over-end rotation. However, recent measurements of viscoelastic properties of dilute solutions have shown that some of these rodlike macromolecules exhibit additional relaxation processes corresponding to internal modes of motion.[2-4] Wada and collaborators have used an elastic cylinder model to investigate this phenomenon theoretically, and have calculated the fundamental relaxation time for flexure, which has been assumed to correspond to the slowest internal mode of motion. In the present report an analogous method has been used to calculate the relaxation time for the fundamental elongational, or accordion-like, mode.

Consider an elastic cylinder of equilibrium length L, diameter d, and Young's modulus E. A Cartesian coordinate system is placed at the center of the cylinder with the x axis directed along its length. External forces acting in the axial direction result in a deformation $2\Delta L$; each half is stretched ΔL with respect to the origin of the coordinate system. The external forces will be balanced by the internal elastic forces, F_{el}. Assuming $\Delta L \ll L/2$, these forces are given by

$$F_{el} = (\pi d^2/4)E[\Delta L/(L/2)] \quad (1)$$

Upon removal or relaxation of the external forces, the cylinder will return to its rest length, driven by F_{el} and opposed by viscous forces, F_V. The latter, neglecting end effects, will be:

$$F_V = \int_0^{L/2} \zeta V_x(x)\, dx \quad (2)$$

where ζ is the friction coefficient per unit length of cylinder and $V_x(x)$ is the velocity of the cylinder wall as a function of position relative to the origin. Assuming uniform deformation,

$$V_x(x) = [x/(L/2)]\ [d(\Delta L)/dt] \quad (3)$$

Inserting eq 3 into 2 and integrating yields

$$F_V = [\zeta L/4]\ [d(\Delta L)/dt] \quad (4)$$

As the cylinder retracts, $F_{el} + F_V = 0$; combination of eq 1 and 4 followed by integration shows that there is an exponential decay of ΔL with a characteristic relaxation time, τ_L:

$$\tau_L = \zeta L^2/2\pi d^2 E \quad (5)$$

The friction coefficient may be obtained from Broersma's[6] analysis of lengthwise motion of a rigid rod through a medium of viscosity η_s. Neglecting end effects again, the approximate result is:

$$\zeta = 2\pi\eta_s/\ln (L/d) \quad (6)$$

and thus

$$\tau_L = \eta_s L^2/d^2 E \ln (L/d) \quad (7)$$

which is then the relaxation time for the fundamental accordion-like elongational mode.

This result can be compared to the results of previous analyses for rotation[7] and flexure[5] which also neglect end effects. There are, respectively

$$\tau_R = \pi\eta_s L^3/18kT \ln (L/d) \quad (8)$$

$$\tau_F = (5.53 \times 10^{-3})\pi\eta_s L^4/B \ln (L/d) \quad (9)$$

where k is Boltzmann's constant, T is the absolute temperature and B ($=\pi d^4 E/64$) is the flexural rigidity of the cylinder. It is interesting to note the different L dependencies of eq 7–9 and the ratios τ_L/τ_F and τ_L/τ_R

$$\tau_L/\tau_F = 2.8(d/L)^2 \quad (10)$$

$$\tau_L/\tau_R = (9/2)(kT/VE) \quad (11)$$

where V is the cylinder volume.

For typical molecules, (L/d) may be 10 to 100 and hence elongational relaxation will occur on a time scale 2–4 orders of magnitude faster than flexure. This is consistent with flexural mode interpretations of the longest internal relaxation time which have yielded values of B and E for several molecules. For instance, for paramyosin in water at 20 °C, τ_R and τ_F were experimentally determined to be 23 μ and 2.7 μs, respectively. From these results E was calculated to be 1.2×10^{10} dyn/cm^2.[3] From eq 10 or 11, then, τ_L can be estimated to be about 1×10^{-3} μs.

