¹³C NMR Chemical Shifts Calculation for Model Compounds of Ethylene–Propylene Copolymer with a Low Ethylene Content

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ABSTRACT: ¹³C NMR chemical shifts of the model compounds for ethylene–propylene (E-P) copolymer with a low ethylene content were calculated using the gamma-effect of ¹³C chemical shift and Mark's rotational isomeric state matrices of E-P copolymer. The carbons of interest in the model compounds are included in the same monomer unit surrounded by different comonomer sequences due to the substitution of monomer unit between ethylene and propylene. Observed ¹³C chemical shift differences for the carbons of interest were reasonably explained by the calculation. The magnitude of the gamma-effect was found to be sensitive to the change of the comonomer sequences. These estimated chemical shift differences are comparable to the stereosequence dependence of ¹³C chemical shifts. The calculated ¹³C NMR chemical shifts of stereoregular E-P copolymer with a low ethylene content allow the assignments of complicated tactic and comonomer sequence dependent resonances in the methyl resonance region. This calculation method also predicted the ¹³C NMR chemical shift differences for the methylene carbons included in ethylene unit situated in two different comonomer sequences, namely, (I) the ethylene unit surrounded by the isotactic polypropylene chain, and (II) the ethylene unit which is the structural element of the isotactic poly(1-methyltetramethylene) as a model of regularly alternating ethylene–propylene copolymer.

KEY WORDS Ethylene–Propylene Copolymer / ¹³C NMR / Chemical Shift Calculation /

Ethylene–propylene (E-P) copolymers are industrially important materials, since some of their properties, such as impact strength, flexibility, and transparency of polypropylene products are modified by the copolymerization with ethylene. For example, the impact strength of E-P copolymer is two or three times larger than that of polypropylene with a relatively small decrease (30–40%) of the rigidity. Tacticity and comonomer sequence distributions are important factors dominating the mechanical properties of E-P copoly-

mers. ¹³C NMR is the most powerful analytical method to determine these two factors. In recent years, by improvement of sensitivity and resolution of NMR spectra, we can observe tactic- and comonomer-sequence dependent hexad or heptad resonances. Further, the calculation methods of ¹³C NMR chemical shifts have been also improved to allow assignments of hexad or heptad resonances of polypropylene and related polymers.

Chemical shift calculation based on the ¹³C NMR gamma-effect and the rotational iso-

meric state model has been applied to the assignments of the ^{13}C NMR spectra of polypropylene,¹⁻⁶ poly(1-butene),⁴ and ethylene-propylene (E-P) copolymer.^{7,8} Recently, ^{13}C NMR chemical shifts of regioirregular polypropylene have been also estimated by the calculation methods mentioned above.⁹ These results indicate that their stereosequence-dependent ^{13}C NMR chemical shifts can be explained by the gamma-effect. Tonelli¹⁰ calculated the ^{13}C NMR chemical shifts of poly(1-methyltetramethylene) using the

gamma-effect and the Mark's¹¹ rotational isomeric model. It is demonstrated that the sensitivity of ^{13}C NMR chemical shifts to the long range stereosequence depends on the probability of bond conformations which produce a gauche arrangement between the carbon atoms of interest and the carbon atoms in the gamma position.

Otherwise, for the comonomer sequence distributions, some empirical rules^{12,13} have been applied to assign the ^{13}C NMR spectra of ethylene-propylene copolymers. However,

Figure 1. (a) Methyl resonance region of the ^{13}C NMR spectrum of highly-stereoregular ethylene-propylene copolymer with a low ethylene content at 120°C . (b) Expanded spectrum of (a). Spinning side bands are marked by asterisks and ^{13}C means ^{13}C satellite signals.

(1) Calculated ^{13}C NMR chemical shifts of methyl carbons, 1, 2, 3, 4, 5, in highly stereoregular ethylene-propylene copolymer using Mark's RIS model are illustrated by stick spectrum.

