# Articles

## Comments on the Elucidation of Stereochemical Control in $\alpha$-Olefin Polymerization via $^{13}C$ NMR Spectroscopy of Ethylene–Propylene Copolymers

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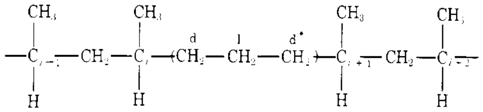
ABSTRACT: Ethylene–propylene (E–P) copolymers of low ethylene content, which insures a preponderance of isolated ethylene units

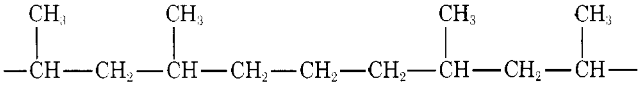


$$-\underset{\displaystyle H}{\overset{\displaystyle CH_3}{C_{i-1}}}-CH_2-\underset{\displaystyle H}{\overset{\displaystyle CH_3}{C_i}}-(\overset{d}{CH_2}-\overset{l}{CH_2}-\overset{d^*}{CH_2})-\underset{\displaystyle H}{\overset{\displaystyle CH_3}{C_{i+1}}}-CH_2-\underset{\displaystyle H}{\overset{\displaystyle CH_3}{C_{i+2}}}-$$

have been studied to determine the $^{13}C$ chemical shifts expected at each of the methylene carbons in ($-^dCH_2-^lCH_2-^{d*}CH_2-$) as a function of the stereosequence of the surrounding polypropylene chain segments. A slightly modified version of Mark's rotational isomeric state model for E–P copolymers was used to determine the average number of three-bond carbon–carbon gauche or $\gamma$ interactions involving the d, l, d* methylene groups as a function of the surrounding polypropylene stereoregularity. Each $\gamma$ interaction was assigned a shielding effect of −5.3 ppm. The calculated chemical shifts led to the following conclusions: (i) the chemical shift expected at $-^lCH_2-$ is independent of the polypropylene stereosequence, (ii) the chemical shifts calculated for $-^dCH_2-$ and $-^{d*}CH_2-$ are independent of the meso ($m$) or racemic ($r$) arrangement of propylene units $i$, $i + 1$ across the ethylene fragment, (iii) chemical shift differences of ca. 1 ppm are expected for $-^dCH_2-$ and $-^{d*}CH_2-$ carbons adjoining an $m$ propylene dyad $i - 1$, $i$ or $i + 1$, $i + 2$ relative to those next to an $r$ propylene dyad, and (iv) $^{13}C$ NMR spectroscopy of E–P copolymers cannot be expected to elucidate the mechanism of stereospecific catalysis in $\alpha$-olefin polymerization.

$^{13}C$ nuclear magnetic resonance (NMR) spectroscopy has been successfully used[1–8] to study the stereochemical configuration of polypropylene. Significant information concerning the tacticity and the nature of steric defects in polypropylene homopolymers has been obtained.

Similar studies[1,8–16] have been conducted on copolymers of ethylene with propylene (E–P) with the intent of obtaining insights into the mechanisms of steric control exerted by Ziegler–Natta catalysts in the polymerization of $\alpha$-olefins. In these investigations E–P copolymers of low ethylene content, some[9,10] with $^{13}C$ enriched ethylene carbons, were polymerized with several stereospecific catalysts leading to polypropylene chain segments with different stereosequences. A great majority of the ethylene units were isolated by polypropylene segments as in



$$-\overset{\displaystyle CH_3}{CH}-CH_2-\overset{\displaystyle CH_3}{CH}-CH_2-CH_2-CH_2-\overset{\displaystyle CH_3}{CH}-CH_2-\overset{\displaystyle CH_3}{CH}-$$

In each of the $^{13}C$ NMR studies only a single resonance was observed[9,10,16] for the $-^lCH_2-$ carbon and either a single or two resonances for the $-^dCH_2-$ and $-^{d*}CH_2-$ carbons (d, l denote the terminal, central $CH_2$ groups in the ethylene fragment and imply nothing about the asymmetry of the propylene fragments, see Figure 1) depending on whether or not an isospecific catalyst was employed in the polymerization. Based on these observations, the following conclusions were drawn.[10,16] (1) In E–P copolymers obtained with isospecific catalysts, the ethylene units occur only in meso ($m$) situations regarding the neighboring propylene units $i$, $i + 1$. This implies that dissymmetry around the metal catalyst atom, and not asymmetric induction involving only the last unit of the growing chain end, provides control of the stereochemistry of addition. (2) The ethylene units in E–P copolymers obtained with syndiospecific catalysts occur with similar frequency between propylene units $i$, $i + 1$ in $m$ and racemic ($r$) situations. Steric control is therefore apparently exerted by the last unit of the growing chain end in syndiospecific catalyzed polymerization.

