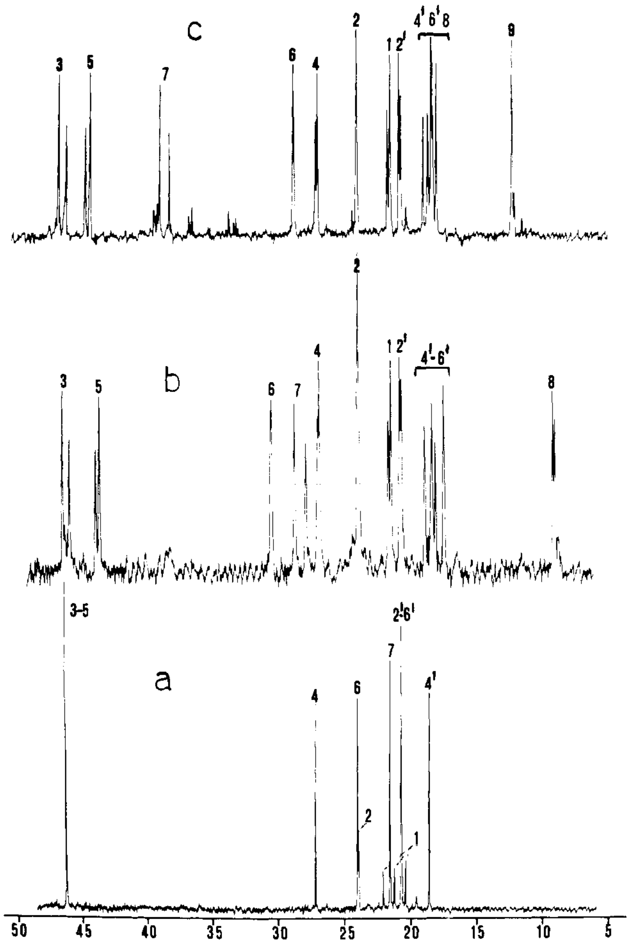

Figure 2. ^{13}C NMR spectra of a, (2*R*,4*R*-2*S*,4*S*)-1 deuterio-2,4,6-trimethylheptane, b, 2,4,6-trimethyloctane, and, c, 2,4,6-trimethylnonane. Labeling of the resonances is according to carbon numbering of Figure 1. By convention C_1 is always the e methyl and C_2 the t one.

diastereomeric methyl carbons of a, b, and c are compared with the corresponding differences, calculated by means of the stereospecific additivity parameters proposed in ref[3] for estimating the chemical shifts of side methyl carbons of paraffinic chains of practically infinite length. The agreement between the experimental and the so calculated differences is satisfactory especially for diastereomeric carbon pairs.

If the previous definition of e and t methyl carbons of the isopropyl group is extended to the diastereomeric (methylene) carbons C_7 of the (4*R*,6*R*-4*S*,6*S*) and (4*R*,6*S*-4*S*,6*R*) forms of b and c,[13] it could be observed for C_7's a similar agreement between the experimental differences of the chemical shifts and that calculated by the just mentioned stereospecific parameters ($\delta_{C_{7\delta e}} - \delta_{C_{7\delta t}}$ = 0.5$_5$ ppm (calcd), (b) 0.8$_5$ ppm, and (c) 0.7$_3$ ppm).

These observations suggest that it might be possible to extend the estimation of chemical shift by additive stereospecific parameters to open chain molecules shorter than those considered in ref 3 and, reasonably, also to the methylene carbons. As to the main goal of this paper, ^{13}C-NMR analysis of the quoted model compounds allows one to evaluate saturated end groups in polypropylene and consequently to reach mechanistic conclusions on polymer chain initiation, metal-chain bond hydrolysis, regioregulation, and stereoregulation.[4]