(2) Calculated ^{13}C NMR chemical shifts of methyl carbons, 1, 2, 3, in highly isotactic polypropylene chains using Suter-Flory's RIS model are illustrated by a stick spectrum.

these rules cannot always provide useful means for the assignments of ^{13}C NMR spectra in E-P copolymers, since tactic and comonomer sequence dependent resonances coexist to make their spectra complicated. A typical example is the methyl carbon region of ^{13}C NMR spectrum of the stereoregular E-P copolymer with a low ethylene content, as shown in Figure 1. Figure 1(a) indicates that this sample is highly isotactic, because the intensity of the peak at 21.84 ppm which is assigned to *mmmm*-pentad is much larger than those of the other peaks. According to the previous assignments for E-P copolymer¹⁴ and isotactic polypropylene,⁶ tactic heptad and pentad comonomer sequence dependent resonances should coexist in the spectrum in Figure 1(b). ^{13}C NMR chemical shift differences from various comonomer sequences should be estimated as well as those from different stereosequences in the assignments of these resonances. In this paper, we investigated the applicability of the chemical shift calculation *via* the gamma-effect to the prediction of ^{13}C chemical shifts of tactic and comonomer sequence dependent resonances of the E-P copolymer with a low ethylene content. In order to confirm the validity of the method, ^{13}C NMR chemical shifts were calculated at first for 2,4,6-trimethyloctane, 2,4,8,10-tetramethylundecane, 3,5,7,9,11,13,15-heptamethylheptadecane, and 2,6,8,10,12,14-hexamethylpentadecane. By a comparison between calculated and observed chemical shifts¹⁵⁻¹⁸ of the model compounds, the magnitude of the gamma-effect was found to be also sensitive to the changes of the comonomer sequences. This means that conformational probability of the bond to take a gauche arrangement between the carbon of interest and the carbons in the gamma position indirectly depends on the existence of methyl substituent in the sequences of the model compounds. The calculation method is applied to the calculation of ^{13}C NMR chemical shifts in the stereoregular E-P

copolymer with a low ethylene content and isotactic poly(1-methyltetramethylene), as a model compound of a regularly alternating ethylene-propylene copolymer. The calculated results for the former allow the assignments of the complicated tactic and comonomer sequences dependent methyl resonances in E-P copolymers with a low ethylene content. By a comparison between calculated and observed chemical shifts¹⁹ for the latter, confirmation was made of the good correspondence of the calculated ^{13}C NMR chemical shift differences with that observed, between the methylene carbons included in the ethylene unit situated in two different comonomer sequences, namely, (I) the ethylene unit surrounded by the isotactic polypropylene chain, and (II) the ethylene unit which is the structural element of the isotactic poly(1-methyltetramethylene) chain.

EXPERIMENTAL

Material

The ethylene-propylene copolymer (E-P) with a low ethylene content polymerized with stereospecific Ziegler-Natta catalytic system, $\delta\text{-TiCl}_3/\text{Et}_2\text{AlCl}$, was a generous gift from Tokuyama Soda Co., Ltd. From ^{13}C NMR, it was confirmed that each ethylene unit was isolated from another ethylene unit in the isotactic polypropylene chain and this sample did not contain any detectable amounts of head-to-head and tail-to-tail arranged propylene units, referring to the study of regiorregularity in the chain.^{9,18} The ethylene content of this sample was determined to be 0.7 mol% from the relative peak areas of methylene resonances ($S_{\alpha\alpha}$, $S_{\alpha\gamma}$, and $S_{\beta\beta}$ carbons). ($S_{\alpha\delta}$, $S_{\beta\delta}$, $S_{\gamma\gamma}$, $S_{\gamma\delta}$, and $S_{\delta\delta}$ carbons were not detected.)

NMR Measurements

The ^{13}C NMR spectrum was recorded at 120°C on a JEOL JNM-GX 270 spectrometer at 67.8 MHz. The sample solutions, in a 10 mm

o.d. glass tube, were prepared in *o*-dichlorobenzene (90 vol%)/benzene- d_6 (10 vol%) to give 0.1 g (polymer)/cm³ (solvent). Benzene- d_6 provided the signal for the ²H NMR internal lock. In all measurements, broad band noise decoupling was used to remove ¹³C–¹H couplings, the pulse angle was 45°, the pulse repetition time was 10 s, and free induction decays were stored in 32 K data points using a spectral window of 10000 Hz. Hexamethyldisiloxane was used as the internal reference (2.03 ppm downfield from the resonance of tetramethylsilane).

