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Polymer 40 (1999) 4353–4363

polymer

Synthesis and characterization of carbon-13 labelled 2-ethylidene-5-norbornene containing EPDM rubber. Observation of crosslinking and oxidation

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Received 7 May 1998; received in revised form 14 September 1998; accepted 14 September 1998

Abstract

[2,8-$^{13}C_2$] ENB was synthesized from labelled acetic acid and terpolymerized in a batch reactor to [2,8-$^{13}C_2$] ENB–EPDM rubber ($M_w = 4.8 \times 10^5$, $d = 3$, ENB content ~ 8 wt.%, ethene to propene ratio ~ 1.8). Labelled ENB, its precursors and the EPDM were characterized by NMR spectroscopy. ENB is incorporated in the polymer chain through the *endo* cyclic double bond. Upon high temperature exposure to air of an NMR sample, the number of double bonds decreases due to crosslinking via addition of backbone radicals to double bonds. Some oxidation of double bonds occurs, giving rise to acetyl norbornene units. No significant cleavage of double bonds takes place. The labelling/NMR approach provides an excellent tool for studying (minor) chemical conversions in EPDM rubber. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: 2-ethylidene-5-norbornene; Labelling; EPDM

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1. Introduction

EPDM rubbers are commercially produced by terpolymerizing ethene, propene and a diene monomer, usually 2-ethylidene-5-norbornene (2-ethylidene-bicyclo[2.2.1]-hept-5-ene, ENB). The *endo* cyclic C(5)– C(6) double bond of ENB takes part in the polymerization process [1–3], leaving the C(2)– C(8) *exo* cyclic double bond intact. The polymer backbone of EPDM rubber does not contain unsaturations, which make it resistant to breakdown by UV degradation and ozone attack. Hence, EPDM is used for high temperature and outdoor applications such as cooling water tubes and window profiles. The residual ENB unsaturation is essential for further reaction of EPDM. During the accelerated sulfur vulcanization of EPDM the actual crosslinking reaction involves the allylic carbon atoms C(3) and C(9)[4,5]. Although EPM rubber can be crosslinked with peroxides, the introduction of a diene monomer results in a major enhancement of the peroxide crosslinking efficiency [6]. The residual ENB unsaturation is also essential for phenol–formaldehyde crosslinking of EPDM, as performed during PP/EPDM thermoplastic vulcanizate production [7]. The diene monomer content of EPDM is usually low, less than 10 wt.% which corresponds to (1 C=C unsaturation per 100 carbon atoms. As a result, it is normally very difficult to characterize reaction products of EPDM involving the unsaturation using spectroscopic techniques.

Chemical transformations of structural units in polymers can be investigated spectroscopically using a three stage strategy of: (i). synthesis of a ^{13}C enriched monomer; (ii). its incorporation into the polymeric chain; and (iii). investigation with ^{13}C NMR spectroscopy. This labelling/NMR strategy has been successfully used earlier to elucidate the molecular structure of the grafts in maleic anhydride functionalized polyolefins [8]. For studying the polymerization of ENB and the sulfur vulcanization of ENB containing EPDM, ^{13}C enriched ENB monomer is required. Since it is not commercially available, it will have to be synthesized, preferably starting from cheap, simple, labelled molecules. During the synthesis, which should be as efficient as possible, scrambling or dilution of the label should not occur.

Labelling the allylic carbon atoms of the ENB unit would allow a direct study of the atoms involved in sulfur vulcanization. However, the NMR signals from the allylic carbon atoms may be obscured by the other, large signals from the aliphatic carbons in the ethene and propene monomeric

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0032-3861/99/$ - see front matter
PII: S0032-3861(98)00665-X

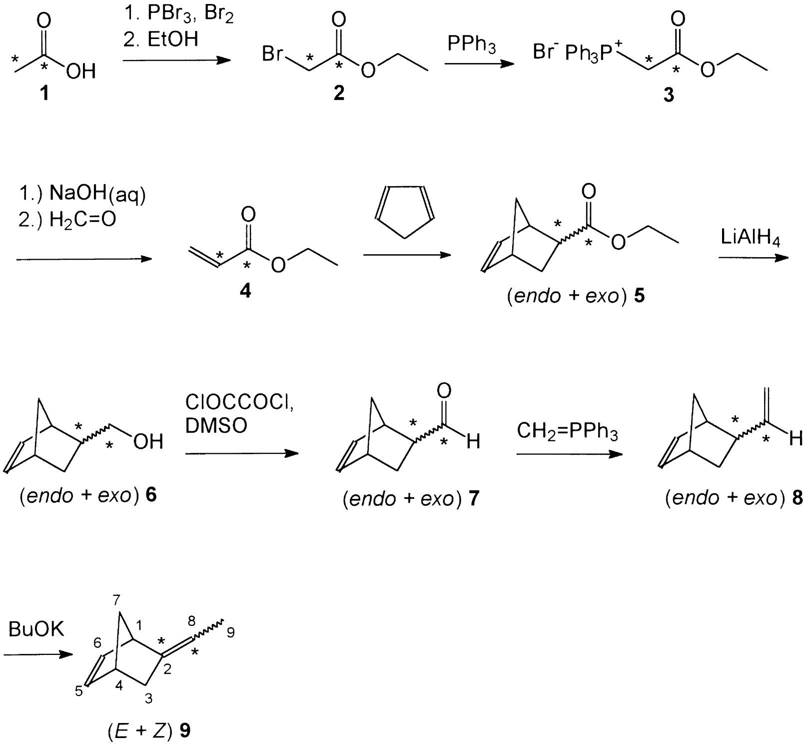

Fig. 1. Synthetic scheme for the preparation of [2,8-$^{13}C_2$] ethylidenebicyclo [2.2.1] hept-5-ene ([2,8-$^{13}C_2$]ENB). Asterisks denote the sites of the ^{13}C labels. Numbering of the carbon atoms is indicated.