Finally it should be noted that the above analysis, derived to describe macromolecules in solution, is not applicable to the solid state where viscous forces no longer dominate. For such systems other analyses must be applied.[8]

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Carbon-13 Nuclear Magnetic Resonance Analysis of Model Compounds of Saturated End Groups in Polypropylene

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Macromolecular structure is a valuable source of information on the stereochemical polymerization mechanism. Actually, in previous papers, we have been able to contribute to the elucidation of the mechanism of the steric control and the regiospecificity in propylene polymerization by comparing the ^{13}C NMR spectra of polypropylene and of ethylene–propylene copolymers with the spectra of suitable model compounds for methylene and methyl carbons of monomeric units in different sterochemical sequences, as well as in different chemical arrangements.[1-3]

As several other details of the macromolecular structure do, also the end groups can reveal important features of the polymerization mechanism, especially if their sterochemistry is considered. In the next paper[4] it is shown how the sterochemistry of chain initiation and propagation is related to the stereochemical structure of some saturated end groups (isopropyl, 2-butyl, and 2-pentyl) of isotactic, syndiotactic, and atactic polypropylene.

In view of the ^{13}C NMR analysis of the just mentioned saturated end groups, we report in this paper the ^{13}C-NMR spectra of three methyl branched hydrocarbons chosen as reasonable model compounds (see Figure 1): (a) (2*R*,-

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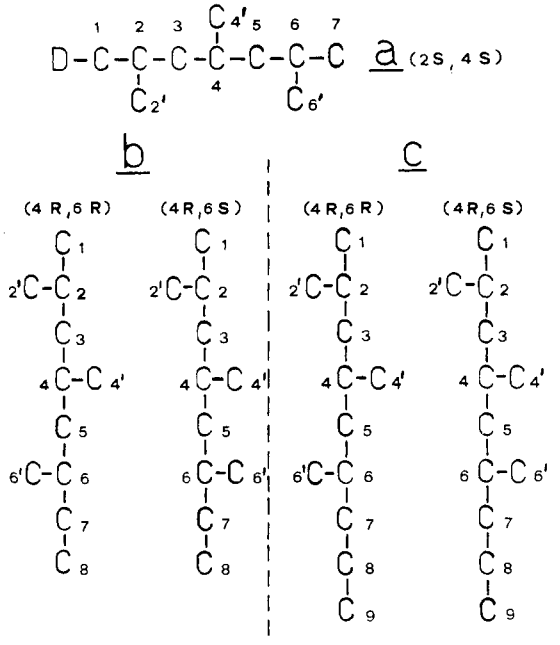

Figure 1. Fisher[9] projections and carbon numbering for the prevailing diastereomer of a[5] and for the diastereomeric forms of b and c. One enantiomer is reported for each diastereomer.

4*R*-2*S*,4*S*)-1-deuterio-2,4,6-trimethylheptane,[5] (b) 2,4,6-trimethyloctane, (c) 2,4,6-trimethylnonane.

The spectrum of 2,4,6-trimethylheptane has been previously reported by Carman and co-workers[6] and consists of six ^{13}C resonances for the pairs of enantiotopic carbons C_1–C_7, C_2–C_6, C_3–C_5, $C_{2'}$–$C_{6'}$ and for C_4 and $C_{4'}$ (see Figure 1 for carbon numbering). As observed by these authors the pair C_1–C_7 and $C_{2'}$–$C_{6'}$ (methyl carbons of isopropyl groups) are diastereotopic and therefore have different chemical shifts. The experimental assignment of the resonances of the diastererotopic carbon pairs C_1–C_7 and $C_{2'}$–$C_{6'}$ is easily achieved by selective deuteration on C_1. In fact (see spectrum of a in Figure 2a) the resonance of C_1 is split for D–^{13}C coupling ($J_{^{13}C\text{-}D}$ = 19.0 Hz) and shifted 0.3_1 ppm upfield (triplet centered at 21.3_4 ppm in Figure 2a) because of the D isotopic effect.[7] The resonances of C_7 and of the pair of enantiotopic carbons $C_{2'}$–$C_{6'}$ of course are unaffected and can be assigned by inspection of the relative intensities, 1:2.[5] It may also be observed that the resonance of C_2 is shifted 0.07 ppm upfield and broadened, as expected[7] for the deuteration on C_1.