Experimental Section

(2*R*,4*R*-2*S*,4*S*)-1-Deuterio-2,4,6-trimethylheptane has been prepared after hydrolysis with D_2O of 1-lithio-(2*S*,4*S*-2*R*,4*R*)-2,4,6-trimethylheptane.[2,5] 2,4,6-Trimethyloctane and 2,4,6-trimethylnonane have been prepared from 2-ethyl- 4,6-dimethylheptanoic acid methyl ester and 2-propyl-4,6-dimethyl heptanoic acid methyl ester after: (1) reduction to alcohol with $LiAlH_4$ in ethyl ether, (2) chlorination of the alcohol with dichlorotriphenylphosphorane,[14] and (3) transformation of the halomethyl group into the lithiomethyl group in diethyl ether and subsequent hydrolysis with H_2O.

2-Ethyl-4,6-dimethylheptanoic acid and 2-propyl-4,6-dimethylheptanoic acid have been prepared after reaction of 1-bromo-2,4-dimethylpentane with diethylethylsodiomalonate and diethylpropylsodiomalonate respectively and subsequent hydrolysis and decarboxylation.[11,12] Proton noise decoupled ^{13}C NMR spectra were measured at 140 °C in 1,2,4-trichlorobenzene solutions (10% v/v) by adding 1% hexamethyldisiloxane (HMD) as internal reference. These conditions where chosen since they are typical for the analysis of hydrocarbon polymers. An HX-90 Bruker spectrometer operating at 22.63 MHz in the PFT mode was used as described previously.[3]

References and Notes

(1) A. Zambelli, G. Gatti, C. Sacchi, W. O. Crain, Jr., and J. D. Roberts, *Macromolecules*, **4**, 475 (1971).
(2) A. Zambelli, G. Bajo, and E. Rigamonti, *Makromol. Chem.*, **179**, 1249 (1978).
(3) A. Zambelli and G. Gatti, *Macromolecules*, **11**, 485 (1978).
(4) A. Zambelli, P. Locatelli, and E. Rigamonti *Macromolecules*, following paper in this issue.
(5) Diastereomeric purity of a was evaluated ~80% on the basis of the purity of the materials used in the synthesis. Neglecting the presence of ~20% of the 2'-deuterio-(2*R*,4*S*-2*S*,4*R*) diastereomer does not affect the assignment of the diastereotopic methyls of isopropyl groups (see later in the text) but is reflected in the relative intensities of the resonances 7 and 2'–6' of Figure 1a (~1.2/1.8 instead of 1/2 and in the presence of a further triplet ($\delta = 20.52 J_{D-^{13}C} = 19$ Hz) partially overlapped with the more intense one centered at 21.34 ppm, also due to $D-^{13}C$ coupling and revealed by the small peak at 19.6$_9$ ppm.
(6) C. J. Carman, A. R. Tarpley, Jr., and J. H. Goldstein, *Macromolecules*, **6**, 719 (1973).
(7) For the effect of deuteration on ^{13}C-NMR spectra see for instance F. W. Wehrli and T. Wirthlin, "Interpretation of ^{13}C Carbon Spectra", Heiden, 1976, pp 107–110, and references therein.
(8) D. M. Grant and E. G. Paul, *J. Am. Chem. Soc.*, **86**, 2984 (1964).
(9) M. A. Rosanoff, *J. Am. Chem. Soc.*, **28**, 114 (1906).
(10) K. F. Elgert and W. Ritter, *Makromol. Chem.*, **178**, 2857 (1977).
(11) G. Odham, *Ark. Kemi*, **26**, 367 (1967).
(12) G. Odham, *Ark. Kemi*, **23**, 431 (1965).
(13) According the definition which takes into consideration the steric relationship of C_7 with $C_{4'}$, the positions of $C_{6'}$ and C_7 are diastereotopic; therefore C_7 is δ_e in the (4*R*,6*R*-4*S*,6*S*) forms of b and c, and δ_t in the (4*R*,6*S*-4*S*,6*R*) forms.
(14) G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *J. Am. Chem. Soc.*, **86**, 964 (1964).

