Tacticity-Dependent ^{13}C NMR Chemical Shifts for Poly(vinyl alcohol) Models Studied by ab initio Gauge-Included Atomic Orbital Calculations

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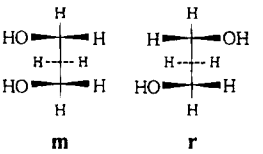
ABSTRACT: Large differences in the experimental ^{13}C NMR chemical shifts for three resonance peaks assigned to the methine carbons in solid poly(vinyl alcohol) (PVA) are attributed not to the intramolecular hydrogen-bond effect but to the conformation effect due to tacticity on the basis of ab initio GIAO calculations for model compounds: 1,3-propanediol, 1,3,5-pentanetriol, pentane, and 4-methylheptane. The experimental chemical-shift differences of the methine carbons are well reproduced by the calculated shifts for not only the triad models of 1,3,5-pentanetriol but also those of 4-methylheptane. The strong intramolecular hydrogen bonds in the m tacticity maintain the *all-anti* conformation of the main chain of PVA. Both the inter- and intramolecular hydrogen-bond effects on ^{13}C chemical shifts are found to be small for carbons connected to hydroxyl groups forming a hydrogen-bond system, where the hydroxyl oxygens can serve as either donor or acceptor in the hydrogen bonding.

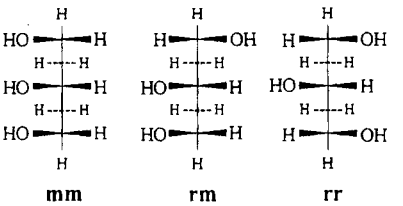
Introduction

^{13}C CPMAS NMR spectra for solid poly(vinyl alcohol) (PVA) are interestingly characterized by resonance lines assigned to the methine carbons bonded to the hydroxyl group, which consist of three rather broad peaks with a large separation of ca. 6 ppm each, named as peak 1, peak 2, and peak 3 in order of increasing shielding, accompanying a decrease of intensity for peak 1 and an increase for peak 3 compared to the intensities for the apparently corresponding three peaks observed in solutions.[1-3] Since the conformation of the main chain in the crystalline part of PVA is planar zigzag or *all-anti* regardless of its tacticity,[4] the relative arrangements of the hydroxyl groups are nearly fixed according to the tacticity. From their NMR measurements for PVA samples with different tacticities Terao et al.[1] proposed that the large separation of the methine resonance peaks can be attributed to the fixation of the intramolecular hydrogen bonds in solids: the deshielding shifts are well correlated with the possible numbers of the strong intramolecular hydrogen bonds (0, 1, and 2 for the rr, rm, and mm triads, respectively). On the other hand, applying the substituent-induced shifts by Duddeck[5] to the triads of PVA, Ketels et al.[2] claimed that the separations can be explained with the conformation effect due to tacticity and without an explicit consideration of the hydrogen-bond effect.

In order to elucidate the hydrogen bonding and conformation effects on the ^{13}C NMR chemical shifts for the methine carbons in solid PVA, we investigated the ^{13}C chemical shifts for 1,3-propanediol (**1**) and 1,3,5-pentanetriol (**2**) as diad and triad models, respectively, of PVA, and those for pentane (**3**) and 4-methylheptane (**4**) as diad and triad models, respectively, of polypropylene assuming the *all-anti* main-chain conformation (hereafter we call the diad and triad models simply as the diad and triad, respectively)[6] by ab initio GIAO (gauge-included atomic orbital) calculations.[7] It is noted that the present calculated chemical shifts are obtained as the shielding constants in ppm; therefore, positively large values correspond to upfield or shielding shifts, opposite to the conventional definition for the experimental chemical shifts.[8]



1,3-propanediol (**1**)



1,3,5-pentanetriol (**2**)

Experimental Section

NMR Measurements. The ^{13}C chemical shifts of methanol, ethanol, and 1- and 2-propanols in $CDCl_3$ solutions (1 kg/mol) at room temperature were measured on a Varian Gemini 200 spectrometer operating at 200 MHz. Chemical shifts were referenced to $CDCl_3$ (76.85 ppm from Me_4Si) as a secondary standard.

