2334 *Macromolecules* **1991,** *24,* 2334-2340

Carbon-13 NMR Spectral Assignment of Five Polyolefins Determined from the Chemical Shift Calculation and the Polymerization Mechanism

Tetsuo Asakura,* Makoto Demura, and Yûkô Nishiyama

Department of Polymer Engineering, Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan

Received September 26, 1990; Revised Manuscript Received November 29, 1990

ABSTRACT: Assignments of the ^{13}C NMR spectra of five polyolefins, poly(1-pentene), poly(1-hexene), poly(1-heptene), poly(1-octene), and poly(1-nonene), to tacticity were performed from the ^{13}C NMR chemical shift calculation on the basis of the ^{13}C NMR γ effect and application of the rotational isomeric state model. The origin of the complex spectral behavior of the methylene backbone carbon, C1, among a series of polyolefins including polypropylene and poly(1-butene) was also successfully interpreted through the chemical shift calculation. The mechanisms of olefin polymerization were analyzed from the values of pentad tacticities obtained from the C3 carbon peak of the side chain on the basis of the bicatalytic sites model. The relative area of hexad peaks calculated with the three parameters optimized in the bicatalytic sites model was also used in the assignment of the C1 carbon peak.

Introduction

^{13}C NMR is the most powerful method for the study of the microstructure of polyolefins.[1,2] However, the assignment of the ^{13}C NMR peaks to the tacticity of polyolefins is a difficult task. For the case of polypropylene, PP, which is a very important polymer commercially, the successful approach to the assignment was the well-planned synthesis of accurate model compounds and of polymers of known structure and modified or ^{13}C labeled ones.[1] However, this approach is very time consuming and is not generally used.

The tacticity assignment of PP reported experimentally has been well reproduced by the ^{13}C chemical shift calculation on the basis of the γ effect with the rotational isomeric state, RIS, model.[3-7] The γ effect is recognized in ^{13}C NMR studies of paraffinic hydrocarbons as an upfield shift of ca. −5 ppm accompanying gauche arrangement of carbon atoms separated by three bonds (γ substituents) relative to their trans arrangements. The actual magnitude of the γ effect will depend on the probability of this bond conformation. For the case of PP and corresponding model compounds, a "bond rotation probability" can be calculated using the Suter–Flory RIS model.[8]

On the other hand, in the case of poly(1-butene), PB, only a brief and incomplete tacticity assignment had been reported experimentally[9] prior to the calculation of the theoretical chemical shift.[5] Thus, the assignment of PB is a good example for judging the potential of such a theoretical approach to assignment. Through the calculation, we showed how the dramatic change in the observed ^{13}C NMR spectra of the backbone methylene carbons between PP and PB could be well interpreted.[5] The observed spread of the backbone methylene chemical shift of PP exceeds 2 ppm, while that of PB is only 0.2 ppm. On the basis of the chemical shift calculation, the methylene peaks of PP can be interpreted in terms of the hexad tacticity of the main chain. In the case of PB, if only the chemical shift contribution of the γ shielding effect from the carbons of the backbone chain to the specified methylene carbon was taken into account, then the peak spread of the hexad level splitting is also still large (2 ppm). However, in contrast to the case of PP, there is an additional γ effect between the methylene backbone and methyl side-chain carbons. The additional contribution from the side-chain methyl carbon to the ^{13}C chemical shift of the methylene carbons of the backbone chain can be estimated. The most striking aspect is the compensation of the γ-effect contribution to the specified methylene carbon from the backbone methine carbons and the side-chain methyl carbons. As a result, the sum of these two contributions reflects the remarkable decrease of the chemical shifts due to the tacticity of the chain, which coincides with the observed spectra. For other carbons of PB such as backbone methine and side-chain methylene and methyl carbons, successful assignments could also be made on the basis of the theoretical chemical shift calculation. This success has demonstrated the usefulness of such calculations.

Table I
Observed ^{13}C NMR Chemical Shifts of Isotactic Polyolefins (in ppm from Internal TMS)[a]

carbon	PP	PB	PPE	PHEX	PHEP	PO	PN
C1	46.37	40.13	41.30	40.91	40.85	40.85	40.85
C2	28.30	34.93	33.33	33.09	33.06	33.04	33.05
C3	21.76	27.69	38.01	34.91	35.06	35.30	35.31
C4		10.79	19.94	28.86	26.22	26.59	26.68
C5			14.69	23.20	32.47	29.91	30.28
C6				13.86	22.58	31.91	29.35
C7					13.81	22.57	31.90
C8						13.79	22.53
C9							13.79

[a] Only the chemical shifts of the main isotactic peak were listed. Detailed chemical shift data of the tacticity peaks were listed later (Table III for C3 and Table V for C1).

In this paper, we will report the tacticity assignment of ^{13}C NMR spectra of a series of polyolefins with longer linear side chains than PB: poly(1-pentene) (PPE), poly(1-hexene) (PHEX), poly(1-heptene) (PHEP), poly(1-octene) (PO), and poly(1-nonene) (PN), which are performed from the ^{13}C NMR chemical shift calculation on the basis of the ^{13}C NMR γ effect and application of the RIS model. The mechanisms of olefin polymerization will be analyzed from the values of pentad tacticities obtained from the C3 carbon of the side chain on the basis of the bicatalytic sites model, where polymerization at one site proceeds according to the Bernoullian model of selection between meso and racemo configurations and at the other site according to selection between dextro and laevo.[10,11] The relative areas of hexad peaks calculated with the three

