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Polymer 45 (2004) 2651–2656
polymer
www.elsevier.com/locate/polymer

Monomer sequence characterization of propylene-1-olefin copolymers by carbon-13 NMR spectroscopy

Yudong Zhang*,[1]

Beijing Research Institute of Chemical Industry, SINOPEC, No. 14 beishanhuadonglu, 100013 Beijing, People's Republic of China

Received 19 November 2003; received in revised form 7 January 2004; accepted 3 February 2004

Abstract

Complete comonomer sequence assignments were made for a series of propylene-1-olefin copolymers, including 1-butene, 1-hexene, and 1-octene, to establish the effect of branch length on the sequence sensitivity of the backbone carbon chemical shifts. Particular attention was paid to the effect of branch length on the monomer sequence sensitivity of the αα carbon chemical shifts. As opposed to the ethylene-1-olefin copolymers where the reported αα carbon chemical shifts were exclusively tetrad sensitive regardless of the branch length, the αα carbons in each of the three propylene-1-olefin systems examined showed apparent tetrad, triad, and dyad monomer sequence sensitivities as the center dyad changed from PP to PX to XX where X represents the individual 1-olefin.

Keywords: Propylene-1-olefin copolymers; Configurational Sequence; Comonomeric sequence

1. Introduction

It is an important way to characterize the sequence of polyolefin molecule by using carbon-13 NMR technique. This study was undertaken to establish carbon-13 NMR chemical shift assignments for propylene-1-butene, propylene-1-hexene, and propylene-1-octene copolymer systems, and to examine the effect of varying branch lengths on the behavior of the observed chemical shifts. Up to now, a few of characterization have been done among these three copolymer systems, that is, the propylene-1-butene copolymer [1–9], the propylene-1-hexene copolymer [10] and the propylene-1-octene copolymer [11]. However, in this report, we are interested in the relationship of chemical shifts of similar backbone carbons for propylene-1-olefins with various branch lengths. One interesting aspect, which was noted but not emphasized in those reports, was the fact that the chemical shifts of the αα carbons in the propylene-1-olefin copolymers were tetrad, triad, and dyad sequence sensitive depending upon whether the central dyad sequence was PP, or PX, or XX, respectively. This behavior is quite different from that observed in the ethylene-1-olefin copolymers where the αα carbon chemical shifts were at least tetrad sequence sensitive [12–15]. In this report, we will address this issue in detail while giving complete chemical shift assignments for a series of propylene-1-olefin copolymers.

2. Experimental

The samples used in the study were synthesized with an isospecific Ziegler–Natta catalyst. Carbon-13 NMR spectra were recorded on a Varian XL-200 NMR spectrometer at 50.3 MHz with broadband decoupling. Experimental conditions were:

pulse angle	90°
pulse delay	10 s
acquisition time	1 s
spectral width	8000 Hz
number of data points per spectrum	16 K
number of transients taken per spectrum	5000
temperature	125 ± 1 °C.

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* Tel./fax: +86-10-8463-4663.
E-mail address: yz@ecs.soton.ac.uk (Y. Zhang), *Permanent E-mail:* doctorydzhang@yahoo.com.cn (Y. Zhang).

[1] Present address: School of Electronics and Computer Science, University of Southampton, UK.

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doi:10.1016/j.polymer.2004.02.011

Sample solutions were prepared at 15 percent by weight in 1,2,4-tri-chlorobenzene. Trace amounts of HMDS were added for internal peak reference. However, it was observed that the HMDS peak position varies substantially in different polymer solutions. When it was used as the reference peak, the resulting chemical shift value for the same polymer peak may vary as much as 0.1 ppm. For this particular system, we had chosen the αα (PPPP) peak as the internal reference, and it was set at 46.515 ppm with respect to the TMS standard. The chemical shift values thus obtained were quite reproducible to ± 0.02 ppm.