Carbon-13 Nuclear Magnetic Resonance Analysis of Tail-to-Tail Monomeric Units and of Saturated End Groups in Polypropylene

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Previous papers concerning ^{13}C-NMR analysis of model compounds of polypropylene[1,2] have shown that the methyl spectrum may be diagnostic for identification of tail-to-tail units (⊢●●⊣, where ⊢● = CH_2–$CH(CH_3)$ and ●⊣ = $CH(CH_3)$–CH_2) and of end groups.

This fact prompted us to carefully examine the methyl spectra of polypropylenes prepared in the presence of typical syndiospecific, nonstereospecific, and isospecific catalytic systems.

Figure 1 shows the methyl spectra of four low molecular weight samples of 30% enriched poly([3-^{13}C]propylene).

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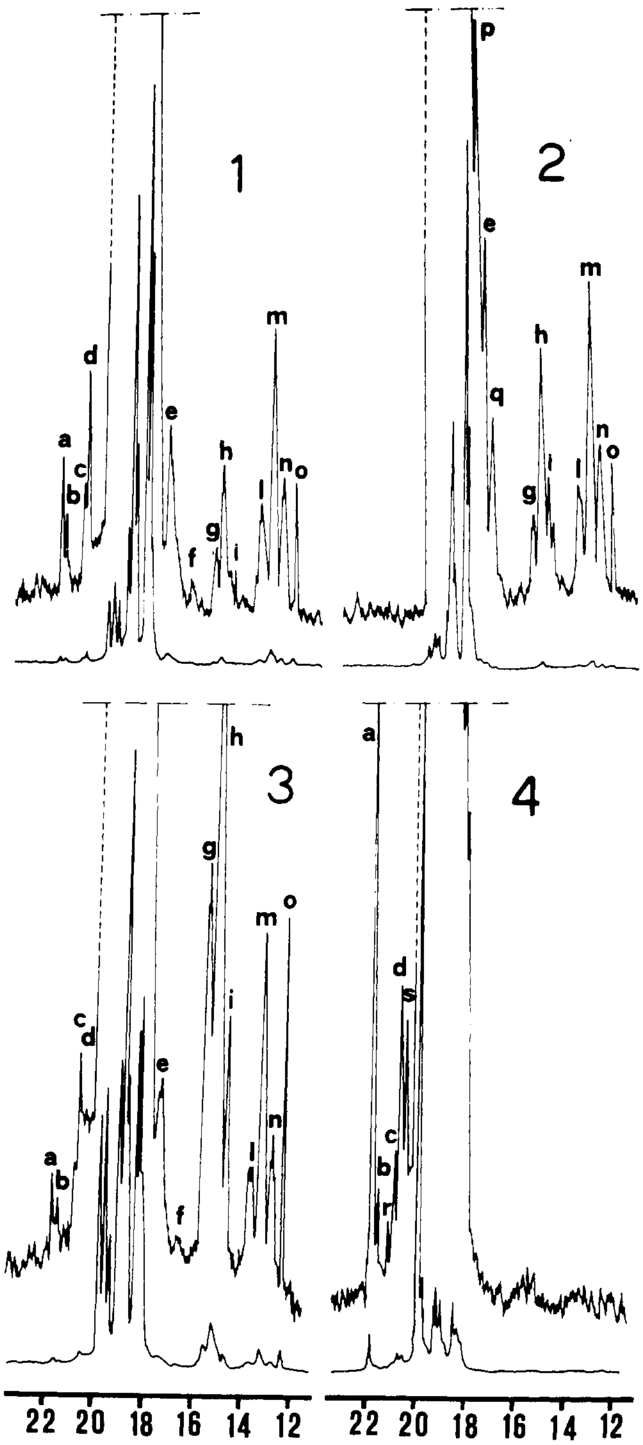

Figure 1. Proton noise-decoupled methyl ^{13}C-NMR spectra of poly([3-^{13}C]propylene) prepared with different catalytic systems. Two amplifications are reported for each spectrum in order to appreciate both methyl resonances of steric pentads (lower amplification) and lower intensity peaks arising from head-to-head units and end groups (higher amplification). Note that due to the fact that only monomer is ^{13}C selectively enriched the observed signals are due to methyl arising from monomer only, and never from organometallic cocatalysts. Chemical shift is relative to HMD.

