Determination of Monomer Sequence Distribution in EPDM by ^{13}C-NMR: Third Monomer Effects

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ABSTRACT: The methods for sequencing ethylene–propylene copolymers (EPMs) by ^{13}C-NMR were extended to account for third monomer effects. The equations for calculating the ethylene content and monomer sequence distribution in EPMs were corrected for the presence of the third monomers 1,4 hexadiene, 2-ethylidene-5-norbornene, and 5,8-dicyclopentadiene that display resonances that overlap with the main chain EPM carbons. These corrections dramatically reduce the standard deviation among equivalent calculation methods. We also examined the effects of experimental conditions on the sequencing data including the choice of solvent, Cr^{3+} doping, and the presence of the nuclear Overhauser effect. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 523–530, 1999

Key words: ^{13}C-NMR; ethylene–propylene–diene terpolymer; sequencing; rubber

INTRODUCTION

Ethylene–propylene–diene terpolymers (EPDMs) are among the most versatile synthetic rubbers. Their applications range from roofing materials, weather stripping, and radiator hoses to additives for motor oil. This versatility is made possible by the range of physical properties spanned by adjusting the copolymer microstructure, including average monomer composition, sequence length distribution, and diene type and concentration. For example, copolymers with long ethylene sequences have a higher degree crystallinity as measured by DSC, resulting in enhanced tensile strength, although at the expense of low temperature elasticity.

^{13}C-NMR is one of the best ways of elucidating the microstructure of EPDM; it yields not only the average monomer composition, but information about the sequence distribution as well. Randall[1] and Cheng[2] developed methods involving the combination of ^{13}C spectral integrals to yield the ethylene content of EP rubber (EPM). Recently Di Martino and Kelchtermans developed a standardized methodology for the NMR sequencing experiment and validated the four commonly used calculation methods with a round-robin study.[3] Although this was a significant improvement for the analysis of EPMs, it results in some problems if applied without modification to EPDMs. The overlap of the third monomer resonances with the main chain EPM resonances causes errors in the integrals used for the calculations. Further, in the choosing of a solvent for the NMR of EPDM, one must consider possible reactions with the double bonds that are introduced into the system by the presence of the third monomer. In this article we extend the methodology of Di Martino and Kelchtermans[3] to generate methods that are formally correct for both EPM and EPDM and explore some additional possibilities for improving the efficiency of the experiment.

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EXPERIMENTAL

A dozen commercial EPDM rubber samples were used in this study. The EPDM-2-ethylidene 5-norbornene (ENB), EPDM-dicyclopentadiene (DCPD), and EPDM-1,4 hexadiene (HD) samples were supplied by DSM Copolymer, DSM Elastomers Europe, and E.I. DuPont, respectively. All polymers were made with a Ziegler–Natta type vanadium based catalyst.

NMR spectra were acquired on a Bruker AC-300 pulsed NMR spectrometer (Bruker Instruments, Billerica, MA) equipped with a 7.4-T superconducting magnet operating at ^{1}H and ^{13}C frequencies of 300 and 75 MHz, respectively. ^{1}H spectra were acquired as 2.5% solutions in *ortho*-dichlorobenzene-d_4 (ODCB-d_4) (Isotec, Miamisburg, OH), typically using 64–512 scans with a recycle time of 15 s. EPDM containing HD required a 60-s recycle time for quantitation of the slowly relaxing diene resonances. ^{13}C spectra were run as 10% solutions in ODCB-d_4 at 125°C in 10-mm NMR tubes and were referenced to $S_{\delta\delta}$ = 30.0 ppm. Recycle times were typically 20 s with 2000 scans being used with inverse gated decoupling or 512 scans with the nuclear Overhauser enhancement (NOE).

Method

Third Monomer Spectral Effects

A third monomer is commonly incorporated into an EPM that renders the resulting terpolymer (EPDM) capable of sulfur vulcanization. Three third monomers are used in industrial rubber production (ENB, HD, and DCPD) that distinguish themselves based upon reactivity, selectivity of incorporation, and subsequent cure properties. The structure of these third monomers as they would appear incorporated into the polymer chain is illustrated by Figure 1. The identification of these third monomers and their quantification can easily be accomplished with ^{1}H-NMR. Figure 2 illustrates the ^{1}H-NMR spectra of EPDMs with the three different third monomers incorporated. EPDM–ENB has two resonances at 5.3 and 5.1 ppm in a 3 : 1 ratio, reflecting the $E : Z$ conformational ratio; HD displays one resonance at 5.45 ppm; and DCPD exhibits 2 diene resonances of equal intensity at 5.5 and 5.7 ppm. The diene concentration can be easily calculated by integrating the olefinic region and the aliphatic region from 0 to 3.3 ppm and taking the appropriate