3. Results and discussion

For each propylene-1-olefin copolymer system, five model polymers with varying comonomer content were made by controlling the monomer feed ratio. Peak assignments were then derived from the model polymer spectra by comparisons of peak intensity changes in reference to variations in monomer feed ratio. Selected model polymer spectra are presented in Figs. 1–3. The peak assignments for propylene-1-butene, propylene-1-hexene, and propylene-1-octene are listed in Tables 1–3, respectively.

In a propylene-1-olefin copolymer molecule with exclusively head-to-tail polymerizations, every other backbone carbon is a branching point. Peak broadenings and splittings due to configurational differences within a given 1-olefin comonomer sequence are evident in our spectra. Configurational splitting are easiest to distinguish from the comonomeric sequence splittings among resonances associated with the first branch carbons at the branching point, i.e. the 1B carbon of methyl branch, the 2B carbon of ethyl branch, the 4B carbon of a butyl branch, and the 6B carbon of a hexyl branch. In most other cases, configurational splittings overlap with comonomeric sequence splittings.

Table 1
Chemical shift assignments in carbon-13 NMR spectra of propylene-1-butene copolymers

Region	Carbon	Sequence	δ (ppm)	Peak number
A	αα	BPPB	47.13	1
	αα	PPPB	46.82	2
	αα	PPPP	46.51	3
B	αα	BPBB + BPBP	43.68	4
	αα	PPBB + PPBP	43.38	5
C	αα	PBBP + PBBB + BBBB	40.27	6
D	CH	PBP	35.32	7
	CH	PBB	35.20	8
	CH	BBB	35.07	9
E	CH	PPP + PPB + BPB	28.91	10
	2B	PBP	28.27	11
			28.17	
	2B	PBB	28.03	12
			27.92	
	2B	BBB	27.78	13
			27.72	
F	CH$_3$	PPP	21.84	14
	CH$_3$	PPB	21.67	15
	CH$_3$	BPB	21.51	16
G	1B	PBP	10.95	17
	1B	PBB	10.88	18
	1B	BBB	10.80	19

Table 2
Chemical shift assignments in carbon-13 NMR spectra of propylene-1-hexene copolymers

Region	Carbon	Sequence	δ (ppm)	Peak number
A	αα	HPPH	47.13	1
	αα	PPPH	46.82	2
	αα	PPPP	46.51	3
B	αα	HPHH + HPHP	44.21	4
	αα	PPHH + PPHP	43.94	5
C	αα	PHHP + PHHH + HHHH	41.38	6
D	4B	PHP	35.72	7
			35.67	
	4B	PHH	35.53	8
			35.47	
	4B	HHH	35.36	9
			35.27	
E	CH	PHP	33.84	10
	CH	PHH	33.70	11
	CH	HHH	33.56	12
F	3B	PHP	29.34	13
	3B	PHH	29.26	14
	3B	HHH	29.19	15
	CH	PPP + PPH + HPH	28.91	16
G	2B	HHH + PHH + PHP	23.47	17
H	CH$_3$	PPP	21.84	18
	CH$_3$	PPH	21.69	19
	CH$_3$	HPH	21.56	20
I	1B	PHP	14.12	21
	1B	PHH	14.10	22
	1B	HHH	14.07	23

The chemical shift changes associated with comonomer sequence differences are generally small, for the methine and the branch carbons. Therefore, it was relatively easy to characterize these peaks with the available model polymer spectra. In Fig. 1, for instance, peak 14, 15, and 16, observed at 21.84, 21.67, and 21.51 ppm, have peak heights of 115, 124, and 49 mm, respectively in spectrum (A). On the same scale, the corresponding peaks have peak heights of 60, 160, and 180 mm, respectively, in spectrum (B), which is from a model copolymer having a higher 1-butene content. From the polypropylene homopolymer spectrum, the isotactic CH$_3$ (PPP) peak was observed at 21.84 ppm. Therefore, peaks 15 and 16 must correspond to CH$_3$ (PPB) and CH$_3$ (BPB), respectively. These sequence assignments for the methyl peaks agree well with those reported by Bunn and Cudby [1,6]. A change from a 'P' to a 'B' unit in these 'P'-centered triads of the CH$_3$ peak resulted in a 0.17 ppm shift upfield. For many other carbon resonances, the resulting peak shifts from triad sequence differences were so small that only the direction of such shifts could be resolved. This information is given in Table 4, as a function of copolymer type.