¹³C NMR Chemical Shift Calculation

¹³C NMR chemical shifts of the model compounds and polymers were calculated using the Mark's RIS model¹¹ of E-P copolymer and the gamma-effect of chemical shift. In the Mark's RIS model, the value of the statistical weight, η , was taken to be 1.0, and the values of four-bond pentane interferences (ω) and three bond gauche interactions (τ)²⁰ were characterized with $E_\omega = 8400 \text{ J mol}^{-1}$ and $E_\tau = 2100 \text{ J mol}^{-1}$, respectively. The gamma-effects of methine carbons on methyl carbons and methylene and methyl carbons on methine carbons were taken to be -5.3 ppm , and the gamma-effect of methine carbons on methylene carbons was taken to be -3.7 ppm in the calculation for polypropylene as proposed by Tonelli.² In the case of (E-P) copolymer, the value of -3.7 ppm was assumed as the gamma-effect of methyl and methylene carbons on the ¹³C chemical shift of methylene carbon. The calculation was performed at 120, 137, and 140°C corresponding to the experimental conditions.

Verification of the Calculation Method of ¹³C NMR Chemical Shifts

¹³C NMR Chemical Shifts Calculation of Model Compounds

As shown in Figure 2, compounds, 2,4,6-trimethyloctane (A, B), 2,4,8,10-tetramethylundecane (C, D), 3,5,7,9,11,13,15-hepta-

methylheptadecane (E, F), and 2,6,8,10,12,14-hexamethylpentadecane (G), were selected as appropriate models for E-P copolymer. These model compounds have different sequences due to the substitution of monomer unit between ethylene and propylene. The carbons of interest are numbered 1, 2, 2', and 3 in the compounds (A), (B), (C), and (D), and are marked by asterisks in the compounds (E), (F), and (G). These carbons are included in the same monomer units surrounded by the different sequences. The influence of monomer unit substitution on the ¹³C NMR chemical shifts of the carbons of interest was investigated in these model compounds, and compared with the stereosequence (*meso* and *racemo* configuration)-dependence of ¹³C chemical shifts. The ¹³C chemical shifts of carbons 1, 2, 2', and 3 in the model compounds (A), (B),

Table I. Observed and calculated chemical shifts of carbons, 1, 2', 2, and 3, in the model compounds (A)–(D)

Carbon No.	Compound	Obsd ^a	Δv_{obsd}^b	$\Delta v_{\text{calcd}}^b$
		ppm	ppm	ppm
1	(A)	23.54	−0.20	−0.253
	(B)	23.74	0.0	0.0
	(C)	23.58	−0.16	−0.212
	(D)	23.58	−0.16	−0.222
2'	(A)	22.77	−0.12	−0.226
	(B)	22.89	0.0	0.0
	(C)	22.83	−0.06	−0.009
	(D)	22.83	−0.06	−0.002
2	(A)	26.01	−0.06	−0.052
	(B)	26.01	−0.06	−0.027
	(C)	26.07	0.0	−0.001
	(D)	26.07	0.0	0.0
3	(A)	47.96	−0.60	−0.582
	(B)	48.56	0.0	0.0
	(C)	47.66	−0.90	−0.634
	(D)	47.62	−0.94	−0.602

^a Observed at 140°C in ref 15, 16. Chemical shifts are expressed from the resonance of tetramethylsilane.

^b Chemical shifts are expressed relative to that of peak appearing at the lowest field, set to be 0.00 ppm, and the negative sign indicates the higher field shift.

Figure 2. Model compounds for ethylene-propylene copolymer with a low ethylene content. (A), (B), 2,4,6-trimethyloctane; (C), (D), 2,4,8,10-tetramethylundecane; (E), (F), 3,5,7,9,11,13,15-heptamethylheptadecane; (G), 2,6,8,10,12,14-hexamethylpentadecane; (t), *threo* relationship to delta methyl carbon.