Figure 1 Structure of third monomers discussed in the text as they are incorporated into the polymer backbone, represented by P_n. (A) EPDM–ENB, (B) EPDM–HD, and (C) EPDM–DCPD. The numbering scheme corresponds to Figure 4.

ratios after subtracting the contribution of the third monomer to the aliphatic intensity. For completeness, the third monomer concentration (in weight percent) may be calculated from the following equations for EPDM–ENB:

$$\text{ENB (wt \%)} = \frac{d*120}{d*120 + \frac{1}{2}(a - 11d)*14} * 100 \quad (1)$$

for EPDM–HD:

$$\text{HD (wt \%)} = \frac{\frac{d}{2}*82}{\frac{d}{2}*82 + \frac{1}{2}(a - 4d)*14} * 100 \quad (2)$$

and for EPDM–DCPD:

$$\text{DCPD (wt \%)} = \frac{\frac{d}{2}*132}{\frac{d}{2}*132 + \frac{1}{2}(a - 5d)*14} * 100 \quad (3)$$

Figure 2 ^{1}H-NMR spectra of EPDM with incorporated ENB (top), 1,4 HD (middle), and DCPD (bottom). Samples were prepared to 2.5% concentration in *ortho*-dichlorobenzene-d_4. Sixty-four scans were acquired at 100°C with recycle times of 15 s for EPDM–ENB and EPDM–DCPD and 60 s for EPDM–HD.

in which d is the integral of the olefinic region and a is the integral of the aliphatic region. In these calculations the average monomer unit weight is taken to be 14, the mass of ethylene, regardless of the actual composition of the EPDM, in conformance with rubber industry convention.

Choice of Solvent

The solvent of choice for EPM is 1,1,2,2-tetrachloroethane-d_4^3 (TCE). TCE is an excellent solvent for EPDM as well and displays a triplet of ^{13}C resonances centered at 74 ppm, which is well out of the spectral region of either the main chain EP lines or the third monomer resonances. Unfortunately TCE is an extremely reactive solvent at the temperatures necessary to dissolve EPDM, and it rapidly attacks the double bonds in the third monomer leading to crosslinking and, perhaps, chloride addition to the double bond. Figure 3 illustrates this effect quite dramatically through the ^{1}H-NMR spectra of EPDM containing 9.4 wt % ENB in TCE-d_4 at 125°C. The concentration was 2.5% (w/v) to be able to dissolve the sample

within 1 h. The diene resonances at 5.1 and 5.3 ppm decrease with time at 125°C, and a resonance at 3.95 ppm appears to be growing in. The peak at 3.95 ppm is consistent with chloride addition across the double bond, although more evidence is needed to support this idea. Although clear at the beginning of this series, the sample acquires a deep brown color over the course of the experiment and after 24 h displays a significant amount of undissolved material. In addition to chloride addition, possible reactions include crosslinking and chain scission, although the details are beyond the scope of this work.

We can avoid these reactions by lowering the experimental temperatures. We measure the concentration of ENB by integrating the diene resonances of the ^{1}H-NMR spectra and summarize the results for $T = 80$, 100, and 125°C in Table I. At 80°C the sample is stable for 24 h; however, at this temperature the EPDM does not dissolve in concentrations necessary for ^{13}C-NMR. The corresponding experimental results using

Figure 3 ^{1}H-NMR spectra as a function of time of 2.5% EPDM–ENB in TCE-d_4 at 120°C. Sixty-four scans per spectrum were acquired with a recycle time of 15 s.

Table I   Weight Percent ENB by ^{1}H-NMR as Function of Time in Tetrachloroethane

Temperature (°C)	0 h	3 h	7 h	24 h
80	9.3	9.4	9.3	9.3
100	9.7	8.7	7.2	6.8
125	8.5	6.5	4.5	4.0

The ENB level after 33 h at 125°C was down to 2.6%.

ODCB-d_4 are reported in Table II. ODCB is much less reactive, showing only a slight loss in double bonds after 24 h at 125°C. For this reason we used ODCB for all of the sequencing work.