Calculations. Geometries of all the molecular structures in this work were fully optimized by ab initio closed-shell restricted Hartree−Fock (RHF) calculations with the 4-31G basis set. The ^{13}C chemical shifts were calculated by the analytical second derivative method[9] of RHF energies with respect to the external magnetic field and the nuclear magnetic moment. The basis function we employed is the 4-31G GIAO function which is actually the 4-31G function multiplied by a phase factor which originates from the gauge invariance of one-electron eigenstates with respect to the choice of gauge of the external magnetic field. On comparison with experimental values, fractional populations were taken into account with the assumption of the Boltzmann distribution at 298 K on the basis of the calculated RHF energies and the geometrical multiplicities of the conformers.

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Table 1. Calculated and Experimental ^{13}C NMR Chemical Shifts for Methanol, Ethanol, and 1- and 2-Propanols[a]

		C1	C2	C3
methanol	calcd	160.69		
	exptl	50.07		
ethanol	calcd	154.27	189.64	
	exptl	57.72	17.91	
1-propanol	calcd	148.86	184.13	196.06
	exptl	64.09	25.51	9.86
2-propanol	calcd	183.41	148.95	183.41
	exptl	24.97	63.87	24.97

[a] In units of ppm. Experimental values are relative to Me_4Si.

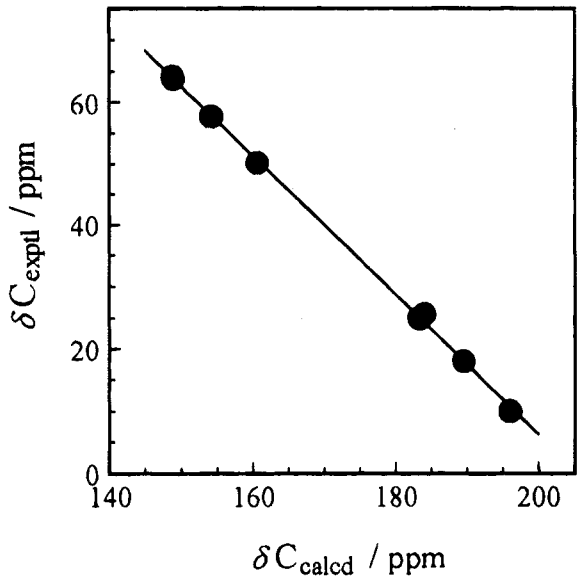

Figure 1. Correlation between the experimental ^{13}C chemical shifts (δC_{exptl}) measured in $CDCl_3$ solutions and the conformationally averaged calculated ones ($\overline{\delta C}_{calcd}$) for methanol, ethanol, and 1- and 2-propanols. The least-squares fitted line is solid.

All the molecular orbital calculations were performed with the ab initio calculation program KOTO[10] on a Hewlett Packard Apollo 9000 Model 715.

Results and Discussion

A. Correlation between Calculated and Experimental ^{13}C Chemical Shifts. In order to estimate the accuracy of the present calculations, we first calculated the ^{13}C chemical shifts for four simple alcohols, methanol, ethanol, and 1- and 2-propanols, which have one, two, five, and two conformers, respectively, due to the rotational isomerism of the hydroxyl groups. On the assumption of the Boltzmann distribution for the conformation equilibrium average, ^{13}C chemical shifts at 298 K were evaluated as listed in Table 1. The experimental chemical shifts measured in $CDCl_3$ solutions at room temperature are also listed in Table 1 and are plotted against the conformationally averaged calculated chemical shifts as shown in Figure 1. The correlation coefficient between them is 0.9996, supporting the adequacy of the present calculations, though the slope of the least-squares fitted line is −1.13, indicating the calculated shifts are systematically smaller than the experimental ones.

