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^{13}C NMR Study of the Nonconjugated Diene Incorporated in Ethylene–Propylene–Diene Terpolymers

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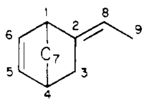
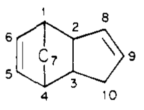
ABSTRACT: The 25-MHz ^{13}C NMR spectra of ethylene–propylene–diene terpolymers show peaks that can be uniquely assigned to the incorporated diene monomer. All diene third monomers studied, viz., 1,4-hexadiene (HEX), 2-ethylidene-5-norbornene (ENB), and 5,8-dicyclopentadiene (DCP), are adjoined on both sides by long (larger than or equal to four) methylene sequences. Evidence has been found for the incorporation of *trans*-HEX, 5-*exo*-6-*exo*-ENB, and 5-*exo*-6-*exo*-DCP. During terpolymerization no isomerization occurs from *endo*-DCP to *exo*-DCP.

Introduction

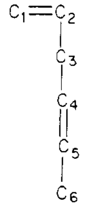
^{13}C NMR has been used sucessfully to determine monomer distributions and number-average methylene sequence lengths in ethylene–propylene (EP) copolymers.[1–3] EP copolymers constitute an important class of hydrocarbon elastomers but terpolymers containing a diene monomer such as 2-ethylidene-5-norbornene (ENB), dicyclopentadiene (DCP), and 1,4-hexadiene (HEX) form an even larger class, known as EPDM rubbers.



ENB



DCP



HEX

So far, the small amount (2–9% by weight) of copolymerized diene monomer, which makes these polymers capable of sulfur vulcanization, has not been the subject of ^{13}C NMR studies. Indeed, ^{13}C NMR measurements of an EP–ENB[1] and EP–DCP[4] rubber have been reported, but Carman and Tanaka et al.[1,4] did not pay attention to a number of small resonances assignable to the diene monomer. These authors merely focused their attention on the EP backbone ^{13}C resonances.

Via ^1H NMR, on the other hand, information can be obtained, if the type of diene used is known, about the double bond through which the diene is incorporated in the EP skeleton and about the concentration of the diene.[5–7] Several questions remain unsolved, at least at proton frequencies of 60–200 MHz, e.g., whether HEX is present as the cis or the trans isomer or both, whether ENB and DCP are linked to the backbone via 5-exo–6-exo, 5-exo–6-endo, 5-endo–6-exo, or 5-endo–6-endo bonds, whether *endo*-DCP isomerizes to *exo*-DCP in the EPDM rubbers, and whether the incorporated diene monomers are adjoined by long or short methylene sequences or even by propylene sequences. These intriguing questions have prompted us to analyze the 25-MHz ^{13}C NMR spectra of EPDM terpolymers, concentrating only on the ^{13}C resonances of the dienes present in them and bearing in mind that measurable shift differences exist between the model compounds *cis*- and *trans*-5-methyl-2-hexene,[8] 5,6-dimethylnorcamphor (i.e., 5,6-dimethyl-2-norbornanone) (four different stereoisomers),[9] and 5,6-dihydro-*endo*- and -*exo*-DCP.[10]

Experimental Section

A series of four EPDM rubbers (unfilled, uncured) is examined here. The commercially available terpolymers A, C, and D are from DuPont, Hüls, and DSM and contain HEX, ENB, and DCP, respectively. *endo*-DCP was used as a starting material for terpolymer D. The fourth terpolymer E, obtained by incorporation of *exo*-DCP, was prepared under the same conditions as terpolymer D (Ziegler–Natta catalysis, using vanadium–aluminum-based catalysts).[6] A copolymer of ethylene and ENB (E–ENB) (B) was prepared under the same conditions as the terpolymers D and E and was found to contain 9 mol % ENB. The composition of the copolymer and the terpolymers was determined by ^1H NMR and IR methods[5–7] and is given in Table I.