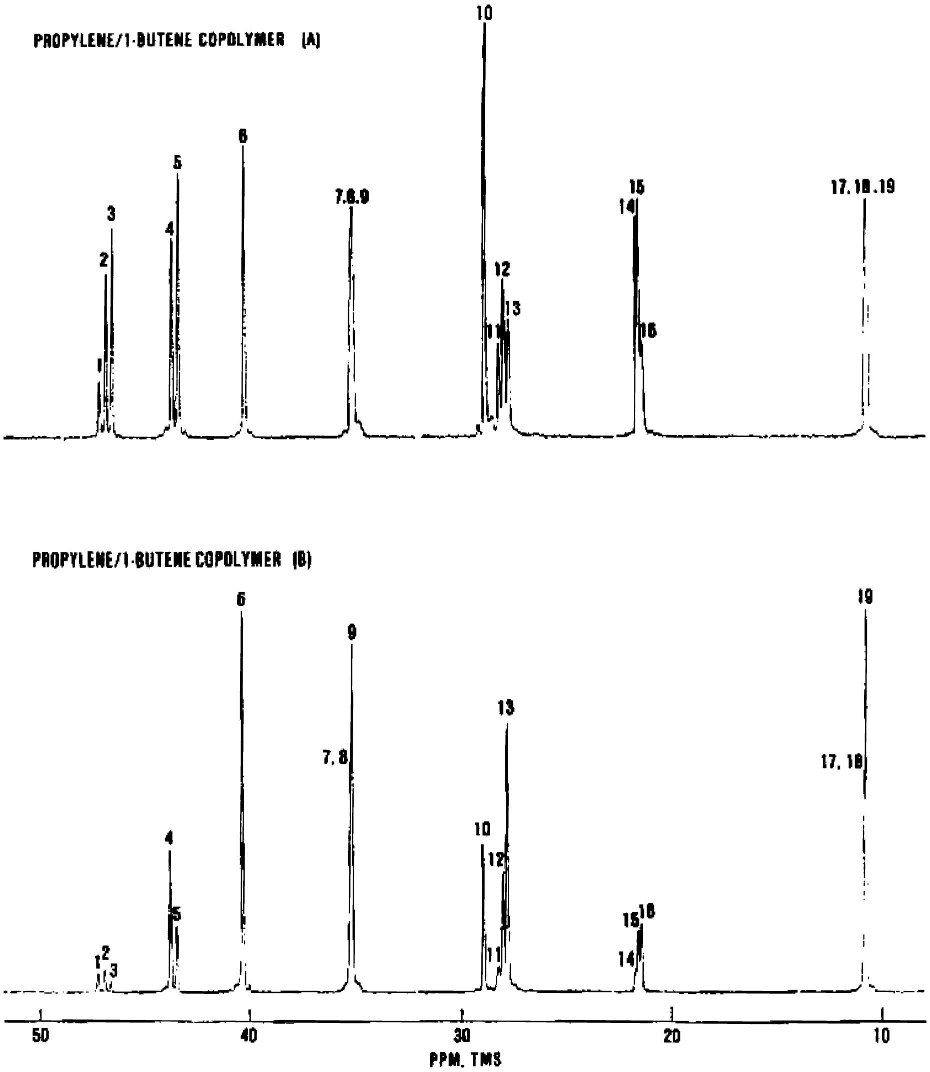

Fig. 1. (A) Carbon-13 NMR spectrum at 50.3 MHz and 125 °C of a propylene-1-butene copolymer ([B] = 47.3 mol%) at 15% by weight in 1,2,4-trichlorobenzene. (B) Carbon-13 NMR spectrum at 50.3 MHz and 125 °C of a propylene-1-butene copolymer ([B] = 70.8 mol%) at 15% by weight in 1,2,4-trichlorobenzene.