B. ^{13}C Chemical Shifts for Methanol Dimer. We examined the intermolecular hydrogen-bond effect on the ^{13}C chemical shift employing a methanol dimer as a model system. Its optimized structure calculated with the present basis set is illustrated in Figure 2, where

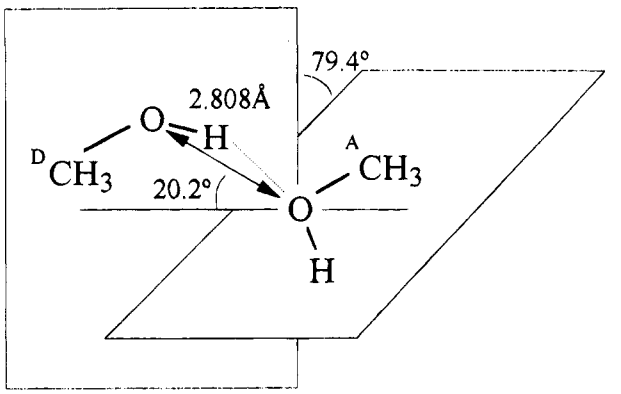

Figure 2. Optimized geometry for the methanol dimer. The OH bond length is 0.959 Å, the O···H distance is 1.851 Å, and the OH···O angle is 176.3°. Carbons marked with D and A stand for those C_D and C_A bonded to the donor- and acceptor-type oxygens, respectively.

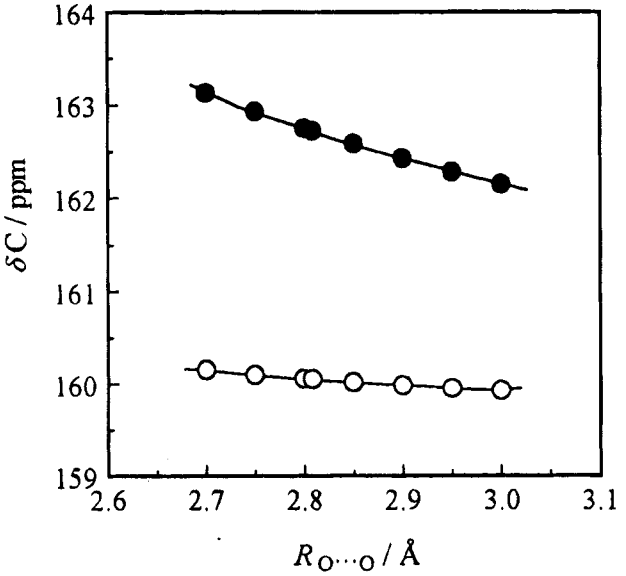

Figure 3. Variation of the ^{13}C chemical shifts (δC) of C_D (closed circles) and C_A (open circles) in the methanol dimer against the O···O dimer ($R_{O\cdots O}$). Solid curves are drawn as a guide for the eye.

the hydrogen-bond distance between the oxygens ($R_{O\cdots O}$) is 2.808 Å, within the region of *the best value* (2.788–2.888 Å) by Jorgensen.[11] As indicated in Figure 2, we denote the carbon bonded to the donor (acceptor)-type oxygen in the hydrogen bond as C_D (C_A). In order to estimate variation of their ^{13}C chemical shifts against $R_{O\cdots O}$, we optimized the dimer structures with fixed $R_{O\cdots O}$ values. The calculated ^{13}C chemical shifts for C_D and C_A are plotted against $R_{O\cdots O}$ in Figure 3. Comparing them with the ^{13}C chemical shift (160.69 ppm) for the isolated methanol, one finds upfield shifts for C_D and downfield ones for C_A in the region of $R_{O\cdots O}$ = 2.7–3.0 Å. Their chemical shift difference (ca. 2.5 ppm) depends slightly on $R_{O\cdots O}$, though the range of the variation is at most 1 ppm, yielding 161.32 ± 0.20 ppm as the average shift for C_D and C_A, which is close to the chemical shift for the isolated methanol. We therefore consider that the intermolecular hydrogen-bond effect on the ^{13}C chemical shift must be small for the case where C_D and C_A exchange rapidly with each other due to proton transfer, molecular rotation, or other processes.

C. 1,3-Propanediol (1) and 1,3,5-Pentanetriol (2). Although we assume the *all-anti* conformation[12] for the

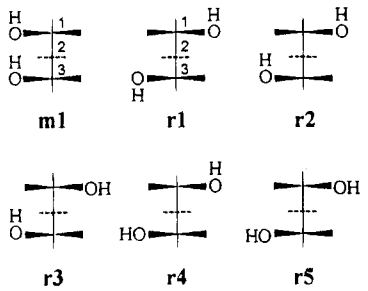

Figure 4. Conformers for the m and r diads of 1,3-propanediol (**1**). Substituents not drawn are hydrogen atoms.