(C), and (D) were calculated and the results are shown in Table I with the observed ones,^{15,16} where the chemical shift difference between the peak appearing at the lowest field and the other one is abbreviated as $\Delta\nu$. The calculated chemical shift difference for the carbon 1 in the compounds (A) and (B) depends on the dif-

ferent configurations of the methine carbon 6. This value coincides with the observed one. The calculated chemical shift difference for the carbon 1 in the compounds (C) and (D) depends on the indirect long range influence¹⁰ from the different configurations of methine carbon 8. The predicted peak positions of the

Figure 3. Observed and calculated ^{13}C NMR chemical shifts of carbons 1, 2, 3 in model compounds (A), (B), (C), and (D) illustrated by stick spectra. Chemical shifts are expressed by ppm relative to that of the peak appearing at the lowest field, set to be 0.00 ppm.

carbon 1 in the model compounds (C) and (D) were calculated to be in the intermediate region between those of (A) and (B). As shown in Figure 3, these calculated results illustrated by stick spectra well reproduce the trends of the observed shifts. The magnitude of the calculated chemical shift differences of the carbon 1 coincides with that observed. Thus, chemical shift differences among the carbon 1 in the compounds of (A), (B), (C), and (D) depend on the change of comonomer sequences, namely, on the existence or the ab-

sence of the methyl substituent 6'. In the case of carbon 2 and 2', a similar description is possible to explain the trends of relative chemical shifts, in spite of the small magnitude of these chemical shift differences.

The observed chemical shifts of the carbons 3 in the model compounds (C) and (D) show upfield shifts of 0.90 and 0.94 ppm from that in the compound (B), respectively. Lindeman-Adams' empirical rule¹³ provides carbon 3 in compounds (C, D) upfield shifts of 0.25 ppm from the chemical shift of carbon 3 in com-

pound (B) due to differences among these 4-bond effects and gives them the same contribution as the 3-bond (gamma)-effect. However, the upfield shifts of carbon 3 in the compounds (C,D) predicted by our calculation *via* the gamma-effect are 0.63 and 0.60 ppm. The total upfield shifts of 0.88 and 0.85 ppm are estimated by additions of upfield shifts from the calculated gamma-effect on upfield shifts from the empirical 4-bond effect. As shown in Figure 3, the calculated total upfield shifts of carbon 3 well coincide with the observed chemical shift differences of these. This suggests that the gamma-effect really depends on the change of conformational probabilities, which would arise whether the methyl carbon 6' are present or not. The assignments of methylene carbon 3 provided by Zambelli *et al.*¹⁶ indicate that carbon 3 in the model compound (C) (*meso* form) is 0.04 ppm downfield from that in (D) (*racemo* form). However, the calculated results suggest that carbon 3 in the *racemo* form is 0.03 ppm upfield from that in the *meso* form. Tonelli¹⁰ demonstrated that both the calculated and observed stereosequence dependence of the ¹³C chemical shifts for poly(1-

Table II. Observed chemical shifts and calculated gamma-effects of carbon 9 in the model compounds (E), (F)

Model	Pentad	Obsd ^a	Calcd
		ppm	gamma-effect ppm
(E)	<i>mmmr</i>	21.55	-6.369
(E)	<i>mrmm</i>	20.85	-6.841
(E)	<i>rmrr</i>	20.85	-6.919
(E)	<i>rrrm</i>	20.17	-7.613
(F)	<i>mmmm</i>	21.78	-6.199
(F)	<i>rmmr</i>	21.33	-6.537
(F)	<i>mmrr</i>	21.01	-6.723
(F)	<i>mrmr</i>	20.71	-7.064
(F)	<i>rrrr</i>	20.31	-7.434
(F)	<i>mrrm</i>	20.04	-7.816

^a Observed at 140°C by Zambelli *et al.*¹⁷ Chemical shifts are expressed from the resonance of tetramethylsilane.

methyltetramethylene) are 0.03–0.06 ppm with good agreement between calculated and observed chemical shifts for all carbon atoms.