Table I
Mole Fractions of Ethylene and Third Monomer in Various Co- and Terpolymers As Obtained by ^1H NMR and IR Measurements

sample	mole fraction of ethylene	mole fraction of third monomer
A	68.0	0.7 (HEX)
B	91.0	9.0 (ENB)
C	69.0	2.2 (ENB)
D	74.5	2.2 (*endo*-DCP)
E	70.0	2.3 (*exo*-DCP)

A mixture of (*E*)- and (*Z*)-2-ethylidenenorbornane (ENA) was obtained via hydrogenation of ENB. No separation of the stereoisomers has been achieved.[11]

The ^{13}C NMR spectra of the copolymer and the terpolymers were recorded using 12-mm tubes at 25.18 MHz and 130 °C on a Varian XL-100/12A spectrometer provided with a Varian 620L computer and an interactive disk unit. The terpolymers were dissolved in a solvent mixture of 83% (v/v) 1,2,4-trichlorobenzene and 17% (v/v) 1,2-dideuteriotetrachloroethane, which provided the internal lock signal. Sample concentration for the terpolymers was 9% (w/v) and 5% (w/v) for the copolymer. The instrumental conditions were pulse angle, 60°; pulse delay, 2.5 s; acquisition time, 1.2 s; sweep width, 5000 Hz; and number of transitions for the terpolymers, 18000 (for the copolymer, 6000). Because the longest T_1 found for EP copolymers is 1.7 s (at 54 °C)[12] and for *endo*-DCP is 8 s,[10] the pulse spacings are not considered adequate for quantitative measurements. Chemical shift calibration was conducted assuming that the $S\delta^+\delta^+$ resonance[1] is to be found at 29.8 ppm. At room temperature, ^{13}C NMR spectra of a mixture of (*E*)- and (*Z*)-ENA were recorded at 25.18 MHz, using $CDCl_3$ as a solvent and internal locking agent.

Nomenclature

The ^{13}C resonances assignable to the incorporated diene are designated by the symbols for the respective carbon atoms (numbered in accordance with Table II) accompanied by subscripts and superscripts. For HEX the subscripts are C (cis) or T (trans), for ENB E (entgegen) or Z (zusammen), and for DCP N (endo) or X (exo). The superscripts are forms like x^5x^6 or n^5x^6, depending on whether the ^{13}C resonances of carbon atoms 5 and 6 in ENB and DCP are due to exo (x) or endo (n) substitution. Moreover, to the left and right are indicated the positions of the nearest methine groups, adopting a nomenclature system based on the one suggested for EP copolymers by Carman and Wilkes.[1] These nearest methine groups belong to either propylene (unparenthesized) or diene side

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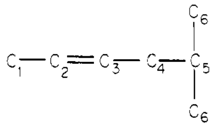
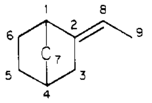
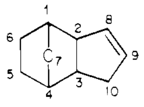
Table II
^{13}C Chemical Shifts for Some Model Olefins[a]

compound		carbon atom 1	2	3	4	5	6	7	8	9	10	ref
	trans	17.9	125.8	130.4	42.3	28.7	22.4					8
	cis	12.8	124.4	129.7	36.3	28.9	22.4					8
	*E*	45.2	145.9	35.5	36.5	28.6	29.8	39.1	110.7	13.4		*b*
	Z	39.6	144.9	38.9	36.3	28.4	29.0	38.7	111.5	14.1		*b*
	endo	39.8	53.2	42.7	41.4	22.1	25.4	41.4	132.8	130.2	32.3	10
	exo	40.6	56.0	44.1	43.3	29.0	29.3	31.8	131.6	132.5	40.0	10

[a] In ppm from internal Me_4Si in $CDCl_3$ solution. [b] See text.

Table III
^{13}C Empirical Increments for 5,6-Dimethyl-Endo- or -Exo-Substituted Norbornanes

	carbon atom 1[a]	2	3	4	5	6	7
5-exo-6-exo-	+8.2	+0.2	+0.4	+7.9	+11.0	+9.7	−6.0
5-exo-6-endo	+7.1	−0.6	+1.0	+6.7	+16.3	+17.6	−2.0
5-endo-6-exo	+8.0	−0.2	−7.0	+5.9	+15.8	+16.0	−1.6
5-endo-6-endo	+7.7	−0.5	−5.7	+5.9	+7.3	+9.7	+0.3

[a] Taken from ref 9, $CDCl_3$ solution, in ppm.

chains (parenthesized). This difference does not appear in the nomenclature if the distance to the nearest methine group (ignoring the methine groups of the dienes DCP and ENB) is equal to or larger than four carbons atoms (δ^+). Hence the terminal methyl group of HEX is represented as $\delta^+C_{1C}\delta^+$ or $\delta^+C_{1T}\delta^+$, and the bicyclo ring carbon atoms 5 and 6, the substituents being present in endo (5) and exo (6) positions and the diene adjoined by long (δ^+) methylene sequences, are indicated as $\delta^+C_{5E}{}^{n^5x^6}\delta^+$ and $\delta^+C_{6Z}{}^{n^5x^6}\delta^+$ for (*E*)- and (*Z*)-ENB or (*E*)- and (*Z*)-ENA.