Assignments and Integral Regions

The resonance assignments and integral regions for EPDM–ENB, EPDM–HD, and EPDM–DCPD are summarized in Tables III–V. The main chain EP resonances are designated according to the notation of Carman et al.[4] and are in correspondence with the assignments of Carman et al.,[4] Smith,[5] and Cheng.[2] The assignments of the third monomer resonances are according to van der Velden.[6] Figure 4 illustrates the ^{13}C-NMR spectra of EPDM containing ENB, HD, and DCPD. There are clearly some resolved lines in the ^{13}C spectrum of each EPDM that can be uniquely attributed to carbons of the third monomer; however, several of the resonances overlap with main chain EPM resonances, particularly in the $S_{\alpha\alpha}$ region of the spectra. It is these overlapped regions that cause a problem for the sequencing calculations as discussed below.

There are many possible ways of combining resonance integrals to obtain the monomer sequence distribution of EPDM. Four of these methods,[1–3] which were developed for EPMs, that were validated by a round-robin study are reviewed by DiMartino and Kelchtermans[3] and follow below.

Table II   Weight Percent ENB by ^{1}H-NMR as Function of Time in o-Dichlorobenzene

Temperature (°C)	0 h	3 h	7 h	24 h
80	9.7	9.8	9.3	9.3
100	9.4	9.4	9.3	9.9
125	9.9	9.6	9.8	7.9

Table III ^{13}C Spectral Assignments and Integral Regions for EPDM–ENB

Assignment	Integration Limits (ppm)
ENB (C_{1E})	52.00–50.00
$S_{\alpha\alpha}$ + ENB (C_5 + C_6) + C_{1Z}	48.50–44.50
ENB (C_4)	43.00–41.00
$S_{\alpha\gamma}$ + $S_{\alpha\delta}$	39.40–36.85
ENB (C_{3E})	36.85–36.20
$S_{\alpha\beta}$	36.20–34.30
$T_{\gamma\gamma}$ + $T_{\gamma\delta}$ + ENB (C_7)	34.29–33.47
$T_{\delta\delta}$	33.47–32.80
$T_{\beta\gamma}$	31.90–31.05
$T_{\beta\delta}$ + $S_{\gamma\gamma}$	31.05–30.61
$S_{\gamma\delta}$	30.61–30.23
$S_{\delta\delta}$	30.23–29.32
$T_{\beta\beta}$	29.15–28.22
$S_{\beta\gamma}$	28.22–27.63
$S_{\beta\delta}$	27.63–26.63
$S_{\beta\beta}$	25.60–23.95
$P_{\beta\beta}$ + $P_{\beta\gamma}$ + $P_{\beta\delta}$	22.50–19.00
ENB (C_9)	15.00–13.00

Method 1: S + T is all secondary and tertiary carbons and P is all primary carbons.

$$\text{mol \% ethylene} = 100\left(\frac{S + T - 2P}{S + T}\right) \quad (4)$$

Table IV ^{13}C Spectral Assignments and Integral Regions for EPDM–HD

Assignment	Integration Limits (ppm)
$S_{\alpha\alpha}$	48.00–44.50
$S_{\alpha\gamma}$ + $S_{\alpha\delta}$ + HEX (C_{4T} + C_{5T})	40.00–36.80
$S_{\alpha\beta}$	36.20–34.55
$T_{\gamma\gamma}$ + $T_{\gamma\delta}$	34.29–33.47
$T_{\delta\delta}$	33.47–32.80
$T_{\beta\gamma}$	31.90–31.20
$T_{\beta\delta}$ + $S_{\gamma\gamma}$	31.20–30.61
$S_{\gamma\delta}$	30.61–30.21
$S_{\delta\delta}$	30.21–29.32
$T_{\beta\beta}$	29.25–28.33
$S_{\beta\gamma}$	28.13–27.63
$S_{\beta\delta}$	27.63–26.63
$S_{\beta\beta}$	25.60–23.95
$P_{\beta\beta}$ + $P_{\beta\gamma}$ + $P_{\beta\delta}$	22.50–19.00
HEX (C_{1T})	18.00–17.30