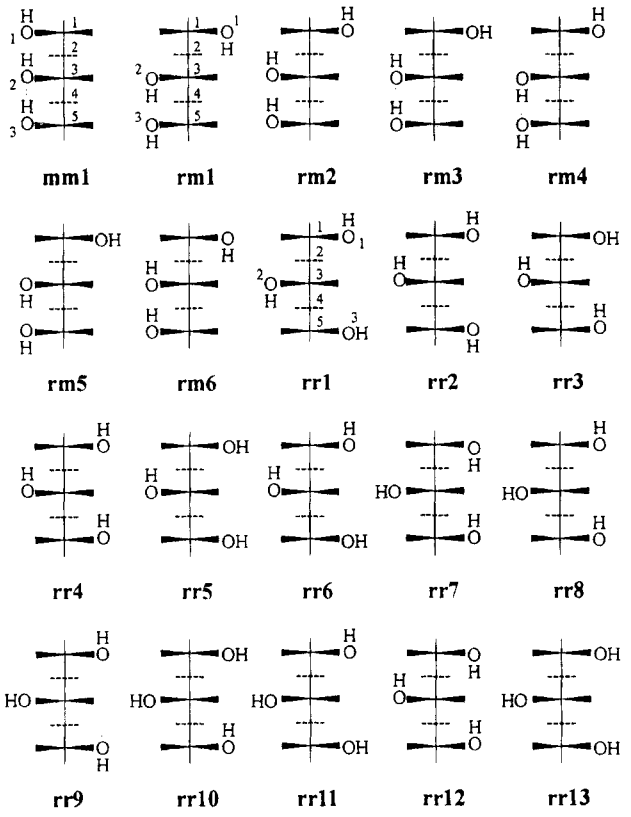

Figure 5. Conformers for the mm, rm, and rr triads of 1,3,5-pentanetriol (**2**). Substituents not drawn are hydrogen atoms.

Table 2. Calculated O···O Distances ($R_{O\cdots O}$), Relative Total Energies (ΔE), Multiplicities of Conformations (m), and Fractional Populations (p) for Conformers of the m and r Diads of 1,3-Propanediol (1)

conformer	$R_{O1\cdots O2}$/Å	ΔE/kcal·mol^{-1} [a]	m	p
m1	2.749	0.0	1	1.0
r1	3.579	1.79	1	0.27
r2	2.979	2.01	2	0.36
r3	2.960	2.21	2	0.26
r4	3.629	2.74	2	0.11
r5	3.694	4.17	1	0.00

[a] Relative to the total energy for m1.

main chain of PVA, there are still many conformers for the conformation of the hydroxyl groups. For **1** and **2** we take into account only conformers with relatively low energies illustrated in Figures 4 and 5, respectively. The calculated values for $R_{O\cdots O}$, relative total energies (ΔE), and populations (p) for the conformers of the m and r diads of **1** and the mm, rm, and rr triads of **2** are collected in Tables 2 and 3, respectively. There is one stable conformer (m1) for the m diad of **1**, which has a strong intramolecular hydrogen bond with $R_{O\cdots O}$ = 2.749 Å. In the five conformers (r1−r5) for the r diad of **1**, r2 and r3 contain weak hydrogen bonds with $R_{O\cdots O}$ = 2.97 ± 0.01 Å, but no hydrogen bonds are found for r1, r4, and r5, since their $R_{O\cdots O}$ values are 3.63 ± 0.05 Å. It is of much interest that the most stable conformer in the r diad is one of the non-hydrogen-bonded ones. The average total energy for the r diad obtained on the assumption of the Boltzmann distribution for the conformation equilibrium among r1−r5 is 2.09 kcal·mol^{-1} higher than the total energy for the m diad (m1). This indicates that the strong intramolecular hydrogen bond contributes to the stabilization of the m1 conformer.