units of EPDM. Fortunately, the chemical shift values of the olefinic ENB carbon atoms C(2) and C(8) will depend on the number and the type of substituents on the allylic carbon atoms, as can be predicted by increment rules [9]. The ^{13}C NMR responses from these double bond atoms are spectrally resolved in the NMR spectrum. Furthermore, the incorporation of two adjacent ^{13}C labels will result in scalar couplings and hence give rise to doublet signals, which are readily distinguishable in the ^{13}C NMR spectrum. The presence of adjacent ^{13}C labels allows the application of NMR filtering techniques such as the INADEQUATE pulse program [10]. The natural abundance of ^{13}C is 1.1%, hence the natural abundance of pairs of adjacent ^{13}C atoms is $\sim$ 0.01%. Labelling of such pairs increases the abundance of spin pairs by a factor of more than 8000, to 98%, which reduces measuring times for INADEQUATE experiments enormously. In summary, the olefinic C(2) and C(8) carbon atoms of the ENB unit offer the optimum sites for isotope enrichment.

This paper reports the total synthesis of [2,8-$^{13}C_2$] ENB starting from [1,2-$^{13}C_2$]acetic acid, as depicted in Fig. 1. The base structure of the norbornene moiety can be obtained by performing a Diels–Alder reaction between cyclopentadiene and ethyl acrylate [11–13]. The resulting *endo* and *exo* isomers of the ester can be converted to the aldehyde, which can be transformed to the vinyl compound using a Wittig reaction. After isomerization [14,15], ENB can be obtained. To eventually obtain [2,8-$^{13}C_2$]ENB, the Diels–Alder reaction has to be carried out with ethyl [1,2-$^{13}C_2$] acrylate, which can be obtained from a Wittig reaction between formaldehyde and ([1,2-$^{13}C_2$] carbethoxymethylene)triphenyl phosphorane. The latter chemical in its turn can be prepared from ethyl [1,2-$^{13}C_2$] bromoacetate, which can be prepared from commercially available doubly labelled acetic acid.

In addition, this paper reports the co-polymerization of the labelled ENB with ethene and propene, and the characterisation of the products. Special attention is paid to some chemical conversions of the labelled EPDM rubber that occurred during NMR data acquisition. In forthcoming papers the results of ^{13}C NMR studies into the vulcanization of EPDM will be presented.

2. Experimental

The spectra of the low molecular weight compounds were recorded on a Bruker WM300, a Bruker DPX300, or a Jeol FX200 spectrometer. Standard ^{1}H and ^{13}C spectra of the EPDM rubber were recorded at 110–115°C using a Varian Unity 300 or Bruker MSL400 spectrometer using a recycle delay of 10 s. Chemical shifts (δ) are given in ppm and referenced relative to TMS. For the spectra of the polymers the tetrachloroethane-d_2 solvent signal was used for internal calibration (δ 74.2 ppm). NMR spectra of low molecular weight compounds were recorded using chloroform-*d* as the solvent, to which TMS was added as an internal standard. Scalar (J) couplings are given in Hz. Elucidation of the

NMR spectra of the labelled low molecular weight compounds was aided by 1D and 2D NMR techniques and the use of the corresponding natural abundance compounds. In the NMR summaries that follow, ‘*endo*’ and ‘*exo*’ indicate signals originating from *endo* and *exo* isomers, respectively. ‘*Z*’ and ‘*E*’ denote signals from *Z*- and *E*-isomers, respectively, while the subscript n is used to indicate a hydrogen atom in an *endo* position and the subscripted x for one in the *exo* position. A subscript a is used to indicate a bridgehead hydrogen atom *anti* to the double bond, while subscript s indicates one that is *syn* to the double bond. The ^{1}H NMR spectra are particularly complex and show many overlapping peak patterns. When appropriate, a remark is made on the difference between spectra from the labelled and the corresponding unlabelled compounds. Only when *J*-couplings can be unambiguously determined is the assignment given. Mass spectra were recorded using a Finnigan MAT900 spectrometer in EI mode. FT–IR spectra of rubber films were recorded using a Perkin Elmer 1720x FT/IR spectrometer in 1-abex mode. Differential scanning calorimetry was performed using a Perkin Elmer DSC-7. Thermograms were recorded over an interval of − 60–100°C with a heating rate of 10°/min. Gel permeation chromatography was performed using a Toyo Soda (TSK) GMHXL-HT mixed bed (4X) set of columns coupled to refractive index and differential viscometer detectors. The polymer was dissolved at 140°C in freshly distilled 1,2,4-trichlorobenzene to which 1 g/l Ionol stabilizing agent was added.

