Analysis of poly(ethene)-based copolymers with low comonomer content by NMR Spectroscopy

Anuttra Nuamthanom

Chemistry Program, Department of Science Service, Ministry of Science and Technology, Bangkok 10400, Thailand

Phone: +66-2201-7216, Fax: +66-2201-7234, E-mail: anuttra@dss.go.th

Introduction

Linear low density polyethylene (LLDPE) are major industrial polymers**.** They were produced by a copolymerization of ethene and α olefin such as propene, butene and hexene. The physical properties of polymer are dependent on the type of short chain branchs, a comonomer content and a comonomer sequence distribution. The information of microstructure can lead to an understanding of the kinetics and mechanism of the copolymerization and the physical properties of the copolymers.

An NMR Spectroscopy is one of the most poweful techniques for studying the composition and microstructure of ethene/α-olefin copolymers. There is a standard test method (ASTM-D5017-96) which is used to determine of a linear low density polyethylene (LLDPE) composition by ^{13}C NMR[1]. Singh, et.al.[2], for example, have used ^{13}C NMR for investingting the triads distribution of ethene-propene copolymers. Sahoo, et.al.[3] have employed multidimensinal NMR (1D and 2D) to studies the tacticity and comonomer sequence distribution of poly(ethene-*co*-butene).

In this work, the equations for calculating the comonomer content and triad sequence distribution of poly(ethene-*co*-propene) and poly(ethene-*co*-butene) with relatively low comonomer contents were developed and compared with those of the standard method ASTM[1] and other previous studies.[2-4]

Experimental

Preparation of polymers for NMR analysis.

The poly(ethene-*co*-propene) and poly(ethene-*co*-butene) copolymers with small amounts of propene and butene were kindly provided by Thai Polyethylene, Ltd. About 5% (w/v) of copolymers and 10% 1,4-dichlorobenzene-d$_4$/90 % 1,2,4 tricholobenzene (w/v) solvent mixture were placed in 5 mm NMR tubes. The sample was rotated at 20 rpm in a Kugelrohr oven at 120°C for 6 hours, after which, a clear uniform solution was obtained. A trace of hexamethyldisiloxane (HMDS) was added to original solvent mixture to serve as an internal chemical shift reference (δ_H = 0.09 ppm, δ_C = 2.03 ppm).

Quantitative ^{13}C NMR.

The ^{13}C NMR spectra were obtained with a Bruker Advance DPX 400 NMR spectrometer at 120 °C using a 5 mm broadband QNP probe, with a 9.57 μs 90 ° pulse, 17 kHz spectral width, 5120 transients, 3s acquisition time, a 10s relaxation delay. The spectra were obtained with WALTZ-16 proton decoupling. Data were exponential weighted with 2 Hz line broadening prior to a Fourier transformation. The ^{13}C NMR chemical shifts were reported relative to internal hexamethyldisiloxane at 2.03 ppm.

Statistical Analysis.

The statistical method, One-way analysis of variance (One-way ANOVA), at the α = 0.01 level was conducted to compare the comonomer contents of poly(ethene-*co*-propene) and (ethene-*co*-butene) calculated in this work and those standard method ASTM D 5017-96 [1] and other previous work.[2-4] The comonomer contents from each method were calculated for eight times. The raw time domain NMR data (FID) were reprocessed for each data. The analysis was performed on Microsoft excel

Results and Discussion

Structure and nomenclature. The general structure of poly(ethene-*co*-olefin) copolymers is shown in Figure 1. The carbons are labeled based on the nomenclature first defined by Carman[5] and later modified by Dorman[6] and Randall.[4] Methylene carbons along the backbone of an ethene/olefin copolymer chain are identified by a pair of Greek letters to indicate the distance to the nearest branch points in either direction. Carbons in the side-chains branches are identified by iB_n where 'i' indicates the position in the branch, starting with the methyl carbon in position 1, and the subscript 'n' indicates the length of the branch. The capital letters "E", "P" and "B" are used to indicate ethene, propene and butene monomer units, respectively.

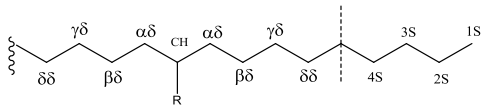

Figure 1. The general structure of poly(ethene-*co*-olefin) copolymers.

The ^{13}C NMR of poly(ethene-*co*-propene) copolymer.