Table 3. Calculated O···O Distances ($R_{O\cdots O}$), Relative Total Energies (ΔE), Multiplicities of Conformations (m), and Fractional Populations (p) for Conformers of the mm, rm, and rr Triads of 1,3,5-Pentanetriol (2)

conformer	$R_{O1\cdots O2}$/Å	$R_{O2\cdots O3}$/Å	ΔE/kcal·mol^{-1} [a]	m	p
mm1	2.697	2.707	0.0	1	1.0
rm1	2.867	2.713	2.00	1	0.63
rm2	2.834	2.744	2.83	1	0.15
rm3	2.835	2.743	3.08	1	0.11
rm4	3.571	2.730	3.09	1	0.10
rm5	3.650	2.727	4.44	1	0.01
rm6	3.801	2.741	7.28	1	0.00
rr1	3.619	2.923	5.09	2	0.38
rr2	2.906	3.627	5.46	2	0.20
rr3	2.862	3.065	5.61	2	0.16
rr4	2.844	3.088	5.73	2	0.13
rr5	2.925	3.677	6.29	2	0.05
rr6	2.975	3.647	6.34	2	0.05
rr7	3.013	3.013	6.84	1	0.01
rr8	3.645	2.948	6.85	2	0.02
rr9	3.625	3.625	7.97	1	0.00
rr10	3.677	2.979	8.13	2	0.00
rr11	3.656	3.660	8.93	2	0.00
rr12	3.872	2.943	9.33	2	0.00
rr13	3.685	3.685	10.64	1	0.00

[a] Relative to the total energy for mm1.

Table 4. Calculated ^{13}C NMR Chemical Shifts for Conformers of the m and r Diads of 1,3-Propanediol (1)[a]

conformer	C1	C2	C3
m1	147.01	178.58	150.52
r1	154.08	177.13	154.08
r2	153.44	178.87	154.45
r3	152.93	178.46	154.61
r4	154.49	175.30	153.36
r5	153.76	173.34	153.76

[a] In units of ppm.

The calculated ^{13}C chemical shifts for all the conformers of the m and r diads of **1** are listed in Table 4. The chemical shifts of the methine carbons in r1−r5 are found to be nearly constant (153.90 ± 0.52 ppm), showing that the hydrogen-bond effect on the ^{13}C chemical shifts in the weak hydrogen-bond system should be as small as that in the non-hydrogen-bond one. These methine carbons can thus be designated as C_N. For m1, containing the strong intramolecular hydrogen bond, not only the chemical shift for the C1 [C_A] carbon (147.01 ppm) but also that for the C3 [C_D] carbon (150.52 ppm) move largely downfield compared to those for C_N's. This contrasts with the above result that only C_A is deshielded in the methanol dimer, though C_A is more deshielded than C_D as in the methanol dimer.

There are 1, 6, and 13 stable conformers for the mm, rm, and rr triads of **2**, respectively (Figure 5). As listed in Table 3, the intramolecular hydrogen bonds can clearly be classified into three types: the strong hydrogen bond with $R_{O\cdots O}$ = 2.73 ± 0.02 Å, the weak hydrogen bond with $R_{O\cdots O}$ = 2.94 ± 0.08 Å, and no hydrogen bond with $R_{O\cdots O}$ = 3.67 ± 0.07 Å. The

Table 5. Calculated ^{13}C NMR Chemical Shifts for Conformers of the mm, rm, and rr Triads of 1,3,5-Pentanetriol (2)[a]

conformer	C1	C2	C3	C4	C5
mm1	147.58	173.67	138.48	172.14	151.25
rm1	153.93	172.12	144.64	174.03	147.53
rm2	152.76	173.22	141.94	172.96	151.01
rm3	152.37	172.72	141.84	172.85	151.01
rm4	153.12	170.17	146.08	173.33	147.41
rm5	152.43	167.88	146.13	173.18	147.64
rm6	154.19	170.23	141.13	172.23	151.17
rr1	152.91	171.67	149.41	172.75	152.13
rr2	152.40	173.10	149.17	171.43	152.87
rr3	152.29	173.01	148.87	172.16	153.51
rr4	152.65	173.24	148.96	172.01	153.34
rr5	152.22	172.55	149.52	169.60	152.33
rr6	152.72	172.84	149.54	169.64	152.41
rr7	154.32	172.99	146.13	172.99	154.32
rr8	153.99	170.43	146.72	173.06	154.11
rr9	153.66	169.81	147.54	169.81	153.66
rr10	153.47	168.67	147.43	172.66	154.14
rr11	153.60	169.49	147.99	168.01	153.19
rr12	154.17	171.15	148.36	172.09	153.78
rr13	153.17	167.53	148.30	167.53	153.17

[a] In units of ppm.