Samples 1 and 2 (Figure 1, parts 1 and 2) are prevailingly syndiotactic and have been prepared in the presence of the homogeneous catalytic systems VCl_4–$Al(CH_3)_2Cl$–anisole and VCl_4–$Al(C_2H_5)_2Cl$–anisole,[3,4] respectively. The stereoirregular sample 3 (Figure 1, part 3) has been prepared with the homogeneous system VCl_4–$Al(CH_3)_3$–$Zn(CH_3)_2$. Sample 4 (Figure 1, part 4) is prevailingly isotactic and has been prepared by the heterogeneous system δ-$TiCl_3$–$Al(CH_3)_3$–$Zn(CH_3)_2$.

Table I
Chemical Shifts and Configurational Relationships of Methyl Carbons of Figure 2[a]

resonance peak	δ	config relationship
a	21.7_6	δe ζe
b	21.5_4	δe ζt
c	20.8_7	δt ζe
d	20.6_9	δt ζt
e	17.5	
f	16.6	
g	15.6	γe
h	15.3	γe
i	14.8	γe
l	13.7	γt
m	13.3	γt
n	12.8	γt
o	12.3_7	
p	17.7_9	
q	17.2_3	
r	21.1_4	
s	20.4_9	

[a] For chemical assignment see Figure 2. Configurational relationships are incomplete because of insufficient resolution (see ref 12).

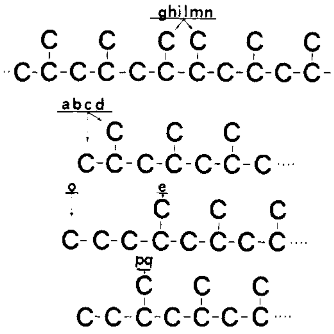

Figure 2. Chemical assignment of the resonances found in Figure 1. See Table I for assignment of configurational relationships.

In the spectrum of sample 1 several methyl resonances (marked by small letters) can be observed beyond those of the methyls of head-to-tail arranged units in pentad stereochemical sequences.[5,6] The assignment and the chemical shifts of all of these resonances but f is given in Figure 2 and Table I on the basis of comparison of the chemical shifts with model compounds previously reported[1,2] (2,4,6-trimethylheptane;[2] 2,4,6-trimethyloctane;[2] 2,4,6-trimethylnonane;[2] and 7′-^{13}C-enriched 2,4,6,7,9,11,13-heptamethyltetradecane[1]). Resonances a, b, c, and d observed in the spectrum of sample 1 are not detected in the spectrum of sample 2 while other resonances appear (p and q).

In the spectrum of sample 3 the same resonances are detected (a to o included) as in sample 1. Finally, in the spectrum of the prevailingly isotactic sample 4, only a, b, c, d, r, and s resonances are detected and a is particularly strong.

Considering the assignment of the resonances found in the four spectra (Figure 2 and Table I) it may be observed that (except for unidentified resonances f, r, and s) they are in good agreement with the stereochemical polymerization mechanism proposed in previous papers[7-11] to which the reader is referred.

Resonances g, h, i, l, m, n call for tail-to-tail arrangements connecting blocks of units having opposite orientation[12] (...├●├●●┤●┤●┤...) in both syndiotactic (1 and 2) and stereoirregular (3) polymers. This fact confirms the conclusion that in the presence of vanadium homogeneous catalytic systems both primary and secondary insertions of the monomer are possible[9-11] and that primary insertion is favored on metal-primary carbon bonds while secondary insertion is favored on metal-secondary carbon bonds (i.e., regiospecific propagation is essentially a Markov process).