The 100 MHz ^{13}C NMR spectrum of poly(ethene-*co*-propene) were illustrated in Figure 2. The spectrum show the signals of $1B_{EPE}$ (δ_C = 19.97 ppm), $\beta\delta_{PEEE}$ (δ_C = 27.44 ppm), δδ (δ_C = 30.00 ppm), $\gamma\delta_{PEEE}$ (δ_C = 30.38 ppm) CH_{EPE} (δ_C = 33.22 ppm) and $\alpha\delta_{PEE}$ (δ_C = 37.52 ppm). The data indicated that the polymer used in the study mostly consisted of EEE, EEP/PEE and EPE triad sequence. However, the signals of PPP, PPE/EPP and PEP were not detected in this polymer.

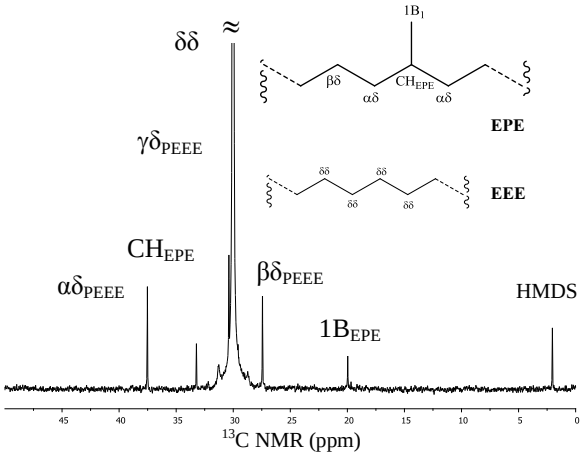

Figure 2. The 100 MHz ^{13}C NMR spectrum of poly(ethene-*co*-propene) containing 0.84 mol % propene.

The integration limits used for calculating the triad sequence distribution and comonomer content for each methods were shown in Table 1.

Table 1. The integration limits for the quantitative analysis of ethene (E) and propene (P) copolymer used in each method.

Area*			Integral region (ppm)		
This work	**Singh[2]**	**ASTM[1]**	**This work**	**Singh[2]**	**ASTM[1]**
A	A	A	38.38 - 36.84	48.00-45.00	47.5 - 44.5
B	B	B	34.16 - 32.71	39.00-36.00	39.8 - 36.8
C	C	C	31.96 - 28.07	33.90-32.81	35.5 - 32.5
D	D	C+D+E	27.94 - 26.55	31.77-29.43	35.5 - 25.8
E	E	F	20.74 - 19.21	29.37-28.10	25.8 - 23.8
	F	G		28.00-27.00	22.5 - 18.5
	G	H		25.22-24.00	Peak at 21.6
	H			20.62-19.02	

***** The capital letters in each method refer to a different integral region.

The compositional analysis of poly(ethene-*co*-propene) was shown in Table 2. The third column of Table 2 is the equations used in the calculation of triad sequence distributions and monomer content

Table 2. Quantitative Analysis of poly(ethene-*co*-propene) copolymer.

Structure	Equations for quantitative analysis			Composition (%)			
	This work	Singh [2]	ASTM [1]	This work	Singh [2]	ASTM [1]	Bernoullian[a]
[EEE]	1/2[(C-(A+D)/2)]+(A+D)/2	½(A-B+C+D+E+F+3G-2H)		97.55	97.19		97.41
[PEE+EEP]	(A+D)/2	1/(-A+0.5B-2G+H)		1.63	1.89		1.71
[PEP]	Not detected	1/(G)		0.00	0.01		0.01
[PPP]	Not detected	½(3A-0.5B+2C-H)		0.00	0.01		0.00
[EPP+PPE]	Not detected	½(-2A+B-4C+2H)		0.00	0.01		0.01
[EPE]	(B+E)/2	1/(C)		0.82	0.75		0.85
[P]	[EPE+EPP/PPE+PPP]	[EPE+EPP/PPE+PPP]	P_1 = (2A+B)/2 P_2= 2A+C-H P'= average : $(P_1+P_2)/2$				
[E]	[PEE/EEP+PEP+EEE]	[PEE/EEP+PEP+EEE]	E'=(C+D+E+F-A)/2				
%[P]	100 x [P]/[P]+[E]	100 x [P]/[P]+[E]	100 x [P]/[P]+[E]	**0.82**	**0.92**	**0.78**	
%[E]	100 x [E]/[P]+[E]	100 x [E]/[P]+[E]	100 x [E]/[P]+[E]	**99.18**	**99.08**	**99.22**	