Table 6. Mean Values for ^{13}C Chemical Shifts ($\overline{\delta C}$) of the Terminal (C1 and C3) Methine Carbons in 1,3-Propanediol (1) and Those of the Terminal (C1 and C5) Methine Carbons and Those of the Central (C3) Methine Carbon in 1,3,5-Pentanetriol (2)[a]

	C_N	C_D	C_A	C_{DA}
1				
$\overline{\delta C}$(terminal)	153.93 ± 0.52	150.52	147.01	
2				
$\overline{\delta C}$(terminal)	153.23 ± 0.70	151.11 ± 0.11	147.54 ± 0.08	
$\overline{\delta C}$(central)	148.30 ± 1.05	145.61 ± 0.69	141.64 ± 0.36	138.48

[a] In units of ppm. Errors are standard deviations.

average total energies for the rm and rr triads obtained on the assumption of the Boltzmann distribution for the conformation equilibrium among rm1–rm6 and that among rr1–rr13 are higher than the total energy for the mm triad (mm1) by 2.37 and 5.51 kcal·mol^{-1} for the rm and rr triads, respectively. The stability of the triads depends obviously on the number of strong intramolecular hydrogen bonds.

The calculated ^{13}C chemical shifts for all the triads of **2** are listed in Table 5. Those of the methine carbons can also be classified according to the hydrogen-bond types as employed for **1**[13] except for the C3 methine carbon in mm1, which is designated as C_{DA}, because it is connected to the O2 oxygen which is simultaneously hydrogen-bonded to the O1 and O3 oxygens with the donor and acceptor types, respectively. Simple mean values ($\overline{\delta C}$) for the ^{13}C chemical shifts of the terminal (C1 and C5) methine carbons and those of the central (C3) methine carbon in **2** together with those of the terminal (C1 and C3) methine carbons in **1** are collected in Table 6. The order of the deshielding shifts for **2**, $C_A > C_D > C_N$, agrees with that for **1**, and C_{DA} is deshielded by nearly the sum of the amounts of the deshielding shifts for C_A and C_D relative to the chemical shift for C_N. The small standard deviations for the $\overline{\delta C}$ values of C_N's in **2** also support the small effect on the ^{13}C chemical shifts due to the weak intramolecular hydrogen bonds. From the result that the $\overline{\delta C}$ values for the terminal methine carbons in **2** are similar to the corresponding values for **1**, the chemical shifts of the central methine carbons in **2** can be regarded as those for the methine carbons in PVA. The populationally averaged chemical shifts for the central methine carbons in **2** are evaluated to be 144.09 and 149.14 ppm for the rm and rr triads, respectively, where those for C_D and C_A in the rm triad are also averaged. Since the chemical shift for the central carbon in the mm triad (C_{DA}) is 138.48 ppm, it is deshielded by 10.66 ppm from the central carbon in the rr triad (C_N), and that in the rm triad is 5.05 ppm deshielded from the latter. By multiplication of the proportionality constant of 1.13 for the experimental shifts against the calculated shifts determined in section A, the deshielding shifts for the mm and rm triads amount to 12.0 and 5.7 ppm, respectively, which are very close to the observed shifts of 12 and 6 ppm for peak 1 and peak 2 relative to peak 3, respectively.

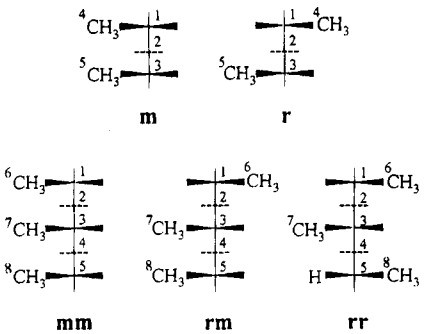

Figure 6. Conformers for the m and r diads of pentane (**3**) and those for the mm, rm, and rr triads of 4-methylheptane (**4**). Substituents not drawn are hydrogen atoms.