Table V ^{13}C Spectral Assignments and Integral Regions for EPDM–DCPD

Assignment	Integration Limits (ppm)
DCPD (C_{2X})	57.00–56.00
DCPD (C_{2N})	54.50–53.50
DCPD (C_{4X})	49.30–48.30
$S_{\alpha\alpha}$ + DCPD ($C_{1X,3X,5X,6X}$ + $C_{1N,4N}$)	47.50–44.00
DCPD (C_{3N},C_{6N},C_{5N})	44.00–40.50
DCPD (C_{10X})	40.50–39.50
$S_{\alpha\gamma}$ + $S_{\alpha\delta}$	39.50–36.85
DCPD (C_{7N})	36.85–36.20
$S_{\alpha\beta}$	36.20–34.30
$T_{\gamma\gamma}$ + $T_{\gamma\delta}$	34.29–33.45
$T_{\delta\delta}$	33.45–32.89
DCPD (C_{10N})	32.89–32.40
$T_{\beta\gamma}$	31.90–31.20
$T_{\beta\delta}$ + $S_{\gamma\gamma}$	31.20–30.58
$S_{\gamma\delta}$	30.58–30.23
$S_{\delta\delta}$	30.23–29.32
$T_{\beta\beta}$	29.15–28.22
$S_{\beta\gamma}$	28.22–27.63
$S_{\beta\delta}$ + C_{7X}	27.63–26.63
$S_{\beta\beta}$	25.60–23.95
$P_{\beta\beta}$ + $P_{\beta\gamma}$ + $P_{\beta\delta}$	22.50–19.00

Method 2:

$$P' = S_{\alpha\alpha} + 0.5(S_{\alpha\beta} + S_{\alpha\gamma} + S_{\alpha\delta}) \quad (5)$$

$$E' = 0.5[S_{\beta\beta} + S_{\beta\gamma} + S_{\beta\delta} + S_{\gamma\gamma} + S_{\gamma\delta} + S_{\delta\delta} + 0.5(S_{\alpha\beta} + S_{\alpha\gamma} + S_{\alpha\delta})] \quad (6)$$

As in another study,[3] for calculation methods 2, 3, and 4 we use $S_{\gamma\gamma} = 0.5(S_{\beta\delta} - S_{\gamma\delta})$ rather than attempting to integrate $S_{\gamma\gamma}$, which is often not resolved from $T_{\beta\delta}$.[2,3]

$$\text{mol \% ethylene} = 100\left(\frac{E'}{E' + P'}\right) \quad (7)$$

Method 3:

$$N_0 = S_{\alpha\alpha} + S_{\alpha\beta} + 3S_{\beta\beta} + 2S_{\beta\gamma} + 5S_{\gamma\gamma} + 3S_{\gamma\delta} + S_{\delta\delta} \quad (8)$$

$$N_1 = P_{\beta\beta} + P_{\beta\gamma} + P_{\gamma\gamma} \quad (9)$$

$$\text{mol \% ethylene} = 100\left(\frac{N_0 - N_1}{N_0 + N_1}\right) \quad (10)$$

Method 4:

$$n_0 = \frac{\begin{array}{c}S_{\alpha\alpha} + S_{\alpha\beta} + 3S_{\beta\beta} + 2S_{\beta\gamma} \\ + 5S_{\gamma\gamma} + 3S_{\gamma\delta} + S_{\delta\delta}\end{array}}{\begin{array}{c}S_{\alpha\alpha} + S_{\beta\beta} + S_{\gamma\gamma} \\ + 0.5(S_{\alpha\beta} + S_{\beta\gamma} + S_{\gamma\delta})\end{array}} \quad (11)$$

$$\text{mol \% ethylene} = 100\left[1 - \frac{2}{1 + n_0}\right] \quad (12)$$

For EPMs under the experimental conditions of DiMartino and Kelchtermans,[3] all four methods are equivalent. For EPDMs different third monomer resonances affect each method to a different extent, giving a large dispersion in the results. To illustrate, consider the sequencing data of Table VI. The four EPDM samples studied contain 0, 4.5, 8.0, and 9.4% ENB by weight as a third mono-

Figure 4 ^{13}C-NMR spectra of EPDM containing (A) 9.4 wt % ENB, (B) 2.8 wt % HD, and (C) 4.3 wt % DCPD as third monomers in ODCB-d_4. Two thousand five hundred scans were averaged using inverse gated decoupling with a recycle time of 20 s. Resonances corresponding to third monomer carbons are designated using the numbering scheme of Figure 1 and are in agreement with the assignments of van der Velden.[6]