[a] Based on P = 0.87 % and E = 99.13 % .

given by Singh, et.al.[2] Based on these equations, the integration of the signals from all of possible triads was used. However, the polymer used in this study had a small amount of propene, therefore, the signals from the PPP, PPE/EPP and PEP triad sequences were not visible in the spectrum. The equations for calculating of the low propene content copolymer were conducted in the current work and shown in the first column of Table 2.These equations were derived based on the detected signals in this polymer. The results of the Bernoullian statistics were shown in the last column of the table. The comomomer sequence distributions determined by ^{13}C NMR were fitted to the Bernoullian statistics indicating that the polymer used in this study is a random copolymer.

Statistical Analysis of poly(ethene-*co*-propene) copolymer.

It was found that there were no statistically significant differences between the comonomer content calculated by three different methods (This work, Singh and standard method ASTM D 5017-96) as determined by One-way ANOVA [F(2,21) =4.70, p= 5.78]

The ^{13}C NMR of poly(ethene-*co*-butene) copolymer.

The 100 MHz ^{13}C NMR spectrum of poly(ethene-*co*-butene) is presented in Figure 3. The spectrum shows the signals of $1B_{EBE}$ (δ_C = 11.19 ppm), $2B_{EBE}$ (δ_C = 26.70 ppm), $\beta\delta_{EBEE}$ (δ_C = 27.29 ppm), $\delta\delta$ (δ_C = 30.00 ppm), $\gamma\delta_{BEEE}$ (δ_C = 30.48 ppm), $\alpha\delta_{EBEE}$ (δ_C = 34.02 ppm) and CH_{EBE} (δ_C = 39.64 ppm). The spectrum shows that this polymer mostly consists of EEE EEB/BEE and EBE triad sequence. Nevertheless, the signals of BBB, BBE/EBB and BEB are not seen in the spectrum.

The integration limits used for calculating comonomer sequence distribution and comonomer contents for each methods were shown in Table 3.The compositional analysis is shown in Table 4. The third and forth column of Table 4 show the equations to calculate the triad sequence distributions and comonomer content given by Randall[4] and Sahoo, et.al.,[3] respectively. In these equations, the signals from all of possible triads are used for the calculations.

The polymer used in this work has low butene contents therefore the signals from BBB, BBE/EBB and BEB triad sequences were not found in the spectrum.The equations for calculating of the low butene content copolymer were shown in the second column of Table 4. These equations were derived only based on the detected signals in the polymer.

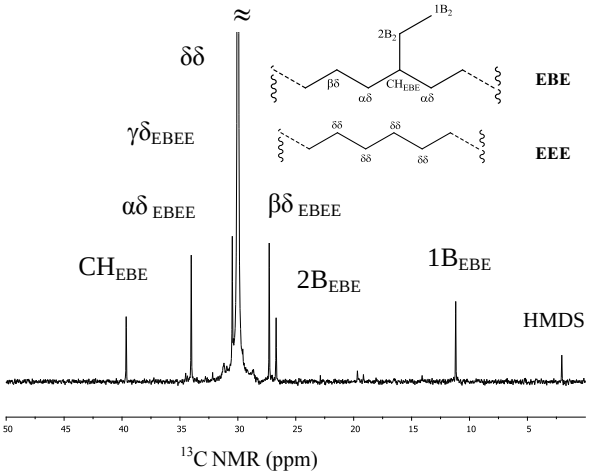

Figure 3. The 100 MHz ^{13}C NMR spectrum of poly(ethene-*co*-butene) containing 1.58 mol % 1-butene.

The comomomer sequence distribution determined by ^{13}C NMR were fitted to Bernoullian statistics revealed that the polymer analyed in the presented work is considered as a random copolymer.

Statistical Analysis of poly(ethene-*co*-butene) copolymer.

It was found that there were no statistically significant differences between comonomer contents calculated by four difference methods (This work, Randall, Sahoo and standard method ASTM D 5017-96) as determine by One-way ANOVA [F(3,28) =4.38 ,p= 4.57]

Table 3. The integration limits for the quantitative analysis of ethene (E) and butene (B) copolymer used in each method.