Because no evidence has been found of diene monomers adjoined by short methylene sequences (i.e., sequences of less than four groups), the left and right additions are abandoned for the present.

The resonances of methylene carbon atoms near the diene incorporated in the chain are indicated in the manner proposed by Carman,[1] additional parentheses being used to indicate the diene present. In this manner it is possible to discriminate between $\alpha S\beta$ and $\alpha S(\beta)$ for HEX. In the case of ENB and DCP a five-letter combination has to be used due to the presence of two neighboring methine carbons, e.g., $(\delta^+\delta^+)S(\alpha\beta)$. Differences in methylene resonances due to effects of N and X and E or Z have not been observed and have therefore not been provided for in the nomenclature.

Results and Discussion

A. ^{13}C NMR Spectra of Model Olefins. Table II lists the ^{13}C chemical shifts of three selected model olefins. These model olefins were selected bearing in mind that the terminal unsaturation in HEX and the unsaturation in the bicyclo ring system of ENB and DCP are removed[5-7] when the dienes are incorporated in the EPDM rubber. Suitable model compounds for HEX were *cis*- and *trans*-5-methyl-2-hexene. The assignments given by Couperus et al.[8] were used as such in combination with the chemical shift data published by the same authors.

The assignments of the ^{13}C NMR spectra of 2-ethylidenenorbornane (ENA) were made using shift increment data and results from partial decoupling experiments and by comparison of our data with data published for 2-methylenenorbornane and (*E*)- and (*Z*)-ENB.[13]

Finally, the results obtained by other research workers for 5,6-dihydro-*endo*-DCP and -*exo*-DCP are also tabulated.[10]

B. Empirical Additivity Parameters. The Grant and Paul parameter values have been taken from ref 14. It has been tacitly assumed that these hold also for substituted olefins, whereas any temperature-related differences between the room-temperature recorded monomer and high-temperature recorded co- and terpolymer spectra have been ignored. Because of the failure of these Grant and Paul parameters to reflect steric interactions occurring in the 5,6 coaddition in ENB,[15] we have established a new set of increment data for the norbornane skeleton by calculating

$$\Delta_i = \delta_i^r(\text{5,6-dimethyl-2-norbornanone}) - \delta_i(\text{2-norbornanone})$$

for $i = 1...7$ and $r = n^5n^6, n^5x^6, x^5n^6$, and x^5x^6. The reference compounds used in these calculations were selected because of their similarity to the compounds under consideration and because of the ^{13}C NMR data available for the four different isomers 5-exo-6-exo (x^5x^6), 5-endo-6-exo (n^5x^6), etc.[9] The calculated additivity parameters Δ_i are given in Table III.

C. ^{13}C NMR Spectra of Co- and Terpolymers. Figure 1 shows the ^{13}C NMR spectrum of terpolymer A containing HEX, whereas in Figure 2 the five truncated spectra are shown for the terpolymers A, C, D, and E and the copolymer B. In all four terpolymer spectra, several small peaks are observed in addition to the major peaks. These major peaks can easily be assigned to ^{13}C resonances of the EP backbone. No new assignments for ^{13}C chemical

Table IV
Calculated ^{13}C Chemical Shifts (in ppm) for Ethylene-*cis*-HEX and Ethylene-*trans*-HEX Copolymers and Experimentally Determined Chemical Shifts for Terpolymer A

	carbon atom								
	C_1[a]	C_2	C_3	C_4	C_5	$(\alpha)S\delta^+$	$(\beta)S\delta^+$	$(\gamma)S\delta^+$	$(\delta^+)S\delta^+$
E-*cis*-HEX	12.8	124.4	128.9	31.2	38.1	34.4	27.3	30.1	29.8
E-*trans*-HEX	17.9	125.8	129.6	37.3	37.9	34.4	27.3	30.1	29.8
EPDM (A)	17.5	TCB[b]	TCB[b]	(37.4)[c]	38.2	34.1	(27.3)[c]	(30.1)[c]	(29.8)[c]

[a] Nomenclature is explained in text. [b] Obscured by 1,2,4-trichlorobenzene resonances. [c] Coincidence with EP resonances.