0024-9297/91/2224-2334$02.50/0

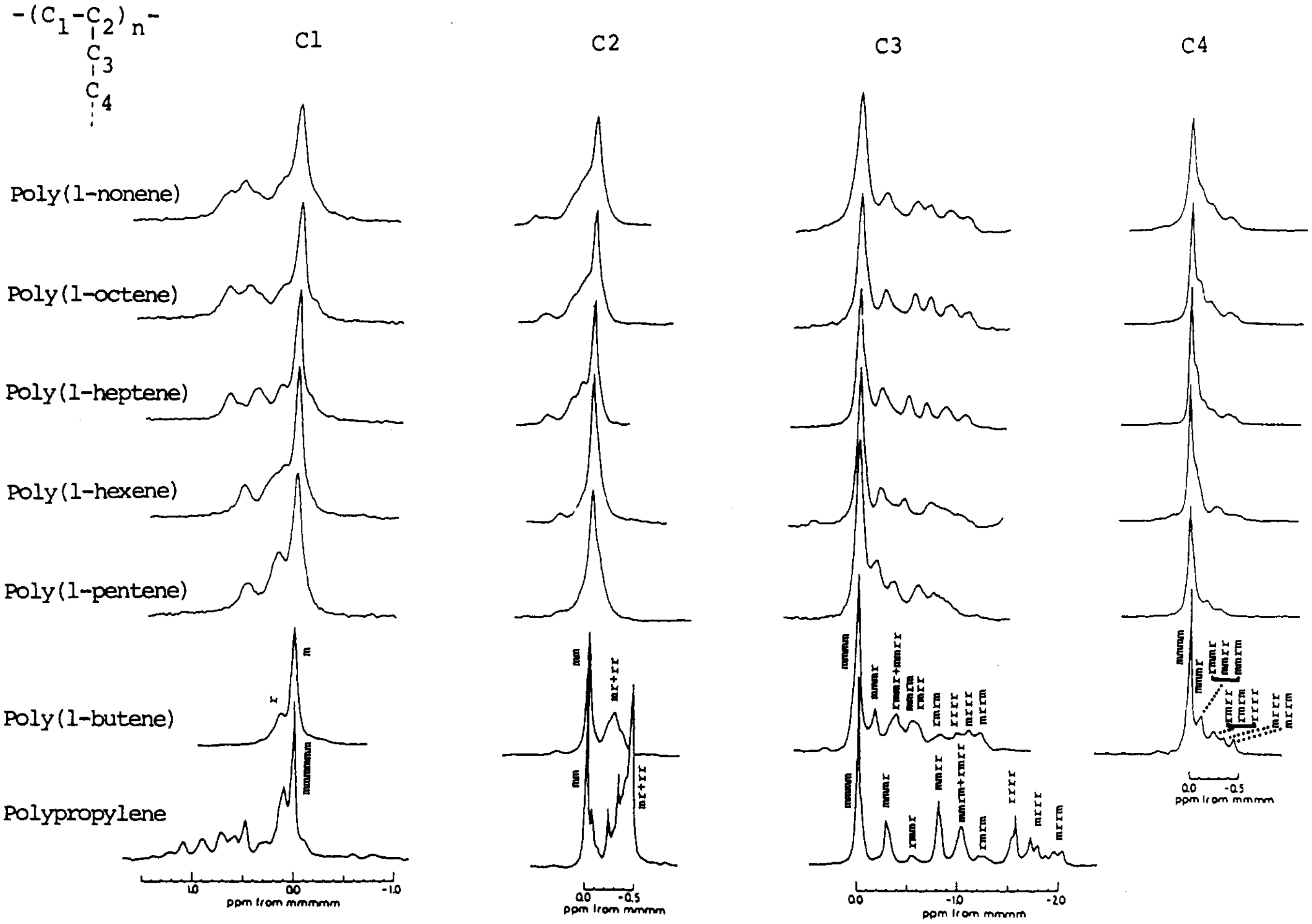


Figure 1. ^{13}C NMR spectra of the C1, C2, C3, and C4 carbons of seven kinds of polyolefins, where the peaks are shown relative to the isotactic ones. For polypropylene and poly(1-butene), the ^{13}C NMR tacticity assignments of all carbons have been reported in detail previously.[3-7,11]

parameters optimized in the bicatalytic sites model will be used in the assignment of the methylene backbone carbons. Since no detailed tacticity assignments have been reported for these polyolefins with a longer side chain than PB, to assign their tacticity is the first trial.

Experimental Section

Materials. All samples used here were kindly supplied by Prof. Y. Doi at the Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Tokyo. PPE and PN samples were polymerized with the Zeigler–Natta catalytic system $TiCl_3$–$MgCl_2$–SiO_2–$AlEt_2$. PHEX, PHEP, and PO samples were polymerized with a similar catalytic system $Ti(OBu)_4$–$MgCl_2$–$AlEt_2Cl$. The polymerization temperature of all samples was 65 °C.

NMR Measurement. ^{13}C NMR spectra were measured at 100 °C with a JEOL FX-200 spectrometer at 50.1 MHz. Polymer solutions were prepared at a concentration of 10 w/v % in an *o*-dichlorobenzene–deuteriobenzene (9:1 (v/v)) mixture. Tetramethylsilane, TMS, was added as an internal chemical shift reference. Each spectrum was recorded with a 2000-Hz spectral width, 8K data points, 3–5-s delay between pulses, and 10 000 scans in the double-precision mode.