The $\alpha\alpha$ carbon chemical shifts were observed to be more sensitive towards differences in comonomer sequencing. In a parallel study of ethylene-1-olefin copolymers [12,13], the observed monomer sequence sensitivity of the $\alpha\alpha$ carbons were at least tetrad regardless of differences in branch length. For the propylene-1-olefin copolymers, there are ten possible tetrad sequences for the $\alpha\alpha$ carbons, but only six peaks were distinctly observed. These $\alpha\alpha$ carbon resonances appeared in three well-separated groups, which could be easily characterized in terms of the center dyad monomer sequences. In more detail, there were three peaks in the 'PP'-dyad-centered group, two peaks in the 'PX'-dyad-centered group (where 'X' denotes the 1-olefin comonomer unit), and one peak in the 'XX'-dyad-centered group. The same pattern was observed for all three P-X copolymer systems. It was noted that the measured separation between centers of adjacent groups was approximately equal for each type of P-X copolymer. But more importantly, the observed separation between peaks within the 'PX' group was also approximately the same as those between adjacent peaks within the 'PP' group. These peak separation values are listed in Table 5.

The three $\alpha\alpha$ carbon peaks in the 'PP'-dyad group correspond to the three 'PP'-centered tetrad monomer sequence XPPX, PPPX, and PPPP from downfield upward. Therefore, the two 'PX'-dyad peaks should correspond to some combination of the four 'PX'-centered tetrads, namely XPXX, XPXP, PPXX, and PPXP, and the broad 'XX'-dyad peak should correspond to the combined three 'XX'-centered tetrads, PXXP, PXXX and XXXX. Based on the observed peak separations described above, it is apparent that whatever is responsible for separating the three 'PP'-centered resonances may also be the cause of the splitting of the 'PX'-centered resonances. Likewise, whatever resulted in the lack of resolution among the three 'XX'-centered tetrad resonances (observed as one broad peak) should also

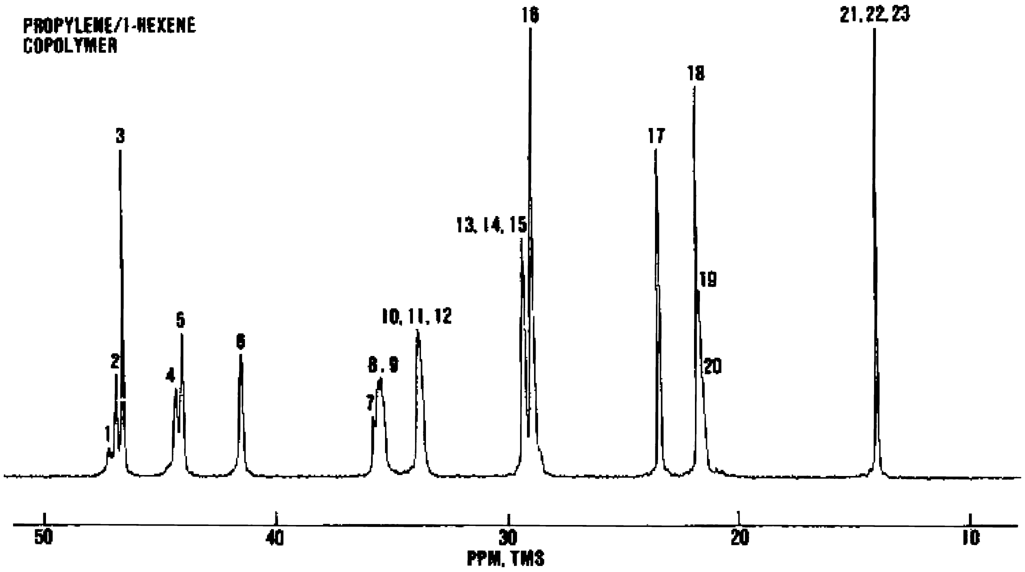

Fig. 2. Carbon-13 NMR spectrum at 50.3 MHz and 125 °C of a propylene-1-hexene copolymer ([H] = 40.0 mol%) at 15% by weight in 1,2,4-trichlorobenzene.