2.1. Syntheses

*2.1.1. Ethyl [1,2-$^{13}C_2$] bromoacetate (**2**)*

An amount of [1,2-$^{13}C_2$] acetic acid (7.67 g, 124 mmol, Cambridge Isotope Laboratories, 99% enriched) was placed in a 250 ml three-necked flask equipped with a nitrogen inlet, a magnetic stirrer bar, a dropping funnel and a reflux condenser with a drying tube. The flask was cooled in an ice bath. From the dropping funnel phosphorus tribromide (33.5 g, 124 mmol) was slowly dosed. Subsequently, bromine (49.4 g, 310 mmol) was slowly added. The mixture was heated to 70°C overnight. After cooling down in an ice bath, ethanol (18 ml, 14.1 g, 307 mmol) was very slowly dosed. The mixture was stirred for 6 h and ethanol (75 ml, 59 g, 1.3 mmol) was added. After dilution with ether, the organic layer was washed with water, a saturated bicarbonate solution and brine. After evaporation of the solvent, 18.7 g of a pale brown liquid was obtained (90%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.31 [*t*, 3H, $^{3}J_{H-H}$ 7.13, CH_3]; 3.84 [*dd*, 2H, $^{2}J_{C-H}$ 4.7, $^{1}J_{C-H}$ 153.0, CH_2Br]; 4.24 [*dq*, 2H, $^{3}J_{C-H}$ 3.1, $^{3}J_{H-H}$ 7.1, OCH_2]. ^{13}C NMR (50 MHz, $CDCl_3$): (13.9 [*d*, $^{3}J_{C-C}$ 1.7, CH_3]; 25.9 [*d*, $^{1}J_{C-C}$ 64.5$^{13}CH_2Br$]; 62.2 [OCH_2]; 167.1 [*d*, $^{1}J_{C-C}$ 64.5, $^{13}C{=}O$].

*2.1.2. [1,2-$^{13}C_2$] carbethoxymethyltriphenylphosphonium bromide (**3**)*

An amount of 17.1 g of triphenylphosphine was dissolved in 50 ml of ethyl acetate and 9.47 g of ethyl [1,2-$^{13}C_2$]-bromoacetate was added. After stirring overnight, the precipitated product was filtered off, washed with ethyl acetate and dried in vacuo at 50°C, after which 20.7 g of a white powder was obtained (88%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.05 [*t*, H, $^{3}J_{H-H}$ 7.1, CH_3]; 4.03 [*dq*, 2H, $^{2}J_{C-H}$ 3.3, $^{3}J_{H-H}$ 7.1, OCH_2]; 5.49 [*ddd*, 2H, $^{1}J_{CH}$134.6, $^{2}J_{CH}$ 7.5, $^{2}J_{PH}$ 13.8 Hz, $P^{13}CH_2$]; 7.65–7.94 [*m*, 15H, aromatic protons]. ^{13}C NMR (50 MHz, $CDCl_3$): δ 13.7 [CH_3]; 33.0 [*dd*, $^{1}J_{PC}$ 56.1, $^{1}J_{CC}$ 59.3 Hz, $P^{13}CH_2$]; 62.9 [OCH_2]; 117.6 [*d*, $^{1}J_{PC}$ 87.9, phenyl P–C]; 129.4 [*d*, $^{3}J_{PC}$ 13.2, phenyl C(3)]; 132.1 [*d*, $^{2}J_{PC}$ 11.7, phenyl C(2)]; 135.1 [phenyl C(4)]; 164.2 [*dd*, $^{2}J_{PC}$ 3.6, $^{1}J_{CC}$ 59.1 Hz, $^{13}C{=}O$].

*2.1.3. endo and exo 2-Carbethoxy[2,8-$^{13}C_2$]-bicyclo[2.2.1]hept-5-ene (**5**)*

An amount of 10 g [1,2-$^{13}C_2$]carbethoxymethyltriphenylphosphonium bromide was dissolved in 50 ml of water, after which 23.1 ml of a 1 M NaOH solution in water and 75 ml of CH_2Cl_2 were added. When two clear phases had been obtained, the organic layer was separated and washed with two portions of 50 ml of water and with brine and dried over $MgSO_4$. Subsequently, the solvent was removed under reduced pressure. The solid phosphorane was transferred to a 250-ml flask equipped with a magnetic stirrer and dissolved in 100 ml of dry dioxane. The flask was purged with nitrogen and 1.05 g of *p*-formaldehyde was added. After stirring for 48 h at 60°C, approximately 3 g of cyclopentadiene was distilled into the flask, which contained the ethyl [1,2-$^{13}C_2$]acrylate formed. The reaction mixture was heated to 70°C for one more hour, after which the reaction mixture was washed with water and brine and dried over $MgSO_4$. After evaporation of the solvent, the product was purified using column chromatography and petroleum ether/diethyl ether = 9/1 as the eluent, yielding 3.14 g of a colourless oil (81%). ^{1}H NMR (300 MHz, $CDCl_3$), δ 1.21 [*t*, *J*7.1 Hz, CH_3, *endo*]; 1.25 [*t*, *J*7.1 Hz, CH_3, *exo*]; 1.25 [*m*, H(7a), *endo*]; 1.33 [*m*, H(3n), *exo*]; 1.40 [*m*, H(3n), *endo*]; 1.40 [*m*, H(7s), *endo*]; 1.41 [*m*, H(7s), *exo*]; 1.53 [*m*, H(7a), *exo*]; 1.88 [*m*, H(3x), *endo*] (In the ^{1}H NMR spectrum of the unlabelled compound splittings from *J*-couplings of 3.7, 9.3 and 11.9 Hz can be observed.); 1.92 [*m*, H(3x), *exo*] (In the ^{1}H NMR spectrum of the unlabelled compound splittings from *J*-couplings of 3.6, 4.7 and 12.0 Hz can be observed); 2.19 [*m*, H(2n), *exo*] (The $^{1}J_{13C-1H}$ is approx. 130 Hz while from the ^{1}H NMR spectrum of the unlabelled compound ^{1}H–^{1}H *J*-couplings of 1.8, 4.4 and 8.8 Hz can be determined.); 2.88 [*m*, H(1), *exo* and *endo*]; 2.93 [*m*, 1H, H(2), *endo*] (The $^{1}J_{13C-1H}$ is 135 Hz while from the ^{1}H NMR spectrum of the unlabelled compound ^{1}H–^{1}H *J*-couplings of 3.8 and 9.3 Hz can be determined.); 3.02 [*m*, H(4), *exo*]; 3.17