$$\mathrm{Mt{-}CH_2\cdots + C_3H_6 \rightarrow Mt{-}CH_2{-}CH(CH_3){-}CH_2\cdots}\ \text{(primary insertion)}$$

$$\mathrm{Mt{-}CH(CH_3)\cdots + C_3H_6 \rightarrow Mt{-}CH(CH_3){-}CH_2{-}CH(CH_3)\cdots}\ \text{(secondary insertion)}$$

As to the stereochemical environment of these methyl carbons in tail-to-tail units, it may be seen that methyls of tail-to-tail units are somewhat prevailingly in the γt configurational relationship[13] (l, m, n resonances) in **1** and **2** while they are mostly in γe (g, h, i resonances) in stereoirregular polymer **3**.

Considering intensities of the g to n resonances, one may also appreciate that the proportion of tail-to-tail units is higher in stereoirregular than in syndiotactic polymers.

The resonances a, b, c, and d could in principle arise either from the primary insertion of the monomer on a $\mathrm{Mt{-}CH_3}$ bond in the initiation step

$$\mathrm{Mt{-}CH_3 + {}^{13}CH_3CH{=}CH_2 \rightarrow Mt{-}CH_2CH({}^{13}CH_3)CH_3}$$

(Mt indicates the metal atom of the catalytic complex) or after the hydrolysis of a Mt–primary carbon bond at the end of polymerization (see Experimental Section).

$$\mathrm{Mt{-}CH_2CH({}^{13}CH_3)CH_2CH({}^{13}CH_3)\cdots \xrightarrow{H_2O} CH_3CH({}^{13}CH_3)CH_2CH({}^{13}CH_3)\cdots}$$

The fact that a, b, c, and d resonances are present in the spectra of **1** and **3** (where initiation occurs on $\mathrm{Mt{-}CH_3}$ bonds) but are absent in **2** (where initiation starts on $\mathrm{Mt{-}C_2H_5}$ bonds) suggests that these resonances arise essentially from initiation when homogeneous catalyst systems are used. Resonances p and q in the spectrum of **2** should be due to primary insertion on $\mathrm{Mt{-}C_2H_5}$ bonds.

$$\mathrm{Mt{-}C_2H_5 + {}^{13}CH_3CH{=}CH_2 \rightarrow Mt{-}CH_2CH({}^{13}CH_3)C_2H_5}$$

Resonance o (and e) in **1**, **2**, and **3** arises unequivocally from the hydrolysis of Mt–secondary carbon bonds at the end of polymerization.[14]

$$\mathrm{Mt{-}CH({}^{13}CH_3)CH_2CH({}^{13}CH_3)CH_2\cdots \xrightarrow{H_2O} {}^{13}CH_3CH_2CH_2CH({}^{13}CH_3)CH_2\cdots}$$

This fact shows that in the initiation step for **1**, **2**, and **3** primary insertion is favored (as expected[9-11]) because in this step it occurs on Mt–unsubstituted carbon bonds.

Primary insertion is not syndiospecific; in fact, the intensities of the resonances a, b, c, and d (see Table I for stereochemical assignments) have a comparable intensity in the spectrum of **1** in spite of the prevailingly syndiotactic structure of the whole polymer. Of course syndiotactic steric control should come into effect after the propagation had turned from primary to secondary. Such change of insertion entails the presence in the polymer of head-to-head units (●⊣⊢●) which cannot be easily observed in the methyl spectra because of the overlap with the methyl resonances of head-to-tail units.[15] However, these units have already been observed both by IR[10] and on methylene carbon ^{13}C-NMR spectra.[15]

In addition, the presence of such units is a necessary consequence of the presence of tail-to-tail units (resonances g to n). Most probably lack of syndiotactic regularity in sample **3** mainly arises from insufficient tendency of the secondary insertion to persist in the presence of the $\mathrm{VCl_4{-}AlR_3}$ (R = alkyl group) catalytic systems. Finally, in the spectrum of the prevailingly isotactic sample **4** no resonances are detected for tail-to-tail units and a, b, c, and d resonances are the only ones attributable to saturated end groups. Therefore they should account for both ends of the polymer chains, and the corresponding methyl carbons should arise partially from primary insertion of the monomer on $\mathrm{Mt{-}CH_3}$ bonds, and partially from hydrolysis of Mt–primary carbon bonds at the end of polymerization. This means that isotactic polymerization is completely regiospecific (primary insertion) as it was found in a previous paper.[16]