Table VI   EPDM–ENB Sequencing Results

	EPDM-1	EPDM-2	EPDM-3	EPDM-4
ENB (wt %)	0.0	4.5	8.0	9.4
mol % C-2				
Method 1	62.2	68.2	68.0	69.4
Method 2	61.0	65.1	64.8	63.3
Method 3	61.7	67.3	67.5	68.0
Method 4	61.2	65.7	64.6	64.0
$\langle$mol % C-2$\rangle$	61.5	66.6	66.2	66.2
σ (four methods)	0.5	1.4	1.8	3.0

No correction is made to account for the presence of the third monomer.

mer. For the first sample, EPDM-1, which is really an EPM, the four calculation methods give essentially identical results with a standard deviation of 0.5% among them. With increasing ENB content the spread between the "equivalent" calculation methods increases, and EPDM-4 displays over a 6 mol % difference in ethylene content between methods.

Correction of Calculations

The correction of the calculations to account for the overlap of the third monomer resonances is relatively straightforward. One simply obtains the average third monomer concentration by integrating resolved third monomer resonances in the ^{13}C spectrum and subtracting the appropriate intensity from the overlapped integral regions. Corrections for EPDM containing ENB, HD, and DCPD follow: for EPDM–ENB:

$$\langle \text{ENB} \rangle = \frac{1}{4} \left(\frac{4}{3} C_{1E} + C_4 + \frac{4}{3} C_{3E} + C_9 \right) \quad (13)$$

$$S'_{\alpha\alpha} = S_{\alpha\alpha} - 2.25 \langle \text{ENB} \rangle$$

and

$$(T_{\gamma\gamma} + T_{\gamma\delta})' = T_{\gamma\gamma} + T_{\gamma\delta} - \langle \text{ENB} \rangle \quad (14)$$

in which the angle brackets denote the average of the integral values; for EPDM–HD:

$$\langle \text{HD} \rangle = C_{1T} \quad (15)$$

$$(S_{\alpha\gamma} + S_{\alpha\delta})' = S_{\alpha\gamma} + S_{\alpha\delta} - 2 \langle \text{HD} \rangle \quad (16)$$

and for EPDM–DCPD:

$$\langle \text{DCPD} - X \rangle = \frac{1}{3} \left(C_{2X} + C_{4X} + C_{10X} \right) \quad (17a)$$

$$\langle \text{DCPD} - N \rangle = \frac{1}{4} \left(C_{2N} + C_{3N} + C_{5N} + C_{6N} \right) \quad (17b)$$

$$S'_{\alpha\alpha} = S_{\alpha\alpha} - 4 \langle \text{DCPD} - X \rangle - 2 \langle \text{DCPD} - N \rangle \quad (18)$$

$$S'_{\beta\delta} = S_{\beta\delta} - \langle \text{DCPD} - X \rangle \quad (19)$$

in which DCPD $- X$ represents the exo conformation of DCPD and DCPD $- N$ represents the endo conformation. The calculations are corrected by substituting the primed quantities in eqs. (14)–(19) for their unprimed counterparts in eqs. (4)–(13).

The results obtained with corrected calculations for the samples of Table IV are reported in Table VII. The standard deviation between the methods dropped to a maximum of 0.5% and all four calculation methods are once again equivalent.

Similar results were obtained with EPDM containing HD or DCPD as third monomers, and these results are summarized in Table VIII. In both cases we notice a significant improvement, although in EPDM–HD only one integral is affected by overlap.

Sensitivity Optimization

Because the standard protocol for EPM sequencing requires 12 or more h,[3] we investigated ideas for shortening the experimental time without sacrificing the quality of the data. One possibility is the use of a paramagnetic relaxation agent such as Cr(acac)$_3$ to shorten the ^{13}C spin-lattice relaxation times, allowing for more rapid recycling. The longest T_1 values in EPM belong to methyl group carbons, which we measure at 125°C on a 300-MHz spectrometer as $T_1 = 4.4$ s. The 20-s

Table VII   EPDM–ENB Sequencing Results

	EPDM-1	EPDM-2	EPDM-3	EPDM-4
ENB (wt %)	0.0	4.5	8.0	9.4
mol % C-2				
Method 1	61.9	67.5	67.0	67.9
Method 2	61.7	67.0	67.5	67.6
Method 3	61.6	66.8	66.9	67.0
Method 4	61.8	67.5	67.2	68.2
⟨mol % C-2⟩	61.7	67.2	67.1	67.7
σ (four methods)	0.2	0.4	0.3	0.5