Calculation. The method of ^{13}C NMR chemical shift calculation on the basis of γ effect and the RIS model is essentially the same as those reported previously for PB.[5] Only the value of the statistical weight, τ^*, the additional repulsive interaction between the side chain and backbone when both adjacent backbone bonds were trans, was changed because the bulkiness of the side chain of five polyolefins from PPE to PN is larger compared with that of PB.[12]

Spectral simulation assuming a Lorentzian was done iteratively by using peak positions, peak height, trough positions, and trough height.[13]

In the application of the bicatalytic sites model to the polymerization mechanism of polyolefins, the pentad relative intensities were calculated iteratively to the observed intensities of the C3 carbons until the mean-square deviation became a minimum with a simplex algorithm.[11]

Results and Discussion

^{13}C NMR Spectra of Polyolefins. On the basis of the Lindeman–Adams empirical rule concerning aliphatic ^{13}C chemical shift,[14] main peaks of polyolefins were assigned to each carbon as listed in Table I together with the previous data for PP and PB.[5] Since the tacticities of these samples are isotactic rich, the main peaks are assigned to isotactic peaks. Figure 1 summarizes all of the C1, C2, C3, and C4 peaks of seven kinds of polyolefins where the peaks are shown relative to the isotactic ones. For PP and PB, the ^{13}C NMR tacticity assignments of all carbons have been reported in detail previously,[3-7,11] and thus only brief assignments are shown here. For the case of the C1 peak of PP, the peak has been already assigned in the hexad level.[3,4] However, because of the limited space, the assignment is not written here. For the peaks C1–C4, small peaks are observed around each main peak, indicating the tacticity of the chain. Segre et al.[15] reported that the atactic peak was observed at lower field in the C1 resonance region and at higher field in the C3 resonance region of the ^{13}C NMR spectra of poly(octadecylethylene), a polyolefin with a long alkyl side chain. This tendency is found in the five polyolefins used here and also in atactic polyolefins.[16] It is noticed that the line shapes of the C3 or C4 carbons are similar among PPE, PHEX, PHEP, PO, and PN, while the width of the tac-

Table II
^{13}C NMR Chemical Shifts of the C3 and C4 Carbons of Polyolefins Calculated on the Basis of the ^{13}C NMR γ-Shielding Effect and the RIS Model ($\tau^* = 0.5$, in ppm Relative to the Chemical Shift of mmmmmm)[a]

	C3		C4	
	heptad	pentad	heptad	pentad
m(mmmm)m	0.000	0.000	0.000	0.000
m(mmmm)r	0.000		0.000	
r(mmmm)r	−0.116		−0.033	
m(mmmr)m	−0.135	−0.192	−0.035	−0.042
m(mmmr)r	−0.135		−0.035	
r(mmmr)m	−0.248		−0.070	
r(mmmr)r	−0.250		−0.073	
m(rmmr)m	−0.382	−0.348	−0.116	−0.094
m(rmmr)r	−0.382		−0.116	
r(rmmr)r	−0.280		−0.082	
m(mmrr)m	−0.328	−0.383	−0.084	−0.094
m(mmrr)r	−0.328		−0.084	
r(mmrr)m	−0.443		−0.130	
r(mmrr)r	−0.431		−0.121	
m(mmrm)m	−0.438	−0.469	−0.115	−0.118
m(mmrm)r	−0.438		−0.115	
r(mmrm)m	−0.546		−0.156	
r(mmrm)r	−0.455		−0.128	
m(rmrr)m	−0.576	−0.545	−0.183	−0.159
m(rmrr)r	−0.566		−0.177	
r(rmrr)m	−0.472		−0.142	
r(rmrr)r	−0.566		−0.177	
m(rmrm)m	−0.684	−0.660	−0.219	−0.200
m(rmrm)r	−0.689		−0.225	
r(rmrm)m	−0.684		−0.219	
r(rmrm)r	−0.584		−0.179	
m(rrrr)m	−0.671	−0.733	−0.219	−0.234
m(rrrr)r	−0.763		−0.258	
r(rrrr)r	−0.763		−0.258	
m(mrrr)m	−0.887	−0.860	−0.311	−0.290
m(mrrr)r	−0.882		−0.311	
r(mrrr)m	−0.789		−0.269	
r(mrrr)r	−0.882		−0.311	
m(mrrm)m	−1.011	−0.943	−0.372	−0.329
m(mrrm)r	−0.909		−0.324	
r(mrrm)r	−0.909		−0.324	

[a] The pentad chemical shifts were obtained by averaging over the heptad ones.

Table III
Observed Chemical Shifts of C3 Carbons of Isotactic Polyolefins (in ppm Relative to the Chemical Shift of mmmm)

pentad	PPE	PHEX	PHEP	PO	PN
mmmm	0.00	0.00	0.00	0.00	0.00
mmmr	−0.18	−0.21	−0.22	−0.24	−0.25
rmmr	−0.18	−0.21	−0.22	−0.24	−0.25
mmrr	−0.18	−0.21	−0.22	−0.24	−0.25
mmrm	−0.35	−0.46	−0.50	−0.54	−0.55
rmrr	−0.35	−0.46	−0.50	−0.54	−0.55
mrmr	−0.59	−0.72	−0.67	−0.69	−0.69
rrrr	−0.59	−0.72	−0.86	−0.89	−0.88
mrrr	−0.8	−0.9	−0.87	−0.89	−0.88
mrrm	−0.9	-1.0	-1.06	-1.06	-1.04

ticity distribution becomes slightly narrower than that of PB. This implies that it is possible to assign these peaks to the tacticity of five polyolefins on the basis of the chemical shift calculation applied to the tacticity assignment of PB previously.[11]

On the other hand, in the region of the C2 carbons, smaller peaks other than the most intensive isotactic peak shift to lower field relative to the isotactic peak with an increase in the length of the side chain. By taking into account the C2 assignments of PP and PB,[5,15] the relative peak intensity, and the gradual low-field shift of this small peak among a series of seven kinds of polyolefins from PP to PN, the main and small peaks are assigned to mm and mr + rr, respectively.