be responsible for having only two (instead of four) well-resolved peaks in the 'PX'-dyad group. It is thus deduced that a substitution of a 'P' unit by an 'X' unit next to a center dyad 'P' unit should result in a downfield shift of the αα carbon resonance by approximately 0.30 ppm. However, the same change next to a center dyad 'X' unit will not lead to any observable αα carbon chemical shift differences. In other words, the longer branches of the center dyad 'X' units appear to have a 'shielding effect' on the αα carbons to prevent them from sensing any branching differences longer than a methyl group beyond the center dyad 'X' units. According to this observation, peak 4 in Figs. 1–3 must correspond to the XPXX and XPXP tetrad sequences of the αα carbons, and the peak upfield, i.e., peak 5, must occur from overlap of the αα (PPXX) and αα (PPXP) resonances.

This particular set of tetrad sequence assignments proposed above could be verified quantitatively by using measured intensities of peaks 1, 2, and 5. Assuming the assignments are correct, one can calculate the intensity of peak 5 as follows:

$$\alpha\alpha(\mathrm{PPXX}) + \alpha\alpha(\mathrm{PPXP}) = k[\mathrm{PPXX}] + k[\mathrm{PPXP}]$$

$$= k[\mathrm{PPX}] \qquad (1)$$

where '*k*' is a NMR constant. For peaks 1 and 2, we have

$$\alpha\alpha(\mathrm{XPPX}) = k[\mathrm{XPPX}] \qquad (2)$$

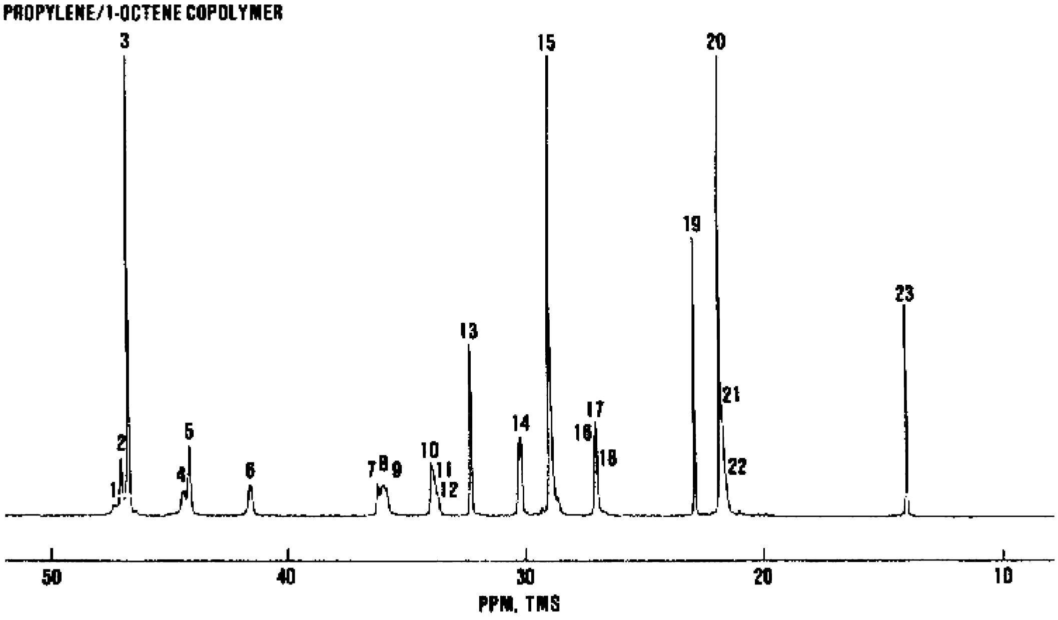

Fig. 3. Carbon-13 NMR spectrum at 50.3 MHz and 125 °C of a propylene-1-octene copolymer ([O] = 25.0 mol%) at 15% by weight in 1,2,4-trichlorobenzene.