The enhanced intensity of a and its stereochemical assignment (see Table I) suggest that this resonance is associated both to the initiation and to the final Mt–C hydrolysis of isotactic chains. The smaller resonances b, c, and d, calling for nonstereospecific placements of the enriched methyls of the first and of the last monomer unit of polymer chains, could arise from very low average molecular weight stereoirregular chains also growing prevailingly through primary insertion. Resonances r and s have not been interpreted. Probably they as well as resonance f are due to traces of irregular oligomers which have little to do with stereospecific polymerization.[17]

Experimental Section

All the solvents used were purified by treatment with $\mathrm{LiAlH_4}$ and distillation, and the reactions were performed in an inert atmosphere (nitrogen or helium). δ-$\mathrm{TiCl_3}$, $\mathrm{VCl_4}$, $\mathrm{AlR_2Cl}$, and $\mathrm{AlR_3}$ were commercial products. Dimethylzinc was prepared as reported in the literature.[18]

Enriched [3-^{13}C]Propene. Enriched [3-^{13}C]propene (30%) was prepared by coupling in tetrahydrofuran vinyl magnesium bromide and ^{13}C enriched methyl iodide. $\mathrm{C_3H_3MgBr}$ (0.18 mol) dissolved in 200 mL of anhydrous tetrahydrofuran was introduced under a helium atmosphere into a 500-mL three-necked flask provided with magnetic stirrer and reflux condenser. Half of the solvent was distilled off in order to eliminate $\mathrm{C_2H_4}$ arising from a trace amount of water; to the Grignard solution cooled to −78 °C was added 0.15 mol of enriched $\mathrm{^{13}CH_3I}$.

The temperature was gently raised until rapid evolution of propene was observed. Propene was passed through the reflux condenser at 0 °C and collected in a trap cooled at liquid nitrogen temperature. Reaction was continued by warming the reaction flask to 50 °C while stirring and stripping with a helium stream. Propene was purified by repeated trap-to-trap distillations in vacuo, treated with $\mathrm{AlEt_3}$, and again distilled. The yield of [3-^{13}C]propene (based on $\mathrm{CH_3I}$) was 90%. The main impurity observed by GLC was 0.2% $\mathrm{C_2H_4}$.

Polymerization Runs. Reagents, polymerization conditions, and yields are reported in Table II. Catalytic systems were prepared by mixing reagents in toluene solution at the preselected temperature under a nitrogen atmosphere. Reaction vessels were then cooled at liquid nitrogen temperature and evacuated at 10^{-4} mm Hg. Subsequently the proper amount of enriched propene was admitted and the temperature raised to the values reported in Table II. Polymerization was stopped by adding dropwise, under a nitrogen atmosphere, HCl-acidified methanol. Care was taken to exclude air in order to prevent the occurrence of oxidation of reactive metal–carbon bonds instead of hydrolysis.

The hydrolyzed reaction mixture was allowed to stand at room temperature for 3 h. Finally, the polymer was precipitated with excess methanol, purified by dissolving in hot toluene and reprecipitating with methanol, and dried under high vacuum at 70 °C.