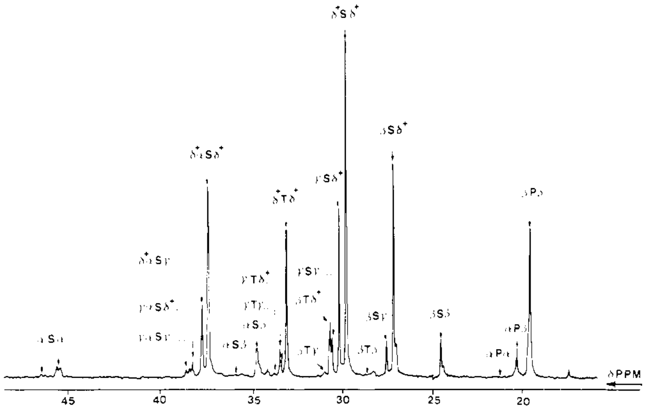


Figure 1. 25-MHz ^{13}C NMR spectrum of terpolymer A, viz., ethylene–propylene–1,4-hexadiene rubber, recorded in 1,2,4-trichlorobenzene at 130 °C. Only the aliphatic region is shown.

shifts have been made since the assignments of Carman and Smith.[1,3] We give a list of resonances of terpolymer A in Figure 1, denoting tertiary, secondary, and primary carbons by T, S, and P, respectively, and using two (sometimes three) Greek symbols to indicate the position of these carbons relative to the nearest tertiary carbons along the polymer chain.[1,2]

Skipping the ^{13}C resonances of the EP backbone, we concentrate on the small resonances due to the diene monomer incorporated in terpolymer A. In Table IV the ^{13}C chemical shifts calculated for hypothetical ethylene-*cis*-1,4-hexadiene (E-*cis*-HEX) and ethylene-*trans*-1,4-hexadiene (E-*trans*-HEX) copolymers have been listed for each carbon, assuming 1,4-hexadiene to be present in low molar ratios. Therefore these calculated shifts only hold for HEX units adjoined by long (≥4) methylene carbon sequences on both sides. We used the experimentally determined chemical shifts for *cis*- and *trans*-5-methyl-2-hexene (see Table II) and added the Grant and Paul parameter values.[14] For comparison, also the experimentally determined values observed for terpolymer A are given. It is evident that only three resonances uniquely assignable to HEX are not obscured by the EP spectrum, viz., the resonances at approximately 17, 34, and 38 ppm. Moreover, the two olefinic resonances are obscured by the solvent resonances of 1,2,4-trichlorobenzene.

The chemical shift of the CH_3 carbon of HEX proves that only *trans*-HEX is incorporated in the EPDM rubber. The agreement between the calculated chemical shifts for E-*trans*-HEX and the experimentally observed chemical shifts (Table IV) for terpolymer A shows that the distance between two methine carbon atoms belonging to HEX (C_{5T}) amounts to at least four carbon atoms. The analysis of the ^{13}C NMR spectra of EPDM terpolymers containing ENB or DCP is much more complex for reasons outlined in section B. Therefore, the ^{13}C chemical shifts of an E-ENB copolymer were calculated by adding the empirical shift increments listed in Table III to the experimental ^{13}C chemical shifts of ENA (Table II) (assuming the additivity increments to be the same for the *E* and *Z* isomers) and modifying these shifts with the small correction parameters (the Grant and Paul parameters[14]) necessary because of the presence of long (≥4) aliphatic chains instead of methyl groups. The calculated chemical shifts, given in Table V, were then compared with the experimental chemical shifts for copolymer B, focusing mainly on the *E* isomer (*E*/*Z*