Table 3
Chemical shift assignments in carbon-13 NMR spectra of propylene-1-octene copolymers

Region	Carbon	Sequence	δ (ppm)	Peak number
A	αα	OPPO	47.12	1
	αα	PPPO	46.82	2
	αα	PPPP	46.52	3
B	αα	OPOO + OPOP	44.19	4
	αα	PPOO + PPOP	43.95	5
C	αα	POOP + POOO + OOOO	41.39	6
D	6B	POP	36.11	7
			36.03	
	6B	POO	35.92	8
			35.84	
	6B	OOO	35.74	9
			35.71	
E	CH	POP	33.87	10
			33.81	
	CH	POO	33.72	11
	CH	OOO	33.59	12
			33.56	
F	3B	OOO + POO + POP	32.20	13
G	4B	OOO + POO + POP	30.13	14
H	CH	PPP + PPO + OPO	28.91	15
I	5B	POP	27.05	16
	5B	POP + POO	26.99	17
	5B	OOO	26.96	18
J	2B	OOO + POO + POP	22.88	19
K	CH_3	PPP	21.84	20
	CH_3	PPO	21.71	21
	CH_3	OPO	21.60	22
L	1B	POP + POO + OOO	14.06	23

Table 5
αα Carbon chemical shift changes in association with monomer sequence differences in propylene-1-olefin copolymers

	Chemical shift difference (ppm)		
Sequence difference	X = B	X = H	X = O
αα(PP)−αα(PX)	3.29	2.74	2.74
αα(PX)−αα(XX)	3.26	2.70	2.70
αα(XPPX)−αα(PPPX)	0.31	0.31	0.30
αα(PPPX)−αα(PPPP)	0.31	0.31	0.30
αα(XPX?)−αα(PPX?)	0.30	0.27	0.24

and

$$\alpha\alpha(\mathrm{XPPP}) = k[\mathrm{XPPP}] \qquad (3)$$

respectively. Based on the necessary relationship

$$[\mathrm{PPPX}] + 2[\mathrm{XPPX}] = [\mathrm{PPX}] \qquad (4)$$

the measured intensities should satisfy the following equation:

$$I_5 = 2I_1 + I_2 \qquad (5)$$

where I_5, I_1 and I_2 are the intensity of peak 5, peak 1 and peak 2, respectively.

Within experimental error, calculations for all three P-X copolymer systems were in good agreement with Eq. (5). Sample results for two P-B model polymers are shown in Table 6. By this kind of positive quantitative verification, we have not only confirmed the αα peak assignments for the P-B copolymers which had been previously reported [4,5], but also established it as a consistent pattern which holds true for propylene-linear 1-olefin copolymer in general.

Table 4
Peak shifts and associated monomer sequence variations for methine and branch carbons of propylene-1-olefin copolymers

Triad sequence	Carbon	Homopolymer peak position (ppm)	Relative peak order (downfield upwards)	|Δ|★★ (ppm)
'P'-Centered	CH	28.91	PPP, PPB, BPB	★
			PPP, PPH, HPH	★
			PPP, PPO, OPO	★
	CH_3	21.84	PPP, PPB, BPB	0.17
			PPP, PPH, HPH	0.15
			PPP, PPO, OPO	0.13
'B'-Centered	CH	35.07	PBP, PBB, BBB	0.12
	2B	27.72	PBP, PBB, BBB	0.23
	1B	10.80	PBP, PBB, BBB	0.08
'H'-Centered	CH	33.56	PHP, PHH, HHH	0.14
	4B	35.27	PHP, PHH, HHH	0.23
	3B	29.19	PHP, PHH, HHH	0.08
	2B	23.48	HHH, PHH, PHP	★
	1B	14.07	PHP, PHH, HHH	0.03
'0'-Centered	CH	33.56	POP, POO, OOO	0.16
	6B	35.71	POP, POO, OOO	0.20
	5B	26.96	POP, POO, OOO	0.05
	4B	30.25	OOO, POO, POP	0.06
	3B	32.25	OOO, POO, POP	★
	2B	22.89	OOO, POO, POP	★
	1B	14.02	POP, POO, OOO	★

★ Indicate small peak shifts; ★★ |Δ| refers to the absolute value of chemical shift differences between adjacent sequences.