[*m*, H(4), *endo*]; 4.06 *m*, OCH_2, *exo*]; 4.11 [*m*, OCH_2, *endo*]; 5.91 [*dd*, *J*2.9, 5.9 Hz, H(6), *endo*]; 6.09 [*m*, H(6), *exo*]; 6.12 [*m*, H(5), *exo*]; 6.15 [*ddd*, *J*3.1, 5.7 Hz, $^4J_{13C(2)-H} \sim 3$ Hz, H(5), *endo*]. ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8 [OCH_2CH_3, *endo*]; 13.9 [OCH_2CH_3, *exo*]; 28.7 [*d*, $^1J_{C(2)-C(3)}$ 41.3 Hz, C(3), *endo*]; 29.8 [*d*, $^1J_{C(2)-C(3)}$ 40.7 Hz, C(3), *exo*]; 42.7 [*d*, $^1J_{C(2)-(C=O)}$ 57.7 Hz, C(2), *exo*]; 42.9 [*d*, $^1J_{C(2)-(C=O)}$ 61.1 Hz, C(2), *endo*]; In the spectrum of the labelled compound some signals are obscured by the very large $^{13}C(2)$ signal. From the ^{13}C NMR spectrum of the unlabelled compound the following assignments can be made. 41.2 [C(1), *exo*]; 42.1 [C(1), *endo*].) 45.3 [C(4), *endo*]; 46.1 [*d*, *J*3.3 Hz, C(7), *exo*]; 46.3 [C(4), *exo*]; 49.1 [*dd*, $^2J_{C(7)-C(2)}$ 4.4, $^3J_{C(7)-(C=O)}$ 4.4 Hz, C(7), *endo*]; 59.5 [*d*, *J*2.2 Hz, OCH_2CH_3, *endo*]; 59.7 [*d*, *J*2.2 Hz, OCH_2CH_3, *exo*]; 132.2 [*dd*, *J*2.1, 3.1 Hz, C(6), *endo*]; 135.6 [*dd*, *J*3.8, 4.1 Hz, C(6), *exo*]; 137.5 [*d*, *J*2.4 Hz, C(5), *endo*]; 137.9 [*d*, *J*3.0 Hz, C(5), *exo*]; 174.5 [*d*, $^1J_{C(2)-(C=O)}$ 61.1 Hz, C=O, *endo*];176.0 [*d*, $^1J_{C(2)-(C=O)}$ 57.7 Hz, C=O, *exo*]. MS *m/z* 168 [5%, $M]^{\cdot+}$]; 123 [6%, M-$C_2H_5O]^+$]; 103 [14%, M-$C_5H_5]^+$]; 94 [6%, M-O=^{13}C-OEt$]^+$]; 92 [11%]; 78 [6%]; 75 [8%]; 66 [100%, $C_5H_6]^{\cdot+}$].

2.1.4. *endo* and *exo* 2-Methanol[2,8-$^{13}C_2$]-bicyclo[2.2.1]-hept-5-ene (**6**)