However, as noted by Sanders and Komoroski,[16] the two resonances seen for $-^dCH_2-$ and $-^{d*}CH_2-$ by Zambelli and co-workers[10] in the syndiotactic E–P copolymer could be due to structures of type c shown in Figure 1. In fact if $\gamma$ interactions involving carbons separated by three bonds are the principal source[17–21] of the observed chemical shift difference, then structures such as c in Figure 1, rather than a mixture of a and b as was assumed,[10] would be expected to be responsible for the two resonances observed.

Consequently the present study was initiated to test the consistency of the current interpretation[10,16] of E–P copolymer $^{13}C$ NMR spectra with the chemical shifts predicted by a quantitative analysis of the $\gamma$ effects[17–22] experienced by the d, l, and d* methylene carbons in the representative E–P copolymer structures depicted in Figure 1.

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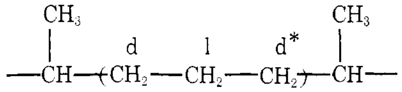
**Table I**
**Calculated Chemical Shifts ($\nu$) for the Methylene Carbons in an Isolated Ethylene Unit of Various E-P Copolymers**



$$-\overset{CH_3}{\overset{|}{CH}}-(\overset{d}{CH_2}-\overset{l}{CH_2}-\overset{d^*}{CH_2})-\overset{CH_3}{\overset{|}{CH}}-$$

| E-P copolymer[a] | $\Delta\nu(-^lCH_2-)$, ppm | | | $\Delta\nu(-^dCH_2-)$, $\Delta\nu(-^{d^*}CH_2-)$, ppm | | |
|---|---|---|---|---|---|---|
| | 50 °C | 100 °C | 150 °C | 50 °C | 100 °C | 150 °C |
| $T^mm\ E^mm\ T^m$ | −0.243 | −0.186 | −0.143 | −1.511, −1.511 | −1.177, −1.177 | −0.932, −0.932 |
| $T^mm\ E^rm\ T^m$ | −0.228 | −0.175 | −0.138 | −1.588, −1.588 | −1.208, −1.208 | −0.957, −0.957 |
| $T^mr\ E^mm\ T^m$ | −0.111 | −0.080 | −0.069 | 0.0, −1.588 | 0.0, −1.208 | 0.0, −0.957 |
| $T^rr\ E^mm\ T^m$ | −0.137 | −0.101 | −0.079 | −0.302, −1.548 | −0.207, −1.203 | −0.143, −0.948 |
| $T^mr\ E^mr\ T^r$ | 0 | 0 | 0 | −0.032, −0.345 | −0.021, −0.233 | −0.015, −0.164 |

[a] As an example, E-P copolymer $T^rr\ E^mm\ T^m$ has an all-racemic or syndiotactic tail $T^A$ ($T^r$) and an all-meso or isotactic tail $T^B$ ($T^m$) (see Figure 1d), racemic dyad $i-1, i(r)$ and meso dyad $i+1, i+2(m)$, and a meso arrangement of propylene units $i, i+1$ across the isolated ethylene unit ($E^m$).