Table III. Observed chemical shifts and calculated gamma-effects of the carbon marked by an asterisk in the model compound (G). Symbols e and t means the *erythro* and *threo* relationship to the carbon marked by an asterisk, respectively

Model	Methyl carbon			Pentad	Obsd ^a	Calcd
	X	Y	Z		ppm	gamma-effect ppm
(G)	e	e	e	P [*] mP [*] mP [*] mPE	21.61	-6.331
(G)	t	e	e	P [*] tP [*] mP [*] mPE	21.42	-6.502
(G)	e	e	t	P [*] mP [*] mP [*] tPE	21.01	-6.733
(G)	e	t	e	P [*] tP [*] tP [*] mPE	20.91	-6.883
(G)	t	e	t	P [*] tP [*] mP [*] tPE	20.85	-6.953
(G)	t	t	e	P [*] mP [*] tP [*] mPE	20.78	-7.010
(G)	e	t	t	P [*] tP [*] tP [*] tPE	20.33	-7.473
(G)	t	t	e	P [*] mP [*] tP [*] tPE	20.19	-7.655

^a Observed at 140°C by Zambelli *et al.*¹⁸ Chemical shifts are expressed from the resonance of tetramethylsilane.

Table IV. Chemical shift differences due to substitution of the propylene unit by ethylene unit

No.	Pentad	Obsd ^a	Calcd ^a
(1)	P [*] mP [*] mP [*] mP [*]	0.0	0.0
	P [*] mP [*] mP [*] mP [*]	-0.23	-0.20
	P [*] mP [*] mP [*] mPE	-0.17	-0.132
(2)	P [*] tP [*] mP [*] mP [*]	0.0	0.0
	P [*] tP [*] mP [*] mPE	0.09	0.03
(3)	P [*] tP [*] tP [*] mP [*]	0.0	0.0
	P [*] tP [*] tP [*] mPE	-0.10	-0.09
	P [*] tP [*] tP [*] tP [*]	-0.16	-0.17
(4)	P [*] mP [*] tP [*] mP [*]	0.0	0.0
	P [*] mP [*] tP [*] mPE	-0.07	-0.17
	P [*] mP [*] tP [*] tP [*]	-0.14	-0.223
(5)	P [*] tP [*] tP [*] mPE	0.0	0.0
	P [*] tP [*] tP [*] tP [*]	-0.02	-0.039
	P [*] tP [*] tP [*] tP [*]	-0.16	-0.140
(6)	P [*] mP [*] tP [*] mPE	0.0	0.0
	P [*] mP [*] tP [*] tP [*]	-0.15	-0.161

^a Chemical shifts are expressed by ppm relative to that of peak appearing at the lowest field, set to be 0.00 ppm.

Thus, our assignments should be applied to the chemical shifts of the carbon 3 in the compounds (C, D). The calculated chemical shifts of the carbons of interest in these model compounds coincide with the observed ones in the order except minor difference in the carbon 3. The magnitude of the chemical shift differences for carbons 1, 2, and 3 are well predicted by the calculation.

The results of ^{13}C chemical shifts calculation of carbons marked by asterisks in compounds (E), (F), and (G), are shown in Tables II and III. This calculation method is applied to the resolution of tactic and comonomer sequence dependent chemical shifts of methyl carbons. The calculated results are shown in Tables II and III and are summarized in Table IV. In

Table IV, the calculated chemical shifts of tactic pentad and the corresponding PPPPE comonomer pentad resonances are compared with the observed ones. In Figure 4, the results are illustrated by stick spectra. The calculated relative peak positions as well as the magnitude of the chemical shift differences are in good agreement with the observed results. For example, the chemical shifts of the resonances $\text{P}^{\text{m}}\text{P}^{\text{m}}\text{P}^{\text{m}}\text{PE}$ and $\text{P}^{\text{m}}\text{P}^{\text{m}}\text{P}^{\text{m}}\text{P}^{\text{r}}\text{P}$ are predicted to be 0.13 and 0.20 ppm upfield from $\text{P}^{\text{m}}\text{P}^{\text{m}}\text{P}^{\text{m}}\text{P}$ pentad, respectively. These calculated results agree with the observed upfield shifts of 0.17 and 0.23 ppm.^{17,18} The empirical rule proposed by Zambelli *et al.*,¹⁸ provides upfield shifts of 0.07 and 0.20 ppm from $\text{P}^{\text{m}}\text{P}^{\text{m}}\text{P}^{\text{m}}\text{P}$ pentad, respectively. The

Figure 4. Observed and calculated ^{13}C NMR chemical shifts of carbons of interest in model compounds, (E), (F), (G), are illustrated by stick spectra corresponding to the summarized results in Table IV. Chemical shifts are expressed by ppm relative to that of the peak appearing at the lowest field, set to be 0.00 ppm.