Calculations are corrected to account for the presence of the third monomer.

recycle time previously recommended, which is 4.5 times the longest T_1, is therefore adequate for quantitative purposes.[3] Adding 20 mg of $Cr(acac)_3$ to the 2.5 mL of ODCB-d_4 in the NMR tube reduces the maximum T_1 to 1.3 s, allowing quantitative acquisition with a recycle time of 7 s. This would appear to be a significant time savings; however, the average linewidth increases upon doping from 2.6 to 3.5 Hz, negating the sensitivity improvement per unit time.

A more significant improvement in sensitivity is obtained via the NOE by leaving the ^{1}H decoupling on during the recycle time. This gives a significant sensitivity enhancement; however, the NOE effect has not been used in EPDM sequencing because of concerns about different relative enhancements for different carbons.[3] In fact, this is not a problem with EPDM because the NOE enhancement appears to be constant for all carbons in the polymer chain.

Table IX reports the sequencing data of two EPDMs acquired under different experimental conditions. The second column is data for undoped EPDM-7 with acquisition under inverse gated decoupling using a recycle time of 20 s. The third column reports sequencing data on a $Cr(acac)_3$ doped sample that was acquired under inverse gated decoupling with a 7-s recycle time. The fourth column reports data acquired on the undoped sample, employing the NOE with a recycle time of 20 s. The last three columns are the corresponding data for a second polymer, EPDM-8. Note that the Cr^{3+} doping and the NOE both give excellent quantitative sequencing results. The enhancement that one obtains from the NOE allows most spectra to be acquired in under 3 h.

CONCLUSIONS

We extended the EPM NMR sequencing procedures to EPDM. Integrals of regions in the [13]C-

Table VIII   Sequencing Results for One EPDM–HD and One EPDM–DCPD

	EPDM-5		EPDM-6	
	Uncorrected	Corrected	Uncorrected	Corrected
Third monomer	HD	HD	DCPD	DCPD
wt % third monomer	2.8	2.8	4.3	4.3
mol % C-2				
1	67.1	66.9	68.8	68.5
2	65.8	66.3	66.2	67.4
3	66.6	66.6	67.9	67.5
4	66.1	66.1	66.4	68.0
⟨mol % C-2⟩	66.4	66.5	67.4	67.9
σ (four methods)	0.6	0.3	1.2	0.5

The results illustrate the effect of compensating for overlap of the third monomer resonances with the EP peaks. The weight percent third monomer content was measured with ^{1}H-NMR.

Table IX ^{13}**C-NMR Sequencing Results for EPDM-7 and EPDM-8 Under Differing Experimental Conditions**

	EPDM-7			EPDM-8		
	Undoped RD = 20 s	Doped RD = 7 s	NOE RD = 20 s	Undoped RD = 20 s	Doped RD = 7 s	NOE RD = 20 s
$\langle$mol % C-2$\rangle$	66.8	66.5	66.3	79.6	79.6	79.5
σ (four methods)	0.4	0.4	0.6	0.5	0.2	0.2
$\langle N \rangle$	4.59	4.55	4.53	6.12	6.11	6.16
$E_{N \geq 3}$	0.43	0.44	0.43	0.71	0.69	0.68
Triad distribution						
EEE	0.30	0.30	0.30	0.51	0.51	0.52
PEE	0.32	0.32	0.32	0.26	0.27	0.28
PEP	0.08	0.07	0.08	0.03	0.03	0.03
EPE	0.19	0.19	0.19	0.15	0.15	0.15
PPE	0.09	0.10	0.10	0.05	0.03	0.02
PPP	0.02	0.01	0.01	0.00	0.01	0.00

$\langle N \rangle$ is the mean number of ethylenes in sequences of three and larger and $E_{N \geq 3}$ is the fraction of ethylene in sequences of three and larger.[7] The triad distribution is calculated according to the method of Kakugo et al.[8]

NMR spectra where the main chain polymer resonances overlap with third monomer resonances are corrected by subtracting the measured third monomer contribution. We also examined the deleterious effect of TCE on the double bonds present in EPDM and recommended a change to ODCB. We showed that the NOE can be employed for EPDM sequencing without sacrificing the quality of the data. This modification reduced the experimental time to 3–6 h.

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