2-Carbethoxy[2,8-$^{13}C_2$]-bicyclo[2.2.1]hept-5-ene (5, 8.00 g, 47.5 mmol, *endo*/*exo* mixture) was dissolved in 150 ml of dry THF and cooled to 0°C in an ice bath. $LiAlH_4$ (2.70 g, 70.5 mmol) was added over a 10 min period. The suspension was stirred for one hour, and subsequently the temperature was slowly raised to room temperature. The progress of the reduction was followed using TLC. When the reaction was complete the reaction mixture was poured onto ice, neutralized and washed with a saturated solution of NaCl in water. After drying over $MgSO_4$ the solvent was evaporated and the residue was purified by column chromatography using silica and petroleum ether/diethyl ether 9/1. A colourless liquid (5.33 g, 43.6 mmol, 92%) was obtained. The assignment of the NMR spectra was aided by the data in Ref.[12]. ^1H NMR (300 MHz, $CDCl_3$), (0.49 [*m*, H(3n), *endo*]; 1.10 [*m*, H(3x), *exo*]; 1.22 [*m*, H(3n), *exo*]; 1.25 [*m*, H(7a), *endo*]; 1.27 [*m*, H(7a), *exo*]; 1.32 [*m*, H(7s), *exo*]; 1.43 [*m*, H(7s), *endo*]; No signal can be discerned between (1.5 and 1.7 ppm. However, in the spectrum of the unlabelled compound, a multiplet signal at (1.60 ppm is present that is attributed to the H(2n) of the *exo* isomer. Clearly, due to the large $^1J_{C(2)-H(2)}$ coupling with the C(2) label, the signals are obscured by the larger signals at $\delta \sim 1.35$ and ~ 1.80 ppm. 1.80 [*m*, H(3x), *endo*]; 2.27 [*m*, H(2), *endo*] (there are in fact two multiplets, 131 Hz apart, equal to $^1J_{C(2)-H(2)}$.); 2.75 [*m*, H(1), *exo*]; 2.79 [*m*, H(4), *endo*]; 2.92 [*m*, H(1), *endo*]; 2.94 [*m*, H(4), *exo*]; 3.20 [*m*, CH*H*–OH, *endo*] (two multiplets, separated by the $^1J_{C-H}$ of 141 Hz.);3.26 [*m*, CH*H*–OH, *endo*] (two multiplets, separated by the $^1J_{C-H}$ of 141 Hz.); 3.48 [*m*, CH*H*–OH, *exo*] (two multiplets, separated by the $^1J_{C-H}$ of 140 Hz.); 3.65 [*m*, CH*H*–OH, *exo*] (two multiplets, separated by the $^1J_{C-H}$ of 140 Hz.); 5.95 [*dd*, *J*2.9, 5.7 Hz, H(6), *endo*]; 6.06 [*m*, H(5), *exo*]; 6.09 [*m*, H(6), *exo*]; 6.12 [*m*, H(5), *endo*]. ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.7 [*d*, $^1J_{C(2)-C(3)}$ 39 Hz, C(3), *endo*]; 29.4 [*d*, $^1J_{C(2)-C(3)}$ 37 Hz, C(3), *exo*] (In the ^{13}C spectrum of the corresponding unlabelled compound, a signal at δ 41.3, attributable to C(4) of the *exo* isomer, is present, in the spectrum of the labelled compound it is obscured by the large signals from the enriched sites.) 41.4 [*d*, $^1J_{C(2)-CH_2OH}$ 40 Hz, C(2), *endo*]; 41.4 [*d*, $^1J_{C(2)-CH_2OH}$ 39 Hz, C(2), *exo*] (In the ^{13}C spectrum of the corresponding unlabelled compound, a signal at δ 42.0, attributed to C(4) of the *exo* isomer, is present, in the spectrum of the labelled compound it is obscured by the large signals from the enriched sites.); 43.1 [*d*, $^1J_{C(2)-C(1)}$ 29 Hz, C(4), *exo*]; 43.4 [*d*, $^1J_{C(2)-C(1)}$ 30 Hz, C(4), *endo*]; 44.7 [*d*, *J*2 Hz, C(7), *exo*]; 49.3 [*t*, *J*3 Hz, C(7), *endo*]; 65.9 [*d*, $^1J_{C(2)-CH_2OH}$ 40 Hz, CH_2–OH, *endo*]; 66.9 [*d*, $^1J_{C(2)-CH_2OH}$ 39 Hz, CH_2–OH, *exo*]; 132.1 [*dd*, *J*2, 3 Hz, C(6), *endo*]; 136.3 [*t*, *J*3 Hz, C(6), *exo*]; 136.5 [*d*, *J*3 Hz, C(5), *exo*]; 137.1 [*d*, *J*2 Hz, C(5), *endo*]. MS *m/z* 126 [5%, $M]^{\cdot+}$]; 92 [10%]; 66 [100%, $C_5H_6]^{\cdot+}$].

2.1.5. *endo* and *exo* 2-Carboxaldehyde[2,8-$^{13}C_2$]-bicyclo[2.2.1] hept-5-ene (**7**)