$\mathrm{Zn(CH_3)_2}$ was used in runs 3 and 4 in order to decrease molecular weights by chain-transfer reaction.[19] Molecular weight of the samples was checked on similar unenriched polymers and was in the range of 1500–4000.[20]

NMR Analysis of Polymers. Proton noise-decoupled ^{13}C NMR spectra were measured at 140 °C in 1,2,4-trichlorobenzene

Table II
3-^{13}C-Enriched Propene Polymerizations with Different Catalytic System

runs[a,b,c,g]	catalytic systems	polymer yield, g
1[d]	VCl_4–$Al(CH_3)_2Cl$–anisole	0.4
2[d]	VCl_4–$Al(C_2H_5)_2Cl$–anisole	0.5
3[e]	VCl_4–$Al(CH_3)_3$-$Zn(CH_3)_2$	0.2
4[f]	δ-$TiCl_3$-$Al(CH_3)_3$-$Zn(CH_3)_2$	0.1

[a] 15 mL of toluene was used as solvent. [b] Polymerization time 24 h. [c] In all the runs 0.7 g of 30% enriched propene was employed. [d] [VCl_4 and anisole] 5×10^{-4} mol; [AlR_2Cl] 5×10^{-3} mol. [e] [VCl_4] 5×10^{-5} mol; [$Al(CH_3)_3$] 11×10^{-3} mol; [$Zn(CH_3)_2$] 5×10^{-3} mol. [f] [δ-$TiCl_3$] 3.2×10^{-3} mol; [$Al(CH_3)_3$] 11×10^{-3} mol; [$Zn(CH_3)_2$] 5×10^{-3} mol. [g] Runs 1, 2, and 3 were performed at −78 °C and run 4 at room temperature.

solutions (10% w/v) by adding 1% of hexamethyldisiloxane (HMD) as internal reference. An HX-90 Bruker spectrometer operating at 22.6_3 MHz in the PFT mode was used as described previously.[1]

References and Notes

(1) A. Zambelli and G. Gatti, *Macromolecules*, 11, 485 (1978).
(2) A. Zambelli, P. Locatelli, and G. Bajo, *Macromolecules*, preceding paper in this issue.
(3) A. Zambelli, G. Natta, and I. Pasquon, *J. Polym. Sci., Part C*, 4, 411 (1963).
(4) G. Natta, A. Zambelli, G. Lanzi, I. Pasquon, E. R. Mognaschi, A. L. Segre, and P. Centola, *Makromol. Chem.*, 81, 161 (1965).
(5) A. Zambelli, P. Locatelli, G. Bajo, and A. Bovey, *Macromolecules*, 8, 687 (1975).
(6) J. C. Randall, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 703 (1974).
(7) A. Zambelli, G. Gatti, C. Sacchi, W. O. Crain, Jr., and J. D. Roberts, *Macromolecules*, 4, 475 (1971).
(8) A. Zambelli, "NMR-Basic Principles and Progress", Vol. 4, Springer, Berlin, 1971.
(9) A. Zambelli and C. Tosi, *Adv. Polym. Sci.*, **15**, 38 (1974).
(10) A. Zambelli, C. Tosi, and C. Sacchi, *Macromolecules*, 5, 649 (1972).
(11) A. Zambelli, G. Bajo, and E. Rigamonti, *Makromol. Chem.*, 179, 1249 (1978).
(12) In the spectrum of 7′ methyl of 7′-^{13}C-enriched 2,4,6,7,9,-11,13-heptamethylheptadecane (the model compound of methyl carbons of monomer units in the considered tail-to-tail arrangement) 16 distinct resonances have been detected[1] due to the configurational effect on chemical shift of 7′ of all methyls six or less bonds distant from the considered one. In polymer spectra these peaks are less resolved. Therefore each of the peaks g to n in polymer spectra accounts for several uncompletely resolved resonances.
(13) The notation of ref 1 and 2 is used in this paper for configurational relationships of methyl carbons.
(14) No chain transfer via β-hydrogen abstraction is expected in these polymerizations due to the experimental conditions (see Experimental Section).
(15) T. Asakura, I. Ando, A. Nishioka, Y. Doi, and T. Keii, *Makromol. Chem.*, **178**, 791 (1977).
(16) G. Natta, P. Pino, E. Mantica, F. Danusso, G. Mazzanti, and M. Peraldo, *Chim. Ind. (Milan)*, **38**, 124 (1956).
(17) G. Mazzanti and P. Longi, *R. Ist. Lomb. Sci. Lett.*, **91**, 755 (1957).
(18) K. Ziegler, Italian Patent 567577 (Feb. 19, 1957).
(19) G. Natta, E. Giachetti, I. Pasquon, and G. Pajaro, *Chim. Ind. (Milan)*, **42**, 1091 (1960).
(20) Unpublished data from our laboratory.