Table IV
Relative Peak Intensities of the C3 Carbons of Isotactic Polyolefins[a]

pentad	PB	PPE	PHEX	PHEP	PO	PN
mmmm	0.583	0.510	0.480	0.479	0.436	0.538
mmmr	0.079	0.155	0.188	0.189	0.168	0.160
rmmr	0.007					
mmrr	0.078					
mmrm	0.036	0.109	0.094	0.105	0.117	0.101
rmrr	0.042					
mrmr	0.032	0.121	0.119	0.071	0.092	0.073
rrrr	0.055			0.103	0.111	0.085
mrrr	0.045	0.062	0.079			
mrrm	0.043	0.043	0.040	0.053	0.076	0.043
β	0.039	0.025	0.055	0.031	0.008	0.012
σ	0.453	0.389	0.313	0.465	0.480	0.495
ω	0.705	0.572	0.640	0.541	0.429	0.546

[a] The three parameters, $\beta = \alpha(1 - \alpha)$, σ, and ω, of the bicatalytic sites model were determined from the observed pentad intensities.

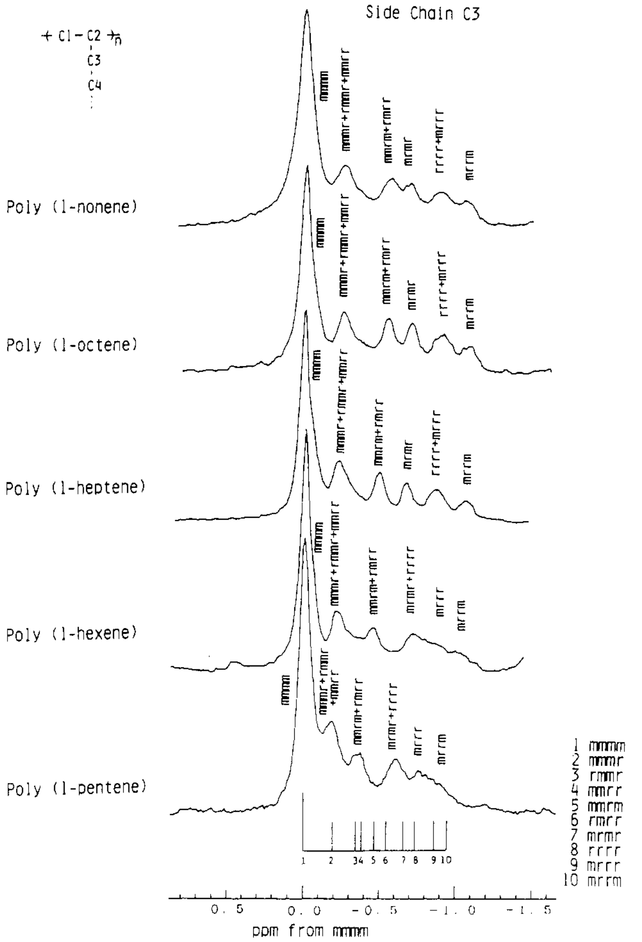


Figure 2. Pentad assignments of the C3 carbons of five polyolefins. The assignments were performed by taking into account the calculated chemical shift and the relative intensities of mm and mr + rr triads evaluated from the C2 peaks of the main chain. The stick spectrum represents the calculated pentad data given in Table II.

However, the tendency of the shift of the C1 peak is very complex. The dramatic change between PP and PB has been interpreted well on the basis of the chemical shift calculation.[5] However, in the case of five polyolefins from PPE to PN, some new peaks appear and the width of the tacticity distribution becomes larger with an increase in the length of the side chain. We will try to assign these peaks in a latter section.

Tacticity Assignment of C3 and C4 Carbon Peaks. In order to assign the C3 peaks to the tacticities of five

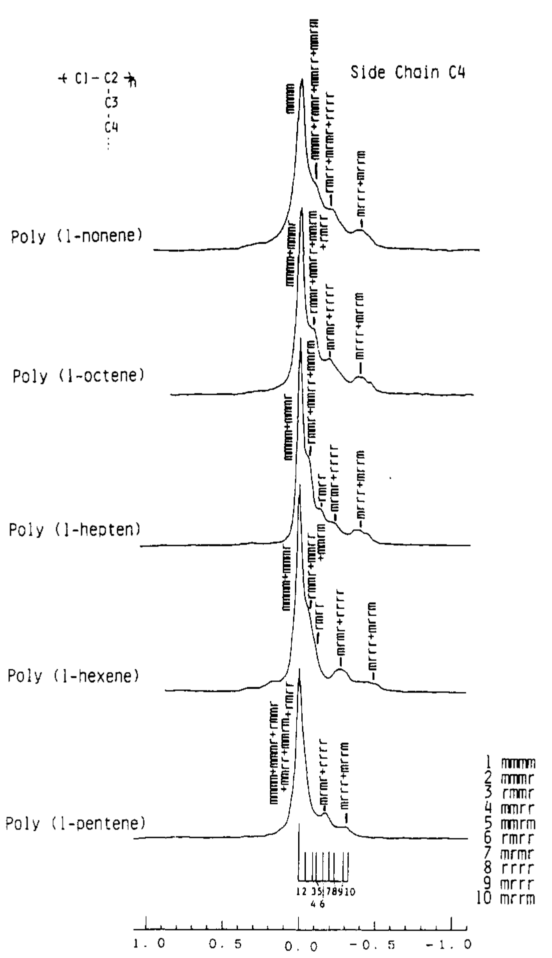


Figure 3. Tacticity assignment of the C4 carbons. The pentad assignments were performed on the basis of the chemical shift calculation (Table II) and the relative pentad intensities calculated with the parameters of the bicatalytic sites model determined from the C3 peak.