10.0 g of oxalyl chloride (78.8 mmol, 1.2 eq) was dissolved in 100 ml of dry dichloromethane and cooled to − 60°C. Dimethyl sulfoxide (12.0 g, 154 mmol, 2.4 eq) and the *endo* and *exo* mixture of 2-methanol [2,8-$^{13}C_2$] bicyclo[2.2.1]hept-5-ene (6, 8.00 g, 64.4 mmol) were mixed and slowly added to the oxalyl chloride solution. After 45 min, 52.5 ml of triethyl amine (38.1 g, 375 mmol, 5.8 eq) was added and the reaction mixture was kept at room temperature for 5 min. The mixture was washed with 150 ml of water. The aqueous layer was washed twice with dichloromethane, and the combined organic layers were washed with slightly acidic water and a saturated sodium chloride solution. After drying over magnesium sulfate, the solvent was removed and the crude product was purified with column chromatography using a mixture of petroleum ether: diethyl ether in the ratio of 9:1 as the eluent. After evaporation of the solvent, 6.03 g of a colourless oil was obtained (48,9 mmol, 76%). ^1H NMR (200 MHz, $CDCl_3$), δ 1.24 [*m*, H(3n), *exo*]; 1.26 [*m*, H(7a), *exo*]; 1.32 [*m*, H(7a), *endo*]; 1.36 [*m*, H(7s), *exo*]; 1.42 [*m*, H(3n), *endo*]; 1.46 [*m*, H(7s), *endo*]; 1.91 [*m*, H(3x), *endo*]; 1.93 [*m*, H(3x), *exo*]; 2.25 [*m*, H(2), *exo*] (the large $^1J_{H(2)-C(2)}$ coupling causes the right-hand part of the signal to coincide with the signal at δ 1.9 ppm, while the low field part is overlapped by a signal from H(2) of the *endo* isomer which makes accurate determination of the $^1J_{C-H}$ impossible); 2.90 [m, H(2), *endo*] (the signal is split by the large $^1J_{H(2)-C(2)}$, causing the high field part of the signal to overlap with the left-hand side of the H(2) of the *exo* isomer, while the low field part overlaps with the signal at δ 3.2 ppm which makes accurate determination of the $^{1}J_{\mathrm{C-H}}$ impossible); 2.97 [*m*, H(1), *endo* and *exo*]; 3.11 [*m*, H(4), *exo*]; 3.24 [*m*, H(4), *endo*]; 5.98 [*m*, H(6), *endo*]; 6.12 [H(6), *exo*]; 6.18 [*m*, H(7), *exo*]; 6.19 [*m*, H(7), *endo*]; 9.41 [*ddd*, $^{3}J_{\mathrm{H(8)-H(2)}}$ 2.4, $^{2}J_{\mathrm{C(2)-H(8)}}$ 22.7, $^{1}J_{\mathrm{C(8)-H(8)}}$ 170 Hz, H(8), *endo*]; 9.78 [*ddd*, $^{3}J_{\mathrm{H(2)-H(8)}}$ 2.4, $^{2}J_{\mathrm{C(2)-H(8)}}$ 23.0, $^{3}J_{\mathrm{C(8)-H(8)}}$ 180 Hz, H(8), *exo*]. ^{13}C NMR (50 MHz, $CDCl_3$) δ 27.1 [*d*, $^{1}J_{\mathrm{C(2)-C(3)}}$ 48.4 Hz, C(3), *exo*]; 27.5 [*d*, $^{1}J_{\mathrm{C(2)-C(3)}}$ 40.0 Hz, H(3), *endo*]; 41.7 [C(4), *exo*]; 42.7 [C(4), *endo*]; 44.2 [*d*, $^{1}J_{\mathrm{C(1)-C(2)}}$ 26.3 Hz, C(1), *exo*]; 44.9 [*d*, $^{1}J_{\mathrm{C(1)-C(2)}}$ 27.8 Hz, C(1), *endo*]; 45.7 [C(7), *exo*]; 49.5 [C(7), *endo*]; 51.2 [*d*, $^{1}J_{\mathrm{C(2)-C(8)}}$ 39.6 Hz, C(2), *exo*]; 51.6 [*d*, $^{1}J_{\mathrm{C(2)-C(8)}}$ 42.5 Hz, C(2), *endo*]; 131.4 [C(6), *endo*]; 134.9 [C(6), *exo*]; 137.6 [C(5), *endo*]; 138.1 [C(5), *exo*]; 204.2 [*d*, $^{1}J_{\mathrm{C(8)-C(2)}}$ 39.5 Hz, C(8), *exo*]; 205.3 [*d*, $^{1}J_{\mathrm{C(2)-C(8)}}$ 43.1 Hz, C(8), *endo*]. MS *m/z* 124 [9%, $M]^{\cdot+}$]; 66 [100%, $C_5H_6]^{\cdot+}$].