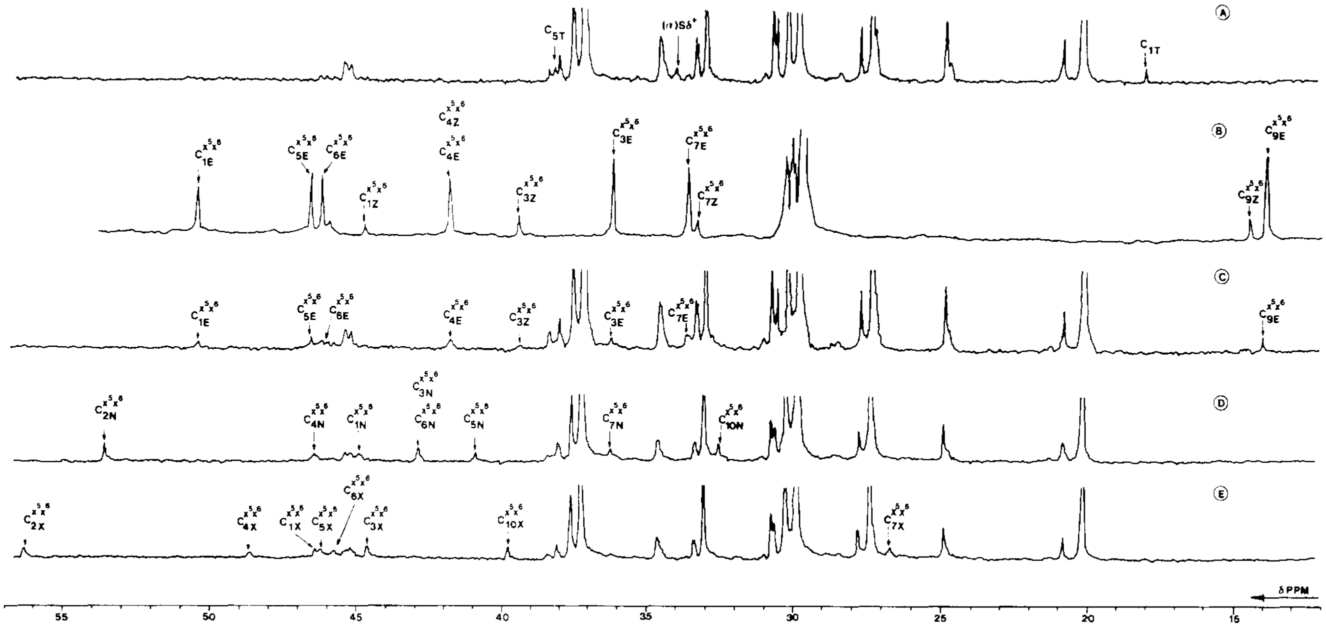


Figure 2. Truncated 25-MHz ^{13}C NMR spectra of copolymer B and four terpolymers A, C, D, and E containing, respectively, HEX, ENB, *endo*-DCP, and *exo*-DCP. All spectra were recorded in 1,2,4-trichlorobenzene at 130 °C. Assignments are discussed in text.

Table V
Calculated ^{13}C Chemical Shifts (in ppm) for Ethylene-ENB Copolymers and Experimentally Determined Chemical Shifts for Copolymer B and Terpolymer C

	carbon atom								
	C_{1E}	C_{2E}	C_{3E}	C_{4E}	C_{5E}	C_{6E}	C_{7E}	C_{8E}	C_{9E}
exo-5-exo-6	51.3	146.5	36.3	42.3	41.7	41.6	33.8	110.7	13.4
exo-5-endo-6	50.2	145.7	36.9	41.1	47.0	49.5	37.8	110.7	13.4
endo-5-exo-6	51.1	146.1	28.9	40.4	46.5	47.9	38.2	110.7	13.4
endo-5-endo-6	50.8	145.8	30.2	40.3	38.0	41.6	40.1	110.7	13.4
E-ENB (B)	51.0	147.1	36.4	42.3	47.0	46.6	33.9	110.2	13.4
EPDM (C)	50.8	147.1	36.5	42.5	47.5	46.7	33.6	111.2	13.2

	carbon atom								
	C_{1Z}	C_{2Z}	C_{3Z}	C_{4Z}	C_{5Z}	C_{6Z}	C_{7Z}	C_{8Z}	C_{9Z}
exo-5-exo-6	45.7	145.5	39.7	42.1	41.5	40.8	33.5	111.5	14.1
E-ENB (B)	46.1	146.3	39.7	41.8	45.5	46.1	33.5	111.8	13.9
EPDM (C)		146.1						110.5	13.9

Table VI
Calculated and Experimental ^{13}C Chemical Shifts (in ppm) for Terpolymers D and E, Containing *endo*- or *exo*-DCP, Respectively

	carbon atom									
	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
endo-DCP										
exo-5-exo-6	45.9	53.7	43.5	47.2	35.2	37.2	36.1	132.8	130.2	32.3
EPDM (D)	45.0	53.7	42.9[a]	46.5	40.9	42.9[a]	36.2			32.4
exo-DCP										
exo-5-exo-6	46.7	56.6	44.9	49.1	42.1	41.1	26.5	131.6	132.5	40.0
EPDM (E)	46.6	56.6	44.7	48.8	46.3	45.9	26.6			39.9

[a] Coincidence of ^{13}C resonances.

ratio for ENB and ENA is 3:1).