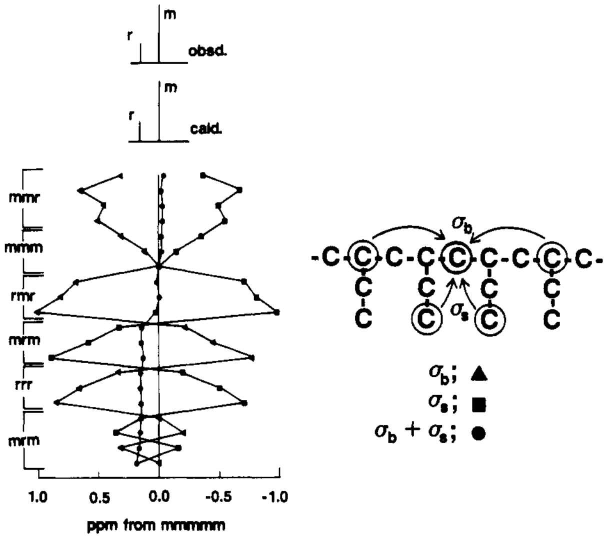


Figure 4. Calculated hexad chemical shifts for the C1 carbon of PB relative to mmmmm.[5] The observed and calculated chemical shifts were shown as stick spectra.

polyolefins, the ^{13}C NMR chemical shifts were calculated at the heptad level. For a comparison of the calculated data with the observed ones, the pentad chemical shifts were calculated again from the heptad ones. A similar chemical shift calculation was performed for the C4 carbon. The calculated chemical shifts were summarized in Table II. The value of 0.5 was used for τ^* in the RIS matrix, which was slightly smaller than $\tau^* = 0.6$ for PB[5] in the calculation of the bond probability of the chain. When we adapted $\tau^* = 0.5$, the width of the tacticity distribution became slightly narrower than that of PB. This is in agreement with the observed tendency of the C3 peaks. By taking into account the calculated chemical shift and the relative intensities of mm and mr + rr triads evaluated from the C2 peaks of the main chain, the pentad assignments were performed for the C3 peaks of five polyolefins as summarized in Figure 2 and Table III (observed chemical shift data). The stick spectrum that appears in the bottom of Figure 2 represents the calculated pentad data given in Table II. Thus, the order of the pentad C3 chemical shifts of five polyolefins from PPE to PN is essentially the same as those reported for PP and PB,[5] although some peaks are overlapped.

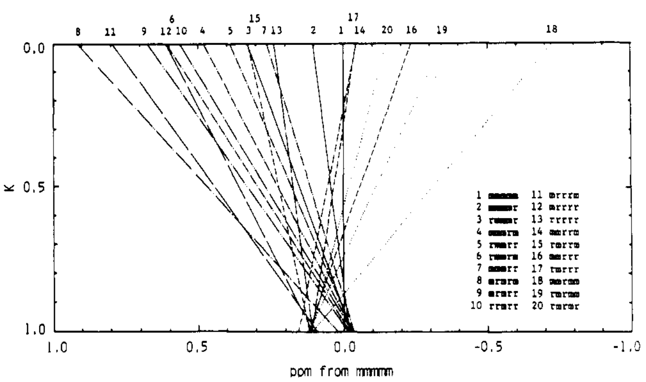
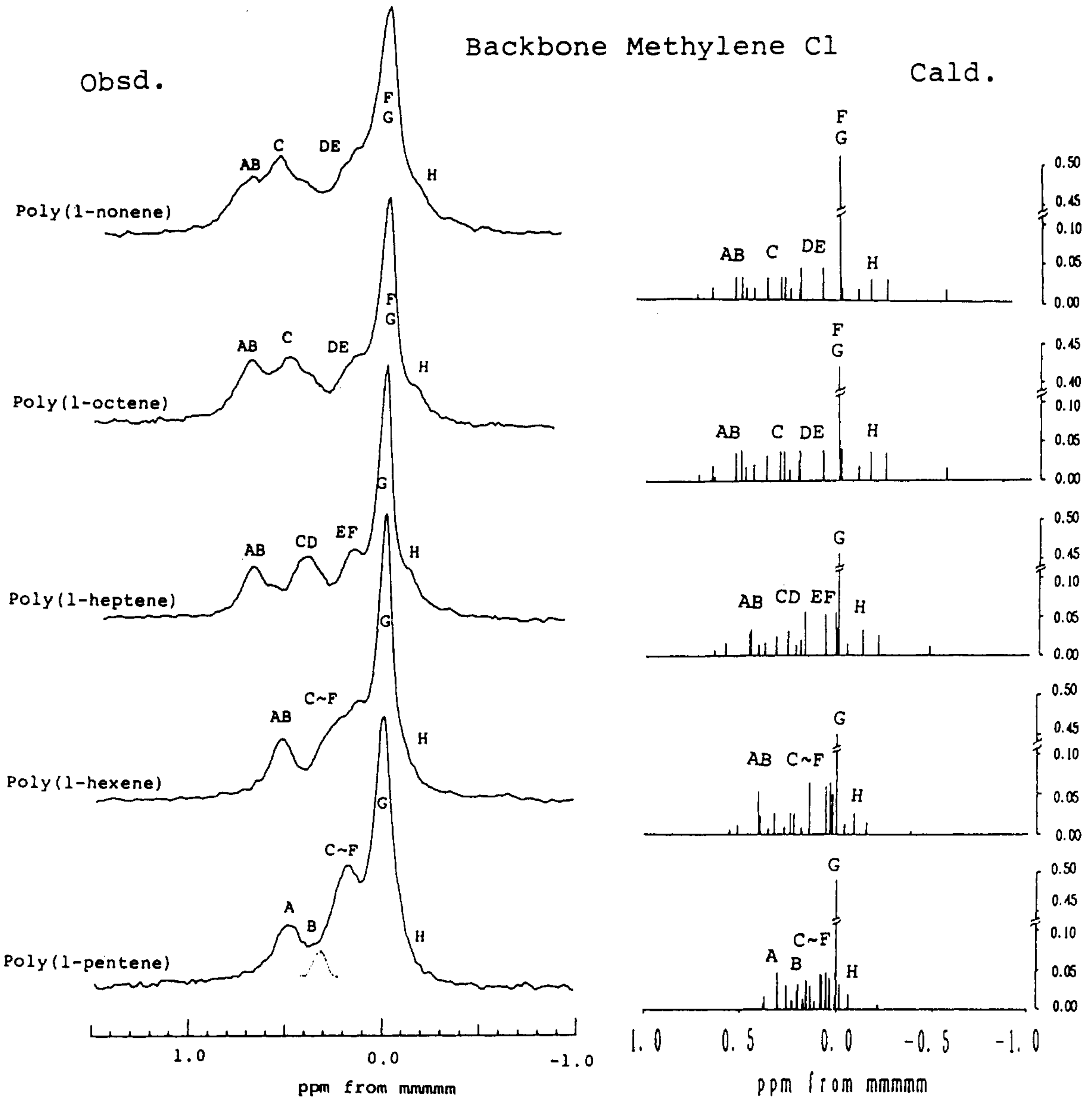