2.1.6. *E- and Z- [2,8-$^{13}C_2$]ethylidene bicyclo[2.2.1]hept-5-ene (**9**)*

A 60% suspension of sodium hydride in mineral oil was washed with dry *n*-pentane and subsequently added to 200 ml of dry dimethyl sulfoxide. The suspension was stirred under a nitrogen atmosphere until a clear solution was obtained. Methyl triphenyl phosphonium iodide (24.0 g, 60.0 mmol) was added and the mixture was stirred for 1.5 h at 60°C. Subsequently, 6.00 g (8, 48, 9 mmol) of the *endo* and *exo* mixture of 2-carboxaldehyde[2,8-$^{13}C_2$] bicyclo[2.2.1] hept-5-ene (48.0 mmol) was added and the mixture was stirred for 3.5 h at 60–C. The mixture was poured onto ice and the organic layer was separated. The aqueous layer was extracted five times with 20 ml of *n*-pentane. The combined organic layers were washed with saturated ammonium chloride and sodium chloride solutions, after which the solution was dried over magnesium sulfate. After evaporation of the solvent, the crude product was dissolved in 350 ml of dry dimethyl sulfoxide and 4.40 g of potassium butoxide (180 mmol) was added. A nitrogen atmosphere was kept over the solution, which was stirred overnight at 60°C. The mixture was poured onto ice, and the organic layer was separated. The aqueous layer was extracted five times with 20 ml *n*-pentane. The combined organic layers were washed with saturated ammonium chloride and sodium chloride solutions, after which the solution was dried over magnesium sulfate. After evaporation of the solvent, the crude product was purified using column chromatography and petroleum ether: diethyl ether in the ratio of 9:1 as the eluent, yielding 3.7 g of colourless oil (31.6 mmol, 65%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.39 [m, H(7a), *Z*]; 1.41 [*m*, H(7a)*E*]; 1.56 [*ddt*, $^{3}J_{\mathrm{H(8)-H(9)}}$ 6.5, $^{3}J_{\mathrm{C(2)-H(9)}}$ 7.9, $^{5}J_{\mathrm{H(3n,\ 3x)-H(9)}}$ 1.2 Hz, H(9), *E*]; 1.58 [*m*, H(7s), *E* and H(7s), *Z*]; 1.68 [*m*, H(3n), *E*]; 1.70 [*m*, H(9), *Z*]; 1.70 [*m*, H(3n), *Z*]; 2.15 [*m*, H(3x), *E*] (The signal consists of two adjacent multiplets with $^{2}J_{\mathrm{H(3n)-H(3x)}}$ 15.3 Hz.); 2.24 [*m*, H(3x), *Z*]; 2.92 [*m*, H(4), *Z*]; 2.98 [*m*, H(4), *E*]; 3.10 [*m*, H(1), *E*]; 3.45 [*m*, H(1), *Z*]; 5.18 [*m*, H(8), *Z*] (The signal consists of two multiplets, $^{1}J_{\mathrm{C(8)-H(8)}}$ 152 Hz.); 5.41 [*m*, H(8), *E*] (The signal consists of two doublets of $^{1}J_{\mathrm{C(8)-H(8)}}$ 153 Hz.); 6.02–6.13 [*m*, C(5), C(6), *E* and C(5), C(6), *Z*]. ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.6 [*d*, $^{1}J_{\mathrm{C(8)-C(9)}}$ 43.0 Hz, C(9), *Z*]; 14.9 [*d*, $^{1}J_{\mathrm{C(8)-C(9)}}$ 43.4 Hz, C(9), *E*]; 31.0 [*d*, $^{1}J_{\mathrm{C(2)-C(3)}}$ 47.3 Hz, C(3), *E*]; 33.5 [*d*, $^{1}J_{\mathrm{C(2)-C(3)}}$ 47.0 Hz, C(3), *Z*]; 41.4 [C(4), *Z*]; 41.7 [C(4), *E*]; 44.6 [*d*, $^{1}J_{\mathrm{C(2)-C(1)}}$ 48.7 Hz, C(1), *Z*]; 49.5 [C(7), *Z*]; 50.2 [C(7), *E*]; 50.5 [*d*, $^{1}J_{\mathrm{C(2)-C(1)}}$ 44.1 Hz, C(1), *E*]; 112.7 [*d*, $^{1}J_{\mathrm{C(2)-C(8)}}$77.0 Hz, C(8), *E*]; 113.1 [*d*, $^{1}J_{\mathrm{C(2)-C(8)}}$ 77.4 Hz, C(8), *Z*]; 141.6 [*d*, $^{1}J_{\mathrm{C(8)-C(2)}}$77.3, C(2), *Z*]; 142.2 [*d*, $^{1}J_{\mathrm{C(8)-C(2)}}$ 77.1 Hz, C(2), *E*]. The ratio of the *E* and *Z* isomers is approximately 9 (mol/mol), as is deduced from the ratio of the areas of the ^{1}H signals and the intensities of the ^{13}C signals of the two isomers. MS *m/z* 122 [53%, $M]^{\cdot+}$]; 107 [72%, $M\text{-}CH_3]^{+}$]; 92 [64%]; 66 [100%, $C_5H_6]^{\cdot+}$].

2.1.7. *Ethene propene [2,8-$^{13}C_2$]ethylidene norbornene terpolymer ([2,8-$^{13}C_2$]ENB–EPDM)*

Since only a small amount of **9** was available, the polymerization was carried out on a small scale in a batch reactor. In order to achieve maximum ENB incorporation and to avoid compositional drift in the EPDM product, additional ethene and propene were dosed during the reaction. Before performing the synthesis with the labelled ENB, the polymerization was attempted with unlabelled ENB, which had been prepared via the same synthetic route as used to prepare **9**.

A 1.5 litre glass Büchi reactor was charged with 400 ml of heptane, 2.0 mol of **9** and 1 μmole of ethyl aluminium sesquichloride. The reactor was pressurized using pure ethene and propene monomers such that the propene: ethene ratio in the atmosphere above the solution was 2:1 (v/v). The temperature was kept at 30°C and the solution was stirred at 40 rpm. An amount of 6.25 μmole of vanadium oxytrichloride and 25 μmole of promoter were added through a pump. During the polymerization, variations in the concentrations of ethene and propene were kept to a minimum by adding them at a rate of 200 and 100 l/h (corrected for pressure difference), respectively. After 10 min another 1.5 ml of 9 and 25 μmole of promoter were added. After all additions the total amount of heptane solvent was 700 ml. After 30 min the reactor was depressurized and the solution was collected in a dry flask under a nitrogen atmosphere. The mixture was stabilized with 28 mg of Irganox 1076 (1 ml of a solution of 14 g in 400 ml of propanol and 100 ml of petroleum ether). Subsequently, the solvent was evaporated at 50°C under reduced pressure. Finally, the material was dried for 15 h at 50°C under reduced pressure, yielding 13.8 g of rubber. The product was stored in the dark under a dry atmosphere. The molecular weights (g/mol) were determined using GPC and the universal calibration method. The M_n is 1.55×10^5, M_w is 4.80×10^5, M_z is 1.35×10^6 g/mol.