As is already clear from Table III, significant chemical shift differences occur between corresponding carbon atoms in the four stereochemical configurations of 5,6-dimethyl-2-norbornanone and hence also between corresponding carbon atoms in the four configurations of 5,6-dimethyl-2-ethylidenenorbornane. This holds especially for carbons 3, 4, 5, 6, and 7. However, small additional terms have to be added as increments to the chemical shifts of carbons 3, 4, and 7, respectively, the Grant and Paul parameter additions δ, $\gamma + 2\delta$, and 2δ. Therefore we have concentrated our analysis on the theoretically calculated and experimentally determined chemical shifts of these three carbons. All calculated chemical shifts are given in Table V, together with the experimental chemical shifts of the E-ENB copolymer and terpolymer C. An exceptionally good agreement is found between the calculated and experimental ^{13}C resonances if ENB is incorporated in long methylene sequences in the 5-exo-6-exo mode, proving also the existence of isolated ENB units present in the E-ENB copolymer. This result is in agreement with the low ENB:E molar ratio (see Table I). Admittedly, the shift difference between the calculated and experimentally found C_5 and C_6 resonances (±5 ppm) could point to the 5-exo-6-endo or 5-endo-6-exo configuration, but there is additional evidence in favor of the 5-exo-6-exo configuration. Carbon atoms 2 and 3 in 2-*exo*-3-*exo*-dimethylnorbornane are configurationally identical with carbon atoms 5 and 6 in incorporated ENA and with carbon atoms 2 and 3 in 5,6,8,9-tetrahydro-*exo*-DCP.[10] The shift difference between carbons 2 and 3 in 2-*exo*-3-*exo*-dimethylnorbornane and their counterparts in 5,6,8,9-tetrahydro-*exo*-DCP must equal $\beta + \gamma + 3°\ (2°)$, which is very similar to the Grant and Paul increment for the resonances 5 and 6 in incorporated ENA ($\beta + 2\gamma + 2\delta + 3°\ (2°)$). The calculated difference of 2.1 ppm is in strong disagreement with the experimental value of +8.5 ppm. Correcting this experimental increment for γ and δ, which are known to hold for these systems (cf. the ^{13}C resonances C_3, C_4, and C_7), one finds the ultimate result of +6 ppm. So apparently in these highly sterically strained systems, the Grant and Paul parameter β does not give a realistic value. These results are in agreement with the results obtained by Stothers et al. for 2,3-dimethylnorbornane.[15] Addition of the values obtained, i.e., +11.0 and +9.7 ppm (Table III) and +6 ppm, yields calculated ^{13}C chemical shifts of 45.6 and 45.5 ppm, which are in reasonable agreement with the experimentally determined chemical shifts of 46.6 and 47.5 ppm.

The ^{13}C NMR spectrum of terpolymer C is in very good agreement with the spectrum of copolymer B (see Figure 2), concentrating only on the diene resonances. Hence the following conclusions can be drawn (only for the E isomer): ENB is incorporated in the EPDM rubber in the 5-exo-6-exo position; ENB is adjoined by long (δ^+) methylene sequences, and there is no evidence of two neighboring ENB units or for the presence of propylene units adjacent to ENB.

As appears from Figure 2, only ^{13}C resonances due to the *E* isomer are seen quite clearly in the spectrum of terpolymer C. Resonances due to the *Z* isomer, which are clearly visible in the copolymer spectrum B (C_{3Z}, C_{7Z}, and C_{9Z}), hardly appear in the terpolymer spectrum. Only three resonances in the terpolymer spectrum can be identified as belonging to the *Z* isomer (C_2, C_8, and C_9). Therefore, the above conclusions can be drawn for the *E* isomer only, and we can only assume them to hold for the *Z* isomer as well.

From Figure 2 it is also clear that the methylene resonances in copolymer B are centered around the $S\delta^+\delta^+$ peak at 29.8 ppm. Comparable resonances in terpolymer A, e.g., $(\alpha)S\delta^+$, can be assigned but no assignment of the methylene resonances in the E-ENB copolymer and terpolymer C (excluding the EP methylene resonances) has been attempted due to the lack of suitable empirical increment parameters.