Figure 5. Change of calculated chemical shift, σ_{cal}, as a function of K, where $\sigma_{cal} = \sigma_b + K\sigma_s$. Numbers, 1–20, indicate the heptad tacticity.

By spectral simulation assuming Lorentzian, the intensities of the pentad peaks are determined and summarized in Table IV. Three parameters, β, σ, and ω, of the bicatalytic sites model, which has been successfully used to analyze the PP and PB polymerization mechanism,[11] were determined and also listed in Table IV. For a comparison, the values of β, σ, and ω of PB reported previously[11] are also included. Thus, the tacticity of the chain and also the polymerization mechanism are similar among these polyolefins including PB reported previously.[17]

The tacticity assignment of the C4 peak was performed on the basis of the chemical shift calculation (Table II) and the relative pentad intensities calculated with the parameters of the bicatalytic sites model determined from the C3 peak. The results are summarized in Figure 3.

Tacticity Assignment of C1 Carbon Peak. As shown in Figure 1, the spectral behavior of the C1 carbon among a series of polyolefins, PP to PN, is very complex. In order to assign the C1 peaks from PPE to PN by reference to the previous assignment for PB,[5] the calculated data for the C1 carbon of PB are shown in Figure 4. As mentioned in the Introduction, a compensation of the γ-effect contribution to the C1 carbons from the backbone methine carbons (σ_b) and the side-chain methyl carbon (σ_s) occurs. As a result, only two peaks, m and r are observed in the ^{13}C NMR spectrum of PB. Even if 0.5 was adapted as the values of τ^* instead of 0.6 (PB), the tendency of the predicted peak for the C1 carbon is essentially the same as the case of $\tau^* = 0.6$. However, as is easily speculated from Figure 4, the appearance of more than two peaks is expected if the compensation between σ_b and σ_s is incomplete. Therefore, we calculated the chemical shift (σ_{cal}) again as a function of K, where $\sigma_{cal} = \sigma_b + K\sigma_s$, as summarized in Figure 5. It is noted that the observed



A;mrmrm,mrrrm,mrrrr,mrmrr,rmmrm

B;rrmrr

C;mmmrm,rmmrr,rmrrm,rmmmr

D;rrrrr,mmmrr

E;mmmmr

F;rmrrr,mmrrm

G;mmmmm

H;rmrmr,mmrrr,rmrmm, mmrmm

Figure 6. Observed and calculated stick spectra of the C1 carbons of polyolefins on the basis of the calculated chemical shift and peak intensities. In the chemical shift calculation, the value of *K* was used as 0.6 (PPE), 0.4 (PHEX), 0.3 (PHEP), and 0.2 (PO or PN). Relative pentad intensities were calculated with the parameters of the two-catalytic sites model determined from the C3 peak.

data can be interpreted if the value of *K* is assumed to be smaller with an increase in the length of the side chain of polyolefins. However, it is difficult to assign the C1 peaks in detail from only these chemical shift data. In order to add the peak intensity data to the chemical shift values, we calculated the relative peak intensities in the hexad level using the three parameters of bicatalytic sites model determined above (Table IV). The calculated stick spectrum of the C1 carbon of PPE is shown in Figure 6 (right) on the basis of the calculated chemical shift and peak intensities, where 0.6 is adapted as the value of *K*. Similar calculations are performed for the other four polyolefins, PPE, PHEP, PO, and PN, and the stick spectra are also shown in Figure 6 (right). In the chemical shift calculation, the value of *K* decreases gradually as 0.4 (PHEX), 0.3 (PHEP), and 0.2 (PO or PN) from PHEX to PN. The changes in the observed spectra among these polyolefins as shown in Figure 6 (left) are well interpreted by these stick spectra. Because the observed peaks are broad, the assignment was performed as the peak area, A, B, ..., H. Especially, the low-field shifts of the peaks A–C and the high-field shift of the peak H relative to the isotactic peak (G) observed are reproduced very well. Details of the observed and calculated results are summarized in Table V. At present, it is difficult to tell the physical meaning of *K* exactly, but it is likely that the value contains useful information about the side-chain conformation of a series of polyolefins.

