## Syndiotactic poly[(S)-4-methyl-1-hexene]<sup>a)</sup>

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In the title paper we reported the <sup>13</sup>C NMR and X-ray diffraction spectra of poly[(S)-4-methyl-1-hexene] obtained in the presence of a catalytic system based on isopropylidene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride and methylaluminoxane which promotes syndiotactic-specific polymerization of a-olefins. The polymer is optically active ( $[a]_D^{25} = 219$ ) and crystalline, and the <sup>13</sup>C NMR and X-ray diffraction spectra are different from the corresponding spectra of isotactic poly[(S)-4methyl-1-hexene]. We concluded that the polymer was syndiotactic and interpreted the splitting of the resonances of the methylene carbons of the backbone observed even in solution at 40,4 and 40,6 ppm as arising from a possibly twofold asymmetric helix conformation of the chain stabilized by the asymmetric substituents. This could be the case but, during a discussion on the matter, Professor M. Farina pointed out that a syndiotactic polymer must have first neighbouring monomer units of opposite configuration<sup>1)</sup>. The truly syndiotactic structure cannot be obtained from homopolymerization of a single enantiomer of a chiral  $\alpha$ -olefin but only from alternate copolymerization of the two enantiomers. The polymer structure we proposed is diastereomeric with respect to both isotactic poly[(S)-4-methyl-1-hexene] and syndiotactic alternating copoly [(R, S)-4-methyl-1-hexene]. The methylene carbons of the first neighbouring monomer units are diastereotopic and, in principle, could have different chemical shifts, no matter what the conformation of the chain. This can be visualized by considering that the only symmetry element of the model cyclodimer reported in Fig. 1(a) is the twofold rotational axis  $(C_2)$  passing through the methylene carbons labelled  $C^1$  and  $C^2$ , and that by this symmetry operation  $C^1$  and  $C^2$  do not interchange to each other.

<sup>&</sup>lt;sup>a)</sup> Reinterpretation of the <sup>13</sup>C NMR spectrum of poly[(S)-4-methyl-1-hexene] (see Makromol. Chem., Rapid Commun. 13, 269 (1992)).

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Fig. 1. a) Pseudo-syndiotactic poly[(S)-4-methyl-1-hexene]; b) pseudo-isotactic poly[(S)-4methyl-1-hexene] (or alternate copoly[(R, S)-4-methyl-1-hexene] with isotactic sequence of the configurations of the substituted carbons of the backbone). The only symmetry element for the cyclodimer b) is the 360° fold rotoreflection S<sub>1</sub> passing through the backbone methylene carbons

In view of the previous considerations it turns out that the observed splitting of the resonance of the methylene carbons provides a self-consistent evidence of the diastereochemical structure of the title poly[(S)-4-methyl-1-hexene], but it is not equally diagnostic of the conformation of the chain.

Having experienced that it can be truly misleading to only consider the stereochemical sequence of the configurations of substituted carbons of the backbone, rather than looking at the entire monomer units, we suggest to define the structure of the title poly[(S)-4-methyl-1-hexene] as pseudosyndiotactic. Conversely the alternating copolymer of (R)-and (S)-4-methyl-1-hexene with isotactic sequence of the substituted carbons of the backbone (see Fig. 1(b)) could be also defined pseudoisotactic, since even in this case the methylene carbons of the backbone of neighbouring monomer units are diastereotopic.

In conclusion, the complete assignment of the <sup>13</sup>C resonances of the title poly[(S)-4-methyl-1-hexene] according to the rules of Lindemann and Adams and DEPT experiments is (C<sup>1</sup>) 40,36; (C<sup>1</sup>) 40,61; (C<sup>2</sup>) 28,71; (C<sup>3</sup>) 41,18; (C<sup>4</sup>) 30,12; (C<sup>5</sup>) 28,75; (C<sup>6</sup>) 9,32; (C<sup>7</sup>) 17,52 (ppm referred to HMDS), where the carbons are numbered as follows:

$$\begin{array}{c} 2 & 1.1' \\ -CH - CH - CH_2 - \\ 3 & CH_2 \\ 1 & 7 \\ 4 & CH - CH_3 \\ 1 \\ 5 & CH_2 \\ - \\ 6 & CH_3 \end{array}$$

 IUPAC Macromolecular Division, Macromolecular Nomenclature Commission, Pure Appl. Chem. 53, 733 (1981)