Table 6
Quantitative verification of monomer sequence assignments for the 'PB'-centered αα tetrads

Polymer	Peak 1 = αα(BPPB)	Peak 2 = αα(BPPP)	Calculated *k*[PPB]	Peak 5 = αα(PPB)
P/B (A)	4.32	10.84	19.48	19.42
P/B (B)	3.09	3.13	9.31	9.03

The observed pattern of variable sequence sensitivity of the αα carbon resonances in a P-X copolymer maybe regarded as an 'exception' to the results predicted by the traditional Grant and Paul parameter methods [16]. However, a closer examination of the data listed in Table 6 indicates that for almost every carbon, the assigned monomer sequences for the observed resonance splittings are out of the 'normal' order from that predicted by the parameter method. For example consider the methine carbon resonances. A substitution of a 'P' unit by a 'X' unit as an outer member of a triad sequence should result in a downfield methine peak shift by a magnitude equal to the 'δ' parameter value if 'X' is 'B', or by $(\delta + \varepsilon)$ if 'X' is either 'H' or 'O'. If the Grant–Paul parameters [16] are used, the estimated magnitude of peak separation corresponding to the triad sequence difference mentioned above should be about 0.4–0.5 ppm. As compared to the predicted 'ε' shift for the αα tetrad sequence resonances, the observed separation is so much larger that a distinct triad sequence sensitivity for methine carbons of a P-X copolymer should be easily observed. The predicted order of triad sequences for the three splittings of a given methine resonance, from downfield upwards, would be XPX, XPP, and PPP for 'P'-centered methines, or XXX, XXP, and PXP for 'X'-centered methines. However, as listed in Table 4, the observed 'P'-centered methine resonance is singlet, and the assigned triad sequences for the three observed 'X'-centered methine resonances are exactly the reverse order from the predicted. The observed peak separation, on the average, is only half of observed separation between αα 'PP'-centered tetrad sequence resonances. It appears that parameter method almost failed completely in the case of P-X copolymers except for locating the general proximity of carbon resonances associated with different structural positions.

It had been recognized in the past that one should not except the parameter values to work correctly for highly branched polymer systems simply because these values were derived from observed chemical shifts of carbons of linear and isolated single branch structures. There simply were not enough chemical shift values available to incorporate the effects of closely neighboring branches into the parameter values.

It is worth noting that Aoki et al. [7,8] used Mark's rotational isomeric state model (RIS model) modified [17] to predict the chemical shift of propyle-1-butene copolymers by chemical shift calculation via the carbon-13 NMR γ effect, which is in agreement with the results in this study, however, the other two copolymers have not performed in this way. Due to the complication and difficulty of the topic, the detailed investigation about the γ effect of propylene-1-olefin copolymers will be given in future papers.

For quantitative studies of monomer sequence distribution of these propylene-1-olefin copolymers, rigorous results can be obtained only for dyad sequences. One may obtain semi-quantitative triad sequence distribution values where the major source of error would come from integral measurements of peaks, which were not so well-separated. As discussed in detail in earlier publications [12,13], the quantitative treatment would involve the use of the necessary relationships and separating peaks into well-spaced and well-defined groups.

4. Conclusion

Carbon-13 NMR chemical shift assignments for propylene-1-butene, propylene-1-hexene, and propylene-1-octene copolymer systems were established. Effect of branch length on chemical shifts of some backbone carbons for propylene-1-olefins with various branch lengths is found to be small, for example, αα carbons. In addition, with increase of branch length, the effect on chemical shifts will become smaller and smaller.

Acknowledgements

I thank Dr Eric. T. Hsieh of Phillips Petroleum Company for his invaluable assistance in this paper.

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