The tacticity chemical shifts of the C1 carbons of PB and PPE were also calculated by using the five-state RIS models proposed by Wittwer and Suter,[18] which assume mutually independent side groups for these polymers. This model eliminates the need for the constant *K*. However, the agreement between the calculated and observed chemical shifts for this more complete RIS modeling was poor compared with the above results. Therefore, at this

Table V
Tacticity Assignments and Peak Intensities of C1 Carbons of Polyolefins

poly-olefin	peak position (Figure 6)	obsd chem shift, in ppm from mmmmm	obsd rel peak intens	calcd chem shift in ppm from mmmmm ($K = 0.6$)		calcd rel peak intens[a]	poly-olefin	peak position (Figure 6)	obsd chem shift, in ppm from mmmmm	obsd rel peak intens	calcd chem shift, in ppm from mmmmm ($K = 0.6$)		calcd rel peak intens[a]
PPE	A	0.50	0.105	mrmrm	0.378	0.006	PPE	D			rrrrr	0.158	0.037
				mrrm	0.375	0.015					mmmrr	0.084	0.045
				mrrrr	0.307	0.047		E			mmmmr	0.034	0.038
				mrmrr	0.260	0.030		F			rmrrr	0.052	0.047
				rmmrm	0.230	0.012					mmrrm	0.075	0.045
	B	0.32	0.010	rrmrr	0.208	0.024		G	0.00	0.610	mmmmm	0.000	0.491
	C	0.18	0.197	mmmrm	0.173	0.013		H	−0.24	0.078	rmrmr	0.012	0.015
				rmmrr	0.137	0.030					mmrrr	−0.019	0.030
				rmrrm	0.202	0.030					rmrmm	−0.063	0.020
				rmmmr	0.117	0.010					mmrmm	−0.218	0.006

poly-olefin	peak position (Figure 6)	obsd chem shift, in ppm from mmmmm	obsd rel peak intens	calcd chem shift, in ppm from mmmmm ($K = 0.4$)		calcd rel peak intens[b]	poly-olefin	peak position (Figure 6)	obsd chem shift, in ppm from mmmmm	obsd rel peak intens	calcd chem shift, in ppm from mmmmm ($K = 0.4$)		calcd rel peak intens[b]
PHEX	A	0.53	0.1701	mrmrm	0.556	0.005	PHEX	D			rrrrr	0.185	0.055
				mrrrm	0.515	0.012					mmmrr	0.144	0.065
				mrrrr	0.408	0.053		E			mmmmr	0.059	0.060
				mrmrr	0.398	0.023		F			rmrrr	0.021	0.051
				rmmrm	0.356	0.008					mmrrm	0.036	0.065
	B			rrmrr	0.325	0.027		G	0.00	0.4849	mmmmm	0.000	0.449
	C	0.24	0.2475	mmmrm	0.275	0.008		H	−0.14	0.0975	rmrmr	−0.042	0.012
				rmmrr	0.222	0.026					mmrrr	−0.091	0.026
				rmrrm	0.244	0.026					rmrmm	−0.155	0.014
				rmmmr	0.188	0.007					mmrmm	−0.386	0.003

poly-olefin	peak position (Figure 6)	obsd chem shift, in ppm from mmmmm	obsd rel peak intens	calcd chem shift, in ppm from mmmmm ($K = 0.3$)		calcd rel peak intens[c]	poly-olefin	peak position (Figure 6)	obsd chem shift, in ppm from mmmmm	obsd rel peak intens	calcd chem shift, in ppm from mmmmm ($K = 0.3$)		calcd rel peak intens[c]
PHEP	A	0.68	0.147	mrmrm	−0.645	0.008	PHEP	D			rrrrr	0.198	0.020
				mrrrm	0.585	0.015					mmmrr	0.174	0.056
				mrrrr	0.459	0.036		E	0.17	0.104	mmmmr	0.071	0.052
				mrmrr	0.467	0.030		F			rmrrr	0.006	0.035
				rmmrm	0.418	0.014					mmrrm	0.017	0.056
	B			rrmrr	0.384	0.018		G	0.00	0.511	mmmmm	0.000	0.456
	C	0.40	0.191	mmmrm	0.327	0.024		H	−0.14	0.047	rmrmr	−0.068	0.015
				rmmr	0.264	0.031					mmrrr	−0.126	0.031
				rmrrm	0.265	0.031					rmrmm	−0.202	0.027
				rmmmr	0.223	0.014					mmrmm	−0.469	0.012

poly-olefin	peak position (Figure 6)	obsd chem shift, in ppm from mmmmm	obsd rel peak intens	calcd chem shift, in ppm from mmmmm ($K = 0.2$)		calcd rel peak intens[d]	poly-olefin	peak position (Figure 6)	obsd chem shift, in ppm from mmmmm	obsd rel peak intens	calcd chem shift, in ppm from mmmmm ($K = 0.2$)		calcd rel peak intens[d]
PO	A	0.70	0.194	mrmrm	0.735	0.009	PO	D	0.17	0.210	rrrrr	0.211	0.022
				mrrrm	0.654	0.019					mmmrr	0.203	0.041
				mrrrr	0.509	0.040		E			mmmmr	0.083	0.038
				mrmrr	0.537	0.037		F			rmrrr	−0.010	0.040
				rmmrm	0.481	0.018					mmrrm	−0.003	0.041
	B			rrmrr	0.443	0.020		G	0.00	0.440	mmmmm	0.000	0.423
	C	0.50	0.137	mmmrm	0.378	0.032		H	−0.16	0.019	rmrmr	−0.095	0.019
				rmmrr	0.306	0.037					mmrrr	−0.162	0.037
				rmrrm	0.285	0.037					rmrmm	−0.248	0.034
				rmmmr	0.258	0.017					mmrmm	−0.553	0.106