Table 7. Calculated C–C–C–C Dihedral Angles (ω), Relative Total Energies (ΔE), Multiplicities of Conformations (m), and Fractional Populations (p) for Conformers of the rr, rm, and mm Triads of 4-Methylheptane (4)

	rr1	rm1	rm2	mm1	mm2	mm3
$\omega_{C6-C1-C2-C3}$/deg	61.5	61.6	61.6	−102.8	−100.0	−64.3
$\omega_{C1-C2-C3-C7}$/deg	61.3	61.2	57.9	61.1	59.2	96.2
$\omega_{C7-C3-C4-C5}$/deg	−61.3	−61.2	−97.1	−61.1	−98.4	−96.2
$\omega_{C3-C4-C5-C8}$/deg	−61.5	102.1	64.3	102.8	64.5	64.3
ΔE/kcal·mol^{-1} [a]	0.0	1.98	2.17	3.95	4.21	5.27
m	1	1	1	1	2	1
p	1.0	0.58	0.42	0.41	0.54	0.04

[a] Relative to the total energy for rr1.

D. Pentane (3) and 4-Methylheptane (4). The m and r diads of **3** and the rr, rm, and mm triads of **4** in the *all-anti* main-chain conformation are illustrated in Figure 6. Owing to the absence of the rotational isomerism for the methyl group, individually unique conformers exist for the m and r diads of **3** and the rr triad of **4**. There are, however, two and three conformers for the rm and mm triads, respectively, of **4** because of the existence of the difference between absolute values for the successive two dihedral angles with opposite signs[14] in the $CH_3–CH–CH_2–CH–CH_3$ sequence with the m tacticity: the calculated C4–C1–C2–C3 and C1–C2–C3–C5 dihedral angles for the m diad of **3** are 63.7° and −95.8°, respectively, whereas those for the r diad are 62.5°. The calculated values for the C–C–C–C dihedral angles (ω), relative total energies (ΔE), and populations (p) for the conformers of the rr, rm, and mm triads of **4** are collected in Table 7. As for the stability of the conformers, m1 is 2.04 kcal·mol^{-1} higher than r1, and on the basis of the populationally averaged total energies for the triads of **4**, the rm and mm triads are more stable by 2.06 and 4.15 kcal·mol^{-1}, respectively, than the rr triad. The

Table 8. Calculated ^{13}C NMR Chemical Shifts for Conformers of the r and m Diads of Pentane (3)

carbon	r1	m1
C1	191.17	183.82
C2	180.38	180.37
C3	191.17	187.04
C4	180.38	193.45
C5	180.38	190.65

[a] In units of ppm.

Table 9. Calculated ^{13}C NMR Chemical Shifts for Conformers of the rr, rm, and mm Triads of 4-Methylheptane (4)[a]

carbon	rr1	rm1	rm2	rr1	rr2	rr3
C1	190.23	190.46	190.21	187.94	187.58	184.85
C2	172.37	172.65	171.02	172.92	171.24	168.38
C3	185.63	178.86	181.07	172.16	174.37	175.78
C4	172.37	172.62	172.25	172.92	172.28	168.38
C5	190.23	187.74	185.34	187.94	185.32	184.85
C6	194.71	194.75	195.00	190.50	190.74	193.55
C7	192.50	191.54	187.53	190.54	186.19	182.20
C8	194.71	190.52	193.52	190.50	193.61	193.55

[a] In units of ppm.

origin of these stability sequences for **3** and **4**, which are just the reverse orders to the corresponding sequences for **1** and **2**, respectively, can reasonably be attributed to the steric repulsion between the methyl groups in **3** and **4**. This repulsion is particularly remarkable for the m tacticity, so that the conformation of the main chain deviates somewhat from *all-anti*: for example, the C1−C2−C3−C4 and C2−C3−C4−C5 dihedral angles for mm1−mm3 are −173.6° and 173.6°, −176.1° and 136.5°, and −139.5° and 139.5°, respectively, contrasting with the result that the corresponding dihedral angles for mm1 of **2** are −169.5° and −174.0°, respectively.