The assignment of all the resonances of 2,4,6-trimethylheptane is shown by numbering the peaks in Figure 2a according to the carbon numbering reported in Figure 1 and agrees qualitatively with the rule of Grant and Paul[8] and with the assignment of Carman,[6] making allowance of the different shift scale and of the different conditions of analysis (see Experimental Section).

As observed by Carman and co-workers,[6] the different shifts of the just considered pair of diastereotopic methyl carbons of isopropyl groups arise from the different steric relationships with the $C_{4'}$ methyl group. We suggest that these relationships will be given, accordingly to a previous paper,[3] by: (1) a greek letter (δ in this case) denoting the number of bonds between the diastereotopic methyl carbons of isopropyl groups and $C_{4'}$; (2) either (a) the symbol e (erythro), which means that one given methyl (C_1 or C_7) is on the same side as $C_{4'}$ when drawing the Fisher projection[9] of the hydrocarbon and considering the geminal methyl ($C_{2'}$ or $C_{6'}$) as belonging to the backbone, or (b) the symbol t (threo) which means that one given methyl ($C_{2'}$ or $C_{6'}$) is on the opposite side with respect to $C_{4'}$ when C_1 or C_7 is considered belonging to the backbone. Note that, by convention, according to Figure 1 and consequently in the tables, δe methyl carbons of isopropyl groups are numbered C_1 and C_7 in a, C_1 in b and c; δt methyls are numbered $C_{2'}$ and $C_{6'}$ in a and $C_{2'}$ in b and c.

The spectra of b and c are reported in Figure 2b,c together with the assignments according to the Grant and Paul rule.[8] Both the hydrocarbons are a diasteromeric pair; the resonances of all the diastererotopic and diastereomeric carbons can be assigned by the following: (1) comparison of the chemical shifts according to previous papers,[2,3,6,10] (2) analogy with a (C_1 and $C_{2'}$), and (3) inspection of the intensities.

Actually both b and c are richer in (4*R*,6*R*-4*S*,6*S*) form because decarboxylation of α-branched alkylmalonic acids (intermediates in the synthesis of title hydrocarbons) is partially stereospecific.[11,12]

The chemical shifts of each carbon of a, b, and c are quoted in Table I. The chemical shifts of b and c are reported separately for each diastereomer.

In Tables II and III, the experimental differences between the chemical shifts of the pair of diastereotopic or

Table I
^{13}C Chemical Shifts of a and of the Diastereomeric Forms of b and c (δ ppm Downfield from Internal HMD)[a]

		b		c	
C_i	a	(*R*,*S*-*S*,*R*)	(*R*,*R*-*S*,*S*)	(*R*,*S*-*S*,*R*)	(*R*,*R*-*S*,*S*)
C_1 (δ_e)	21.6_5	21.7_1	21.5_1	21.7_4	21.5_3
C_2	24.1_3	23.9_8	23.9_8	24.0_4	24.0_4
$C_{2'}$ (δ_t)	20.8_3	20.7_4	20.8_6	20.7_1	20.8_7
C_3	46.3_4	45.9_3	46.4_7	46.0_0	46.5_7
C_4	27.2_9	27.0_4	26.9_3	27.1_2	26.9_9
$C_{4'}$	18.6_9	18.9_5	18.4_0	(19.0_5)	(18.4_1)
C_5		43.9_3	43.6_3	44.5_6	44.2_0
C_6		30.5_8	30.5_2	28.7_9	28.7_5
$C_{6'}$		18.1_3	17.5_3	(18.7_1)	(18.0_9)
C_7		27.9_2	28.7_7	38.1_6	38.8_9
C_8		9.1_3	9.2_7	(18.3_3)	(18.4_5)
C_9				12.3_7	12.3_7

[a] Resonances are numbered according to the carbon numbering of Figure 1. The chemical shifts in parentheses may be uncertain because of insufficient resolution. Note that chemical shifts of C_1 and C_2 of a are freed from the D isotopic effect.