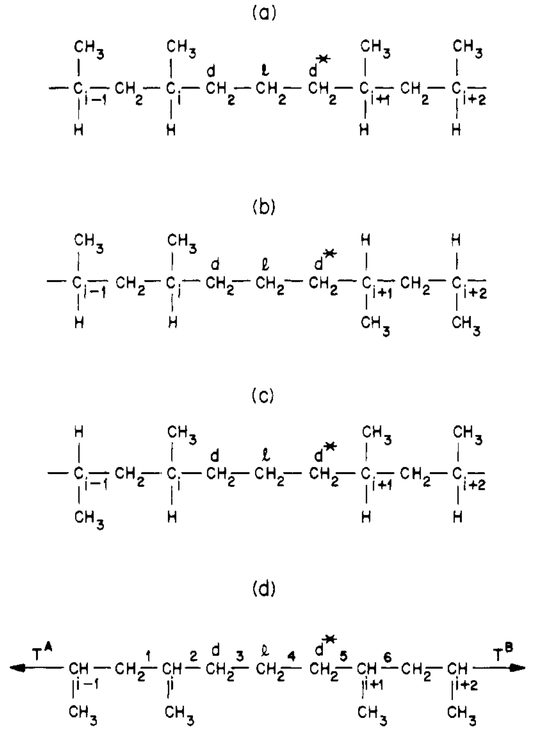


**Figure 1.** (a) Isolated ethylene unit in an all-isotactic E-P copolymer with the meso arrangement of propylene units across the ethylene unit. (b) Same as (a) except replace meso with racemic. (c) Isolated ethylene unit bounded by racemic $i-1, i$ and meso $i+1, i+2$ propylene units. (d) Isolated ethylene unit in a model E-P copolymer chain. $T^A$ and $T^B$ indicate polypropylene tails of 50 repeat units each.

## Description of Calculations

The probabilities of finding bonds 1–6 surrounding and including an isolated ethylene unit in an E-P copolymer chain (see Figure 1d) in their allowed rotational states[23,24] are calculated[24] as a function of the stereosequence at propylene centers $i-1, i, i+1, i+2$. Mark's[25] rotational isomeric state model developed for E-P copolymers is used, where $E_\tau = 0.5$ kcal/mol and $E_\omega = 1.5$ and 2.0 kcal/mol characterize the three-bond gauche interactions and the four-bond pentane interferences,[24–26] respectively, among the CH, $CH_2$, and $CH_3$ groups.

The average number of $\gamma$ effects experienced by d, l, and d* methylene carbons are obtained from these average bond probabilities calculated at 50, 100, and 150 °C. Consistent with a previous study[22] of the $^{13}C$ chemical shifts observed[5,27] and predicted[22] for various stereosequences in polypropylene model compounds based on $\gamma$ effects, a $\gamma = -5.3$ ppm is assumed for each three-bond gauche or $\gamma$ interaction involving $-^dCH_2-$, $-^lCH_2-$, or $-^{d^*}CH_2-$ with CH, $CH_2$, or $CH_3$.

The calculations were actually performed on E-P copolymer chains of 208 bonds, with the isolated ethylene unit fragments shown in Figure 1 positioned at the center of each chain. The polypropylene chain tails $T^A$ and $T^B$ (see Figure 1d) were either both isotactic or one was isotactic and the other syndiotactic.

## Calculated Results and Discussion

Table I presents the chemical shift differences predicted for the d, l, and d* methylene carbons in isolated ethylene units surrounded by polypropylene fragments of various stereosequence at $T$ = 50, 100, and 150 °C. Only results calculated with $E_\omega = 1.5$ kcal/mol are presented, because the calculated chemical shift differences are not changed significantly when $E_\omega$ is increased to 2.0 kcal/mol.

The chemical shift predicted for the central methylene unit $-^lCH_2-$ is virtually independent of the stereosequence of the surrounding polypropylene units. All $^{13}C$ measurements reported on low ethylene content E-P copolymers assign[10,16] a single resonance to $-^lCH_2-$ regardless of the stereospecificity of the catalyst employed, which is consistent with the calculated chemical shifts.

E-P copolymers $T^mm\ E^mm\ T^m$ and $T^mm\ E^rm\ T^m$, which contain the central fragments illustrated in Figures 1a and 1b, respectively, have nearly identical predicted chemical shifts for the d and d* methylene carbons. This means that the arrangement of nearest neighbor propylene units $i, i+1$ across the ethylene unit should not effect the chemical shifts of the terminal methylene groups d, d*.

On the other hand, the stereosequence of the propylene dyads $i-1, i$ and $i+1, i+2$ adjoining the ethylene unit does effect the chemical shifts of the d and d* methylene carbons. An adjacent meso dyad $i-1, i$ or $i+1, i+2$ shields $-^dCH_2-$ or $-^{d^*}CH_2-$ more than a racemic dyad by ca. 1–1.5 ppm.