poly-olefin	peak position (Figure 6)	obsd chem shift, in ppm from mmmmm	obsd rel peak intens	calcd chem shift, in ppm from mmmmm ($K = 0.2$)		calcd rel peak intens[d]	poly-olefin	peak position (Figure 6)	obsd chem shift, in ppm from mmmmm	obsd rel peak intens	calcd chem shift, in ppm from mmmmm ($K = 0.2$)		calcd rel peak intens[d]
PN	A	0.70	0.184	mrmrm	0.735	0.007	PN	D	0.18	0.231	rrrrr	0.211	0.015
				mrrrm	0.654	0.014					mmmrr	0.203	0.041
				mrrrr	0.509	0.029		E			mmmmr	0.083	0.040
				mrmrr	0.537	0.029		F			rmrrr	−0.010	0.029
				rmmrm	0.481	0.014					mmrmm	−0.003	0.041
	B			rrmrr	0.443	0.015		G	0.00	0.446	mmmmm	0.000	0.521
	C	0.56	0.128	mmmrm	0.378	0.028		H	−0.16	0.011	rmrmr	−0.095	0.014
				rmmrr	0.306	0.029					mmrrr	−0.162	0.029
				rmrrm	0.285	0.029					rmrmm	−0.248	0.028
				rmmmr	0.258	0.014					mmrmm	−0.553	0.014

[a] Relative intensities of the hexad peaks of PPE were calculated. Resonances represent the one calculated based on $\beta = 0.025$, $\sigma = 0.389$, and $\omega = 0.572$.
[b] Relative intensities of the hexad peaks of PHEX were calculated. Resonances represent the one calculated based on $\beta = 0.055$, $\sigma = 0.313$, and $\omega = 0.640$.
[c] Relative intensities of the hexad peaks of PHEP were calculated. Resonances represent the one calculated based on $\beta = 0.031$, $\sigma = 0.465$, and $\omega = 0.541$.
[d] Relative intensities of the hexad peaks of PO were calculated. Resonances represent the one calculated based on $\beta = 0.008$, $\sigma = 0.480$, and $\omega = 0.529$.
[e] Relative intensities of the hexad peaks of PN were calculated. Resonances represent the one calculated based on $\beta = 0.012$, $\sigma = 0.495$, and $\omega = 0.546$.

stage, it is still necessary to include such a constant as K.

In conclusion, we could newly assign a series of polyolefins, PPE, PHEX, PHEP, PO, and PN, on the basis of ^{13}C NMR chemical shift calculations. This emphasizes the potential of such a theoretical approach to spectral assignments of polyolefins.

Acknowledgment. We are greatly indebted to Professor Y. Doi at the Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Tokyo, for the gift of polyolefin samples and discussion.

References and Notes

(1) Bovey, F. A.; Jelinski, L. W. *Chain Structure and Conformation of Macromolecules*; Academic Press: New York, 1982.
(2) Ando, I.; Yamanobe, T.; Asakura, T. *Progress in NMR Spectroscopy*; McGraw Hill: London, 1990; in press.
(3) Schilling, F. C.; Tonelli, A. E. *Macromolecules* **1980**, *13*, 270.
(4) Zambelli, A.; Locatelli, P.; Provasoli, A.; Ferro, D. R. *Macromolecules* **1980**, *13*, 267.
(5) Asakura, T.; Omaki, K.; Zhu, S.-N.; Chûjô, R. *Polym. J.* (*Tokyo*) **1984**, *16*, 895.
(6) Asakura, T.; Nishiyama, Y.; Doi, Y. *Macromolecules* **1987**, *20*, 616.
(7) Hayashi, T.; Inoue, Y.; Chûjô, R.; Asakura, T. *Polymer* **1988**, *29*, 138.
(8) Suter, U. W.; Flory, P. J. *Macromolecules* **1975**, *8*, 765.
(9) Mauzac, M.; Vairon, J. P.; Sigwalt, P. *Polymer* **1977**, *18*, 1193.
(10) Chûjô, R. *Kagaku* **1981**, *38*, 420.
(11) Asakura, T.; Demura, M.; Yamamoto, K.; Chûjô, R. *Polymer* **1987**, *28*, 1037.
(12) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Wiley: New York, 1969.
(13) Kato, Y.; Ando, I.; Nishioka, A. *Kobunshi Ronbunshu* **1975**, *32*, 200.
(14) Lindeman, L. P.; Adams, J. Q. *Anal. Chem.* **1971**, *43*, 1245.
(15) Segre, A. L.; Andruzzi, F.; Lupinacci, D.; Magagnini, P. L. *Macromolecules* **1981**, *14*, 1845.
(16) Asakura, T.; Hirano, K.; Demura, M.; Katô, K. *Makromol. Chem., Rapid Commun.*, in press.
(17) Asakura, T.; Doi, Y. *Macromolecules* **1983**, *16*, 786.
(18) Wittwer, H.; Suter, U. W. *Macromolecules* **1985**, *18*, 403.