Table 8 collects the calculated ^{13}C chemical shifts for the m and r diads of **3** and Table 9 those for all the conformers of the mm, rm, and rr triads of **4**. In order to estimate the conformation effect on the ^{13}C chemical shifts in the triads of **4**, those of the central (C3) methine carbons in the rm and mm triads are individually averaged by considering the populations of their conformers. The populationally averaged chemical shifts of the central methine carbons in the rm and mm triads are thus 179.79 and 173.51 ppm, respectively, and are 5.84 and 12.12 ppm, respectively, deshielded from the ^{13}C chemical shift of the central carbon in the rr triad. Surprisingly, these deshielding shifts are close to or rather larger than the corresponding shifts obtained for the triads of **2**. We thus conclude that the conformation effect due to tacticity is the more important factor for the ^{13}C chemical shifts of the methine carbons in PVA and that the strong intramolecular hydrogen bonds in the m tacticity maintain the *all-anti* conformation of the main chain of PVA, because the main-chain conformations are not planar zigzag but helical for the crystalline parts of not only isotactic but also syndiotactic polypropylenes.[15]

Including the results for the methanol dimer, we can state that both the inter- and intramolecular hydrogen-bond effects on ^{13}C chemical shifts are small for carbons connected to hydroxyl groups forming a hydrogen-bond system, where the hydroxyl oxygens interconvert being the donor and the acceptor in the hydrogen bonding.

References and Notes

(1) Terao, T.; Maeda, S.; Saika, A. *Macromolecules* **1983**, *16*, 1535−1538.
(2) Ketels, H.; de Haan, J.; Aerdts, A.; van der Velden, G. *Polymer* **1990**, *31*, 1419−1424.
(3) Horii, F.; Hu, S.; Ito, T.; Odani, H.; Matsuzawa, S.; Yamamura, K. *Polymer* **1992**, *33*, 2299−2306.
(4) Murahashi, S.; Yûki, H.; Sano, T.; Yonemura, U.; Tadokoro, H.; Chatani, Y. *J. Polym. Sci.* **1962**, *62*, S77−81. Fujii, K.; Mochizuki, T.; Imoto, S.; Ukida, J.; Matsumoto, M. *Makromol. Chem.* **1962**, *51*, 225−228.
(5) Duddeck, H.; Wolff, D. *Org. Magn. Reson.* **1977**, *9*, 528−532. Duddeck, H. *Tetrahedron* **1978**, *34*, 247−251 and references cited therein.
(6) Although there is no stereoisomerism for **1**−**4** themselves, in the present work we apply the diad- and triad-type stereoisomerism to classification of conformers of **1** and **3** and **2** and **4**, respectively, because we consider only conformers of **1** and **2** and **3** and **4**, which can be regarded as the corresponding components of PVA and polypropylene, respectively.
(7) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789−807. McMichael, C.; Rohlfing, C.; Allen, L. C.; Ditchfield, R. *Chem. Phys.* **1984**, *87*, 9−15. Chesnut, D. B.; Phung, C. G. *J. Chem. Phys.* **1989**, *91*, 6238−6245.
(8) Imashiro, F.; Masuda, Y.; Honda, M.; Obara, S. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1535−1541.
(9) For reviews, see: Fukui, H. *Magn. Reson. Rev.* **1987**, *11*, 205−274. Jameson, C. J. *Nuclear Magnetic Resonance*; Special Publication of the Royal Society of Chemistry: London, 1987; No. 16.
(10) Obara, S.; Honda, M.; Nakano, H.; Sakano, F.; Takada, S.; Miyake, Y.; Sato, K.; Nakajima, T. Library Program 202 Y4/KOTO91 at the Data Processing Center of Kyoto University, 1991.
(11) Jorgensen, W. L. *J. Chem. Phys.* **1979**, *71*, 5034−5038.
(12) Since all the geometries for the compounds calculated in this work were optimized, the *all-anti* conformation is not identical with the planar zigzag conformation.
(13) C_D or C_A is preferred to C_N to call the C2 methine carbon in the rm triad.
(14) Tsuzuki, S.; Schäfer, L.; Gotō, H.; Eluvathingal, D. J.; Hosoya, H.; Siam, K.; Tanabe, K.; Ōsawa, E. *J. Am. Chem. Soc.* **1991**, *113*, 4665−4671.
(15) Turner-Jones, A.; Aizlewood, J. M.; Beckett, D. R. *Makromol. Chem.* **1964**, *75*, 134−158. Corradini, P.; Natta, G.; Ganis, P.; Temussi, P. A. *J. Polym. Sci.* **1967**, *C16*, 2477−2484. Bunn, A.; Cudby, M. E. A.; Harris, R. K.; Packer, J. K.; Say, B. J. *J. Chem. Soc., Chem. Commun.* **1981**, 15−16; *Polymer* **1982**, *23*, 694−698.

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