text{CH}_2-\text{CH}_2-)_x(-\text{CH}_2-\text{CH}-)_y$   CH <sub>3</sub>	721	13.87

with a wedge of high density polyethylene, the band position of the ethyl branch moved to 770 cm.<sup>-1</sup> (12.99 μ) due to the band overlap correction.<sup>9</sup>

### B. *n*-Propyl Groups

The terminal *n*-propyl group in low molecular weight polypropylene absorbs at 740 cm.<sup>-1</sup> (13.51 μ), and the *n*-propyl branch in poly-1-pentene absorbs at 735 cm.<sup>-1</sup> (13.61 μ). This confirms Natta's<sup>10</sup> terminal *n*-propyl group assignment of 739 cm.<sup>-1</sup> (13.54 μ) (see Table III).

### C. *n*-Butyl Groups

The *n*-butyl branch assignment of 724 cm.<sup>-1</sup> (13.81 μ) from poly-1-hexene is in better agreement with the liquid hydrocarbon data in Table I than the 745 cm.<sup>-1</sup> (13.42 μ) reported for the *n*-butyl group in low density polyethylene by Willbourn.<sup>4</sup>

### D. *n*-Pentyl and *n*-Hexyl Groups

The assignments of 723 cm.<sup>-1</sup> (13.83 μ) for the *n*-pentyl and 722 cm.<sup>-1</sup> (13.85 μ) for *n*-hexyl branches are comparable with those reported for liquid hydrocarbons in Table I.

### E. Long-Chain Methylene Groups

The long-chain methylene group in an ethylene-propylene copolymer has its rocking vibration at 721 cm.<sup>-1</sup> (13.76 μ).

### CONCLUSIONS

Our infrared data show that solid polymers have their infrared rocking vibrations at frequencies

comparable with those shown by liquid hydrocarbons. Applying our values to the infrared spectrum in Figure 1, the 769 cm.<sup>-1</sup> (13.00 μ) band is certainly due to an ethyl group. The 739 cm.<sup>-1</sup> (13.43 μ) band is due to a *n*-propyl group and not to *n*-butyl, to which Willbourn<sup>4</sup> had assigned a frequency of 745 cm.<sup>-1</sup> (13.42 μ). The presence of *n*-propyl and ethyl groups fits our proposed mechanism for this reaction,<sup>1</sup> whereas *n*-butyl groups cannot. However, the cationic polymerization of 1-butene could yield a material containing *n*-butyl, *n*-propyl, and ethyl groups. The infrared spectrum of this 1-butene polymer shows distinct ethyl and *n*-propyl bands at 766 cm.<sup>-1</sup> (13.05 μ) and 736 cm.<sup>-1</sup> and a broad *n*-butyl band with a center at 727 cm.<sup>-1</sup> (13.76 μ).

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### Synopsis

A series of polymers have been prepared that contain ethyl, *n*-propyl, *n*-butyl, *n*-pentyl, and *n*-hexyl branches. We have determined the rocking vibrations of the branches and have shown that branches in solid polymers have their rocking vibrations at frequencies comparable with those shown by liquid hydrocarbons. The ethyl branches in seven different polymers have infrared absorption bands in the 785–760  $\text{cm}^{-1}$  (12.74–13.18  $\mu$ ) region. The terminal *n*-propyl group absorbs at 740  $\text{cm}^{-1}$  (13.51  $\mu$ ) and the *n*-propyl branch at 735  $\text{cm}^{-1}$  (13.61  $\mu$ ). The *n*-butyl, *n*-pentyl, and *n*-hexyl branches in polymers have their infrared absorption at 724  $\text{cm}^{-1}$  (13.81  $\mu$ ), 723  $\text{cm}^{-1}$  (13.83  $\mu$ ) and 722  $\text{cm}^{-1}$  (13.85  $\mu$ ), respectively. The above data have been used to identify ethyl, *n*-propyl, and *n*-butyl branches in polymers produced by the cationic polymerization of propylene and 1-butene.

### Résumé

On a préparé une série de polymères avec des ramifications éthyle, *n*-propyle, *n*-butyle, *n*-pentyle et *n*-hexyle. On a déterminé les vibrations dues à ces ramifications et on a pu montrer que dans les polymères solides, ces groupes ont une fréquence de vibration de "rocking" à une position comparable à celle des hydrocarbures liquides. Les groupes éthyles présents dans 7 polymères différents ont des bandes d'absorption infrarouge entre 785–760  $\text{cm}^{-1}$  (12.74–13.18

$\mu$ ) Le groupe terminal *n*-propyle absorbe à 740  $\text{cm}^{-1}$  (13.51  $\mu$ ) et le groupe *n*-propyle à 735  $\text{cm}^{-1}$  (13.61  $\mu$ ). Les ramifications *n*-butyle, *n*-pentyle et *n*-hexyle au sein des polymères ont leur fréquence d'absorption infrarouge à 724  $\text{cm}^{-1}$  (13.81  $\mu$ ), 723  $\text{cm}^{-1}$  (13.83  $\mu$ ), et 722  $\text{cm}^{-1}$  (13.85  $\mu$ ) respectivement. Les données ci-dessus permettent d'identifier les ramifications éthyles, *n*-propyles et *n*-butyles dans les polymères produits par polymérisation cationique du propylène et du 1-butène.

### Zusammenfassung

Eine Reihe von Polymeren mit Äthyl-, *n*-Propyl-, *n*-Pentyl- und *n*-Hexylseitenketten wurden dargestellt. Die Rockingfrequenzen der Seitenketten wurden bestimmt und es wurde gezeigt, dass diese Seitenkettenschwingungen in festen Polymeren bei vergleichbaren Frequenzen wie in flüssigen Kohlenwasserstoffen liegen. Die Äthylseitengruppen in sieben verschiedenen Polymeren haben Infrarotabsorptionsbanden im 785–760  $\text{cm}^{-1}$  (12,74–13,18  $\mu$ )-Bereich. Die endständige *n*-Propylgruppe absorbiert bei 740  $\text{cm}^{-1}$  (13,51  $\mu$ ) und die *n*-Propylseitengruppe bei 735  $\text{cm}^{-1}$  (13,61  $\mu$ ). Die *n*-Butyl-, *n*-Pentyl- und *n*-Hexylseitengruppen in Polymeren absorbieren im Infrarot bei 724  $\text{cm}^{-1}$  (13,81 $\mu$ ), bzw. 723  $\text{cm}^{-1}$  (13,83 $\mu$ ) bzw. 722  $\text{cm}^{-1}$  (13,85 $\mu$ ). Die obigen Daten wurden zur Identifizierung von Äthyl-, *n*-Propyl- und *n*-Butylseitenketten in kationischen Propylen- und 1-Butenpolymerisaten herangezogen.

Received November 28, 1960