observed chemical shift difference of 0.06 ppm between $P^{m}P^{m}P^{m}P^{r}P$ and $P^{m}P^{m}P^{m}PE$ resonances agree with the value of 0.07 ppm predicted by the calculation. Thus, our calculation can predict the relative positions of these peaks more precisely, compared with those predicted by the empirical rule. From these results, it is confirmed that the ^{13}C chemical shift calculation *via* the gamma-effect provides reasonable chemical shift differences between the carbons of interest, which are included in definite monomer units surrounded by different comonomer sequences. These chemical shift differences are estimated to be comparable to the stereo-sequence-dependent ^{13}C chemical shifts.

RESULTS AND DISCUSSION

 ^{13}C NMR Chemical Shift Calculation of Ethylene-Propylene Copolymer

As shown in Figure 1(a), the sample is highly isotactic, and it is confirmed from the methylene ^{13}C resonances, which is not shown in Figure 1(a), that each ethylene unit is isolated from the another ethylene unit in the isotactic polypropylene chain. Thus, some typical sequences included in this sample are simplified in the models (H), (I), and (J), as shown in Figure 5. The chemical shifts of the carbons 1, 2, 3, 4, and 5 in the model polymer (H), (I), and (J), were calculated using the calculation method confirmed above. The

* : Isotactic-P1MTM

Figure 5. Model structures of isotactic polypropylene (H), *rr*-defect in isotactic polypropylene (I), isolated ethylene unit in the isotactic polypropylene (J), and isotactic poly(1-methyltetramethylene) (K). Isotactic polypropylene and isotactic poly(1-methyltetramethylene) are abbreviated IPP and IP1MTM, respectively.

isotactic polypropylene chain is abbreviated as IPP chain, and it is assumed that the *rr*-configuration and ethylene unit in models (I) and (J) are isolated in the surrounding IPP chains, which are composed of 30 *meso* dyads. Isotactic poly(1-methyltetramethylene), model (K), is a model polymer of regularly alternating ethylene-propylene copolymer. This model was used for the prediction of chemical shift differences for carbons included in ethylene unit situated in the different comonomer sequences of E-P copolymer. The calculated and observed results are shown in Table V. The observed chemical shifts for E-P copolymer in this work correspond to those observed by Sanders *et al.*²¹

As for the assignments for the spectrum shown in Figure 1(b), the chemical shift calculation for the model polymers predicts that the position of P^mP^mP^mP^mPEP resonance is downfield from the P^mP^mP^mP^mP^rP^r. This coincides with the results for the model compounds shown in Figure 4(1). Thus, peaks 1, 4, and 2 are assigned as P^mP^mP^mP^mP^mP^m, P^mP^mP^mP^mPEP, and P^mP^mP^mP^mP^rP^r in this

order from downfield. The peak located at 21.58 ppm (0.02 ppm upfield from the peak of 2) was identified as the ¹³C satellite signal with a coupling constant of 35 Hz, by measurement of ¹³C NMR at 50.1 MHz. Peaks 3 and 5 can be assigned to P^mP^mP^mP^rP^rP^mP^m and P^mP^mP^mPEP^mP, respectively. Since the relative upfield shift of the latter is predicted by addition of the difference (0.476 ppm) in the calculated gamma-effect to the 4-bond effect of 0.49 ppm estimated from Lindeman-Adams rule, the calculated total upfield shift is 0.966 ppm. This value coincides well with the observed one of 0.92 ppm. The former is assigned to P^mP^mP^mP^rP^rP^mP^m owing to the magnitude of the relative upfield shift. These calculated results are illustrated by the stick spectrum (1) in Figure 1 (the calculated ¹³C chemical shift of P^mP^mP^mPEP^mP is expressed by the total upfield shift). Also illustrated as a stick spectrum (2) in the figure are the calculated chemical shifts for the heptad stereoisomers observed in the highly isotactic polypropylene chains using Suter-Flory²² five-state RIS model.⁶ By comparison of two stick spectra

Table V. Observed and calculated chemical shifts of numbered carbons in the model structures of polymers