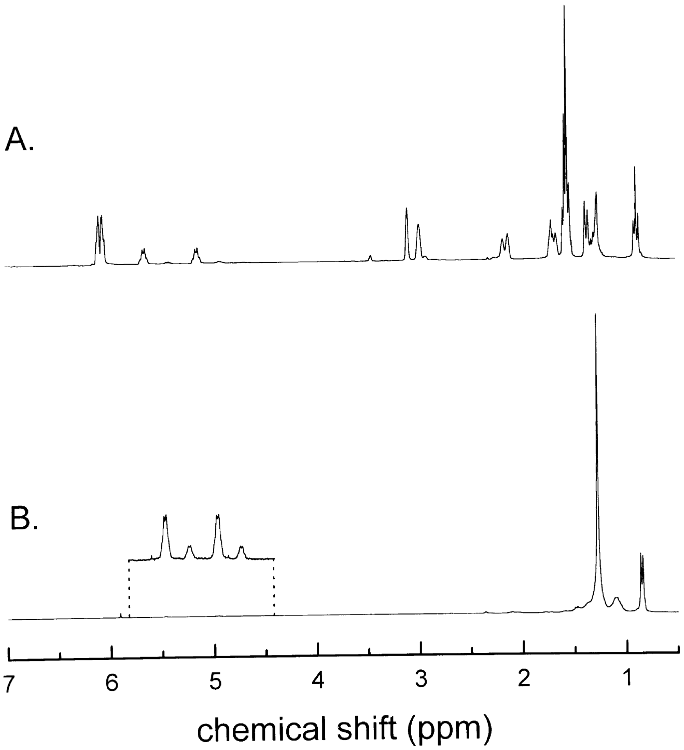

Fig. 2. ^{1}H NMR spectra of: A. [2,8-$^{13}C_2$] ENB (recorded at 300 MHz) and B. [2,8-$^{13}C_2$] ENB–EPDM (recorded at 300 MHz). The inset trace shows the magnified olefinic part of the EPDM spectrum.

3. Results and discussion

3.1. Labelled ENB monomer — synthesis

The strongly lachrymatic ethyl [1,2-$^{13}C_2$] bromoacetate **2** was obtained via conversion of [1,2-$^{13}C_2$] acetic acid **1** in a Hell–Volhard–Zelinskii reaction (Fig. 1). The fluffy white Wittig salt [1,2-$^{13}C_2$]carbethoxytriphenyl phosphonium bromide **3** was formed by reacting **2** with triphenyl phosphine. After deprotonation of **3**, the resulting sticky ylide was treated with *p*-formaldehyde to form ethyl [1,2-$^{13}C_2$] acrylate **4**, to which subsequently distilled cyclopentadiene was added. In the subsequent Diels–Alder reaction, a mixture of the *endo* and *exo* isomers of the sweet smelling 2-carbethoxybicyclo[2.2.2]hept-5-ene was obtained. The ratio of isomers was 3:1 as estimated from ^{1}H and ^{13}C NMR spectroscopy, in line with earlier reports [10]. No effort was made to separate the *endo* and *exo* isomers. Attempts were made to reduce the ester **5** to the aldehyde **7**, either directly using DIBAL-H [16] or by forming the methyl methoxy amide equivalent of **5**, followed by reduction. These procedures proved to be unsuccessful. Presumably, the main reason for this is the difference in reactivity between the *endo* and *exo* isomers. The product mixtures of the trial reductions were found to contain ester, aldehyde and alcohol, indicating some over-reduction. In another attempt, the ester was converted to the acetyl norbornene derivative using methyl lithium. The product, a mixture of *endo* and *exo* 2-acetyl-5-norbornene, was used as the substrate in a Shapiro reaction, which was expected to result in the formation of an unsaturated compound. However, this reaction did not give satisfactory results when performed on the mixture of stereoisomers. In the end, the particularly malodorous aldehyde was obtained by reducing the ester **5** to the alcohol **6** using $LiAlH_4$, followed by a Swern oxidation of **6**. The ^{1}H and ^{13}C NMR spectra of **6** are in good agreement with the literature data [12]. Compound **7** was treated with methylenetriphenyl phosphorane, yielding the vinyl compound **8**, which was immediately isomerized to ENB **9** using the strongly basic dimsyl anion [17]. In conclusion, [2,8-$^{13}C_2$]ENB **9** was synthesized from [1,2-$^{13}C_2$] acetic acid in an overall yield of 29%.

The synthetic scheme presented here will also allow the introduction of ^{13}C labels at the C(3) and methyl positions of the product ENB by using isotopically labelled *p*-formaldehyde in the first step and/or labelled C_1-phosphorane in the penultimate step.

3.2. Labelled ENB monomer — characterization

Rigid cyclic compounds are well known for their very complex ^{1}H NMR spectra. They can provide important information on the dependence of the sign and magnitude of *J*-couplings as a function of the number of bonds between the coupling protons, dihedral angles, etc. Important compounds in this class are cyclic terpenes and norbornenes [10–12,18–27]. The presence of two ^{13}C labels in the norbornene compounds prepared in this study gives rise to