Zambelli et al.[10] observe two resonances separated by 1 ppm for the d and d* methylene carbon in E-P copolymers polymerized with either syndiospecific or aspecific catalysts. The magnitude of this observed chemical shift difference is consistent with that calculated for E-P copolymers $T^mr\ E^mm\ T^m$ and $T^rr\ E^mm\ T^m$, which contain the fragment illustrated in Figure 1c.

It seems apparent that the calculated and experimentally observed chemical shifts of the d and d* methylene carbons in low ethylene content E-P copolymers are compatible only if the stereosequence of propylene units adjoining and not spanning the isolated ethylene unit influence their chemical shifts. Contrary to previous interpretations[9,10,16] $^{13}C$ NMR studies of E–P copolymers do not aid in the elucidation of the mechanism of stereospecific catalysis in $\alpha$-olefin polymerization.

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# Structure of Poly(hexamethylene oxamide) [Nylon 62][+]

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ABSTRACT: Poly(hexamethylene oxamide) [Nylon 62] of reasonable molecular weight was prepared by a modification of the Sokolov technique for the preparation of oxamides. This polymer could be stretched and a fiber diagram of the polymer could be obtained. Nylon 62 has a structure similar to that of the $\alpha$ form of Nylon 66.

Polyoxamides are generally high-melting materials which decompose to some extent below their melting point especially when the aliphatic portions of the diamine of the polyoxamides[1,2] are short. As a consequence, polyoxamides have not reached commercial importance inspite of their interesting overall properties. Recently regular copolyamides based on the oxamide linkage have shown promise as materials for desalination membranes.[3–9]

Polyoxamides of reasonable molecular weight cannot be easily prepared by the normal polymerization techniques for polyamides.[1,10,11] Although several oxalic acid derivatives have been used for polyoxamide preparation, polyoxamides normally obtained had an inherent viscosity not exceeding an $\eta$ of 0.3. Only the method utilizing oxalyl chloride gives polymers of substantially higher molecular weight. The specific technique is a gas liquid interfacial polymerization technique first devised by Sokolov[12–15] in which oxalyl chloride diluted with nitrogen is bubbled into an aqueous solution of the diamine. The relationship between the yield and viscosity of various polyoxamides as a function of the reaction temperature, the diamine concentration in water, the concentration of the gaseous oxalyl chloride in the inert gas, and the height of the aqueous phase was investigated. The high reactivity of oxalyl chloride in aqueous solution leads readily to its hydrolysis but the relatively low solubility of oxalyl chloride and also the high reaction temperature which reduces the solubility of the oxalyl chloride favors polymerization. The relationship between reactant and concentration (both gaseous and liquid) was found to be qualitatively similar to that found in liquid–liquid type interfacial polymerizations; consequently it was expected to be possible to prepare, by this gas/liquid interfacial technique, samples of high enough molecular weight Nylon 62 for the determination of its crystal structure.

Structure determinations of Nylon 6,[16,17] Nylon 66,[18] and more recently wholly aromatic polyamides[19] have been carried out. Nylon 6 crystallizes in three forms, the $\alpha$,[16] $\beta$,[16] and $\gamma$ form.[17] The $\alpha$ form is monoclinic, has eight monomeric units per unit cell, and has a fiber period of 17.2 Å. The $\beta$ form is difficult to analyze, as the $\beta$-type specimens all contain a high percentage of the $\alpha$ form. The $\gamma$ form is again monoclinic but has a twisted molecular structure with 0.3 Å shorter fiber period than that of the $\alpha$ form. Nylon 66[18] also has an $\alpha$ and $\beta$ form; the $\alpha$ form is triclinic and has one polymer chain per unit cell, while the $\beta$ form is monoclinic with two chains per unit cell. Both forms have a fiber period of 17.2 Å. Poly(*p*-phenyleneterephthalamide) and poly-*p*-benzamide are fully extended,[19] while poly(*m*-phenyleneisophthalamide)[20] is twisted with a fiber period about 1 Å shorter than that of the fully extended structure. The characteristic tensile moduli[21] features of these aromatic polyamides were also interpreted in terms of these structures.

It was the purpose of this paper to prepare Nylon 62 of reasonable molecular weight and to fabricate the polymer into samples which could be drawn and for which good x-ray fiber diagrams could be obtained. Identification of the spacing would be suitable for the calculation of the unit cell of Nylon 62 and for fully characterizing the crystal structure of the polymer.

[+] Regular Copolyoxamides. 6.

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