Carbon No.	Assign. abbr.	Obsd ^a	Obsd	Δv_{obsd}^b	Calcd γ -effect	$\Delta v_{\text{calcd}}^b$
		ppm	ppm	ppm	ppm	ppm
1	P ^m P ^m P ^m P ^m P ^m P ^m	21.84	21.82 ^c	0.0	-6.069	0.0
4	P ^m P ^m P ^m P ^m PEP	21.63	21.61 ^c	-0.21	-6.250	-0.181
2	P ^m P ^m P ^m P ^m P ^r P ^r	21.60		-0.24	-6.259	-0.190
3	P ^m P ^m P ^m P ^r P ^r P ^m P ^m	21.04		-0.80	-6.589	-0.520
5	P ^m P ^m P ^m PEP ^m P	20.92	20.90 ^c	-0.92	-6.545	-0.476
8	EPEPEPE		20.03 ^d	-1.79	-7.217	-1.148
6	P ^m P ^m PEP ^m P	37.97	37.96 ^c	0.0	-3.125	0.0
9	PEPEPE		37.94 ^d	-0.03	-2.878	0.247
10	PEPEPEP		24.88 ^d	0.0	-8.663	0.0
7	P ^m P ^m PEP ^m P ^m P	24.62	24.61 ^c	-0.26	-8.944	-0.281

^a Observed at 120°C in this work. Chemical shifts are expressed from the resonance of tetramethylsilane.

^b Chemical shifts are expressed relative to that of peak appearing the lowest field, set to be 0.00 ppm.

^c Observed at 120°C by Sanders *et al.*²¹

^d Observed at 137°C by Zetta *et al.*¹⁹

and the observed spectrum, assignments of peaks 2 and 3 are confirmed to be $\text{P}^{\text{m}}\text{P}^{\text{m}}\text{P}^{\text{m}}\text{P}^{\text{m}}\text{P}^{\text{r}}\text{P}^{\text{r}}\text{P}$ and $\text{P}^{\text{m}}\text{P}^{\text{m}}\text{P}^{\text{m}}\text{P}^{\text{r}}\text{P}^{\text{r}}\text{P}^{\text{m}}\text{P}$ heptads in the isotactic polypropylene chain, respectively. The relative areas of peaks 2, 3, 4, and 5 are determined by the curve resolving method.²³ The relative areas of peaks 2 and 4 correspond to those of peaks 3 and 5, respectively. These results indicate that the provided assignments are reasonable. Although the magnitudes of the gamma-effect on carbons 2 and 3 calculated using Mark's RIS model are underestimated compared with those calculated using Suter-Flory five state RIS model, as illustrated by the stick spectra in Figure 1, their relative positions are reasonably explained.

The chemical shift of the carbon 8 is also predicted by a similar estimation of carbon 5. The total upfield shift from the $\text{P}^{\text{m}}\text{P}^{\text{m}}\text{P}^{\text{m}}\text{P}^{\text{m}}\text{P}^{\text{r}}\text{P}^{\text{r}}\text{P}$ heptad is predicted by addition of the difference in the calculated gamma-effect of 1.148 ppm to the empirical four-bond effect of 0.98 ppm.

Observed chemical shift difference between methylene carbons 6 and 9 is very small. This is also described as follows: the calculated gamma-effect of the carbon 6 is 0.247 ppm larger than that of a carbon 9. Otherwise, the empirical 4-bond effect provides a relative upfield shift of 0.25 ppm for the latter carbon. Therefore, both effects cancel each other out to produce a very small chemical shift difference for these resonances. The observed chemical shift difference between the centered methylene carbons, 10 and 7, is in good agreement with the calculated upfield shift. This indicates that the magnitude of the gamma-effect is sensitive to the change of comonomer sequence, which arises from the existence of the methyl substituent separated 5 bonds from the carbon of interest.

CONCLUSIONS

The chemical shift calculation using the

gamma-effect of ^{13}C chemical shift and Mark's RIS model of E-P copolymer can well predict ^{13}C chemical shift differences for carbons included in definite units, which are surrounded by different comonomer sequences. These predicted ^{13}C chemical shifts depend on differences of comonomer sequences, and are comparable to stereosequence dependence. This calculation method is applicable to predict ^{13}C chemical shifts of comonomer- and stereo-sequence dependent resonances in the E-P copolymer.

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