The analysis of the ^{13}C resonances of *exo*- and *endo*-DCP present in EPDM rubbers (see Figures 2) has been done in the manner presented above. However, no copolymers containing only E–*exo*-DCP or E–*endo*-DCP have been made. In the analysis, we followed the line of reasoning explained for terpolymer C; we used the same empirical increments as used for ENB (Table III) but did not add Grant and Paul increments to the ^{13}C resonances C_8, C_9, and C_{10} of 5,6-dihydro-*endo*- and -*exo*-DCP. The results of the calculations are given in Table VI, where it is assumed that the calculations hold for the respective ethylene–*exo*- or *endo*-DCP copolymers. Only the results for exo–exo additions are given, together with the experimental chemical shifts of terpolymers D and E. The following conclusions can be drawn with respect to terpolymer D and E:

endo- and *exo*-DCP are present in the same 5-exo–6-exo configuration in these polymers.

No isomerization of *endo*-DCP in *exo*-DCP or the reverse takes place for these terpolymers. This result is in agreement with results from IR measurements on similar systems.[16] Cesca et al.[16] have reinterpreted earlier work from our laboratory.[17]

endo- and *exo*-DCP are adjoined by long (δ^+) methylene sequences.

Accidental coincidence of ^{13}C resonances is noted for the C_3 and C_6 resonances in terpolymer D (*endo*-DCP).

Appreciable shift inaccuracies occur for the C_5 and C_6 resonances for both terpolymers.

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Registry No. A, 25038-37-3; B, 26521-87-9; C, 25038-36-2; D, 26589-66-2; E, 26589-67-3; *trans*-5-methyl-2-hexene, 7385-82-2; *cis*-5-methyl-2-hexene, 13151-17-2; (*E*)-ENA, 39173-91-6; (*Z*)-ENA, 39173-92-7; 5,6-dihydro-*endo*-DCP, 1755-01-7; 5,6-dihydro-*exo*-DCP, 933-60-8; 5-*exo*-6-*exo*-dimethyl-2-norbornanone, 51154-52-0; 5-*exo*-6-*endo*-dimethyl-2-norbornanone, 15925-44-7; 5-*endo*-6-*exo*-dimethyl-2-norbornanone, 15780-43-5; 5-*endo*-6-*endo*-dimethyl-2-norbornanone, 27141-85-1; E–*cis*-HEX, 83468-45-5; E–*trans*-HEX, 83815-98-9.

References and Notes

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Intramolecular Photocyclomerization and Excimer Emission of 1,1′-Di(1-naphthyl)diethyl Ethers: Model Systems of Poly(1-vinylnaphthalene)

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ABSTRACT: Temperature-dependent fluorescence spectra and intramolecular excimer decay curves of *meso*- and *rac*-1,1′-di(1-naphthyl)diethyl ether (D1NEE) show the existence of at least two excimers in both diastereomers. Broadening of the ^{13}C NMR absorptions at low temperatures of *meso*- and *rac*-D1NEE and the model compound 1-(1-naphthyl)ethyl methyl ether (1NEME) indicates that hindering of rotations occurs. Photoreaction yields for both isomers an intramolecular exo cycloadduct. Cleavage of the cycloadducts reveals that the hypsochromic excimer in *meso*-D1NEE can be correlated with the exo configuration. The data are interpreted on the basis of hindering of the rotation around the 1-naphthyl carbon–methine carbon bond in combination with steric interactions between the peri H_8, $H_{8'}$ hydrogens and the methyl substituents.

Introduction

The intramolecular photocyclomerization of nonconjugated dinaphthyl compounds with different chains can lead to several possible isomeric photoisomers[1–7] (Figure 1). Todesco et al. have reported a direct correlation between the excimer emission in solution and the configuration of the cyclomers of di(1-naphthyl)dimethyl ether (D1NME).[7] Photocleavage of the endo and exo cyclomer of D1NME in an ethanol matrix at 77 K yields for both products an emission spectrum identical with the excimer emission in solution. Todesco et al. conclude that the excimer precursors of the cyclomers have an identical but not complete sandwich overlap.

In a number of intramolecular excimer-forming systems in solution the spectral distribution and time-dependent fluorescence intensities have been analyzed as derived from one excimer species.[8] In the case of poly(*N*-vinylcarbazole), however, two spectral different intramolecular complexes

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