Comment on a Paper by Fong and Peterlin

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Fong and Peterlin[1] have published a paper which contains some new results that they indicate are in contradiction to earlier work by this author.[2] The purpose of this note is to show that there is actually no contradiction, but that both procedures are correct, alternative methods of handling the same problem.

The discussion is concerned with the algebraic methods used to solve the eigenvalue and eigenvector problem of the Rouse–Bueche beads-springs dynamic-chain model with hydrodynamic interaction. The eigenvalue equation is usually written as

$$\mathbf{Q}^{-1}\mathbf{HAQ} = \Lambda \tag{1}$$

where **H** and **A** are two symmetric matrices, defined in the original papers, Λ is the diagonal matrix of the eigenvalues, and the columns of **Q** are the eigenvectors. Although **H** and **A** are symmetric, their product **HA** is not, so that the transformation **Q** is not orthogonal, that is, there are two sets of eigenvectors, the left-hand set, which are the rows of $\mathbf{Q}^{-1}$, and the right-hand set, which are the columns of **Q**. The question then arises as to how to normalize the length of these vectors, and it is here that Fong and Peterlin have made a choice different from the one that the author made earlier.

The author chose to normalize the right-hand eigenvectors so that their length was unity, leaving the length of the left-hand eigenvectors to be determined from the equation

$$\mathbf{Q}^{-1}\mathbf{Q} = \mathbf{I} \tag{2}$$

where **I** is the unit matrix. If we retain the notation **Q** for the matrix so normalized, and denote Fong and Peterlin's transformation matrix by **Q′**, the two are related through a diagonal matrix **B** as follows

$$\mathbf{Q}' = \mathbf{QB} \tag{3}$$

The diagonal element b_i of **B** multiplies the ith column of **Q**, that is, the ith right-hand eigenvector. Since the sum of the squares of the elements of the ith column of **Q** is unity, the corresponding sum of the squares of the ith column of **Q′** is b_i^2; that is, the length of Fong and Peterlin's eigenvectors is b_i.

In any case, we can define a matrix **M** or **M′** as

$$\mathbf{M} = \mathbf{Q}^{\mathrm{T}}\mathbf{AQ} \tag{4a}$$

$$\mathbf{M}' = \mathbf{Q}'^{\mathrm{T}}\mathbf{AQ}' \tag{4b}$$

It has been shown in eq 2 that **M** is diagonal, with elements μ_i. From eq 3 it follows that the diagonal elements, μ_i', of **M′** are

$$\mu_i' = b_i^2\mu_i \tag{5}$$

Fong and Peterlin show that their method leads to $\mu_i' = \lambda_i$ where λ_i is the ith eigenvalue of **HA**. Thus they have effectively chosen their normalization constants so that the lengths of their right-hand eigenvectors are

$$b_i = (\lambda_i/\mu_i)^{1/2} \tag{6}$$

Not recognizing that two different choices of the lengths had been made, Fong and Peterlin believed that their matrix **M′** should be the same as the author's matrix **M**. It clearly is not; hence the apparent contradiction. When we perceive, however, that the normalizations are different, the contradiction disappears.

Fong and Peterlin's procedure leads to formally simpler basic equations, since the matrices **M′** and Λ become identical. To accomplish this, they introduce a symmetric matrix **C**, such that

$$\mathbf{C}^2 = \mathbf{H} \tag{7}$$

Then they transform **HA** to **CAC**, which is symmetric as opposed to **HA**, and with the advantage that it can be efficiently diagonalized by widely available computer