Area*				Integral region (ppm)			
This work	Randall [4]	Sahoo [3]	ASTM [1]	This work	Randall [4]	Sahoo [3]	ASTM [1]
A	A	A	A	41.57-38.00	40.50-39.10	41.57 - 37.99	41.5 - 38.5
B	B	B	A'	34.80-33.31	37.39-35.36	37.72 - 35.36	Peak at 39.4
C	C	C	B	31.47-28.27	35.20-34.00	34.80 - 33.31	37.8 - 36.8
D	D	D2	C	27.65-26.96	30.90-29.90	31.47 - 28.27	36.0 - 33.2
E	E	D3	D+E	26.91-26.49	27.4-26.60	30.73 - 30.32	33.2 - 25.5
F	F	E	F	11.61-10.83	24.5-24.24	27.65 - 26.50	25.2 - 24.0
	G	E7			11.0-10.50	26.91 - 26.49	
		F1-F3				24.94 - 21.85	
		G				11.61 - 10.00	
		G1				11.39 - 10.95	
		G1-G7				10.79 - 10.18	

*The capital letters in each method refer to a different integral region.

Table 4. Quantitative Analysis of poly(ethene-*co*-butene) copolymer.

Structure	Equations for quantitative analysis				Composition (%)				
	This work	**Randall[4]**	**Sahoo[3]**	**ASTM[1]**	**This work**	**Randall[4]**	**Sahoo[3]**	**ASTM[1]**	**Bernoullian[a]**
[EEE]	½[(C-(B+D)/2)]+(B+D)/2	½(D-½ E +½G)	$D_3/2+D_2/4$		95.42	95.30	97.32		95.41
[BEE+EEB]	(B+D)/2	E-G	E-G		3.06	3.15	1.16		3.01
[BEB]	Not detected	F	$F_1+F_2+F_3$		0.00	0.00	0.00		0.02
[BBB]	Not detected	2A-C	2A-C $G_5+G_6+G_7$ Average		0.00	0.01	0.01		0.00
[EBB+BBE]	Not detected	B	B		0.00	0.00	0.01		0.02
[EBE]	(A+E+F)/3	C-A-½B	G_1 E_7 Average		1.59	1.52	1.51		1.51
[B]	[EBE+EBB/BBE+BBB]	[EBE+EBB/BBE+BBB]	[EBE+EBB/BBE+BBB]	B_1 = (2A+B)/2 B_2=(A'+2C+2B)/4 B'= average : $(B_1+B_2)/2$					
[E]	[BEE/EEB+BEB+EEE]	[BEE/EEB+BEB+EEE]	[BEE/EEB+BEB+EEE]	E'=(2D+2E+2F-A'-B)/4					
%[B]	100 x [B]/[B]+[E]	100 x [B]/[B]+[E]	100 x [B]/[B]+[E]	100 x [B]/[B]+[E]	**1.51**	**1.64**	**1.51**	**1.68**	
%[E]	100 x [E]/[B]+[E]	100 x [E]/[B]+[E]	100 x [E]/[B]+[E]	100 x [E]/[B]+[E]	**98.49**	**98.36**	**98.49**	**98.32**	

[a] Based on B = 1.55 % and E = 98.45%

The results form poly(ethene-*co*-propene) and poly(ethene-*co*-butene) copolymers obtained from the equations developed in this study are not significantly different gather from the standard test method (ASTM-D5017-96)[1] and the pevious work[2-4], however, the process of the analysis of this research is simpler and more straightforward than procedure employed in other works, which normally took into consideration every possible signals in to the calculation even though some signals are not found in the spectrum. In this study, the calculation was only based on the detected signals.

Conclusions

The chemical shift assignments, the determination of comonomer content and triad sequence distributions of poly(ethene-*co*-propene) and poly(ethene-*co*-butene) with low comonomer content were presented in this work.

The statistical analysis (One-way ANOVA) demonstrated that the comonomer contents of poly(ethene-*co*-propene) and poly(ethene-*co*-butene) calculated in the present study were not significantly different from the standard method ASTM[1] and other works. [2-4]

The triad sequence distributions determined by ^{13}C NMR of both poly(ethene-*co*-propene) and poly(ethene-*co*-butene) were complied with the Bernoullian statistics. These results ultimatly indicated that the polymers analyed in the presented work should be considered as a random copolymers.

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References

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