Table II
Experimental and Calculated[3] Differences between Chemical Shifts of the Diastereotopic Methyl Carbons (C_1 and $C_{2'}$) of a, b, and c

	$\delta C_1 - \delta C_{2'}$, ppm	
hydrocarbon	exptl	calcd
a	0.8_2	0.5_5
(4*R*,6*S*-4*S*,6*R*)-b	0.9_7	0.8_5
(4*R*,6*R*-4*S*,6*S*)-b	0.6_5	0.5_2
(4*R*,6*S*-4*S*,6*R*)-c	1.0_3	0.8_5
(4*R*,6*R*-4*S*,6*S*)-c	0.6_6	0.5_5

Table III
Experimental and Calculated[3] Differences between Chemical Shifts of the Diastereomeric Methyl Carbons of b and c

	$\delta C_{i(R,S\text{-}S,R)} - \delta C_{i(R,R\text{-}S,S)}$, ppm		
	exptl		calcd
C_i	b	c	b and c
C_1	0.2_0	0.2_1	0.2_0
$C_{2'}$	-0.1_2	-0.1_6	-0.1_3
$C_{4'}$	0.5_5	0.6_3	0.5_5
$C_{6'}$	0.6_0	0.6_2	0.5_5

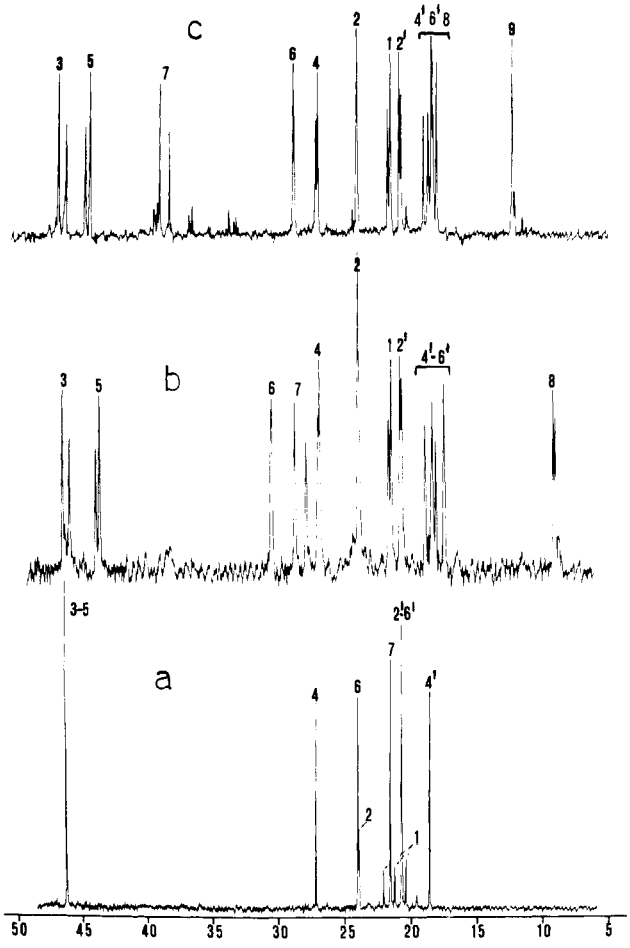

Figure 2. ^{13}C NMR spectra of a, (2*R*,4*R*-2*S*,4*S*)-1 deuterio-2,4,6-trimethylheptane, b, 2,4,6-trimethyloctane, and, c, 2,4,6-trimethylnonane. Labeling of the resonances is according to carbon numbering of Figure 1. By convention C_1 is always the e methyl and C_2 the t one.

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 ($\delta_{C_{7e}} - \delta_{C_{7t}} = 0.5_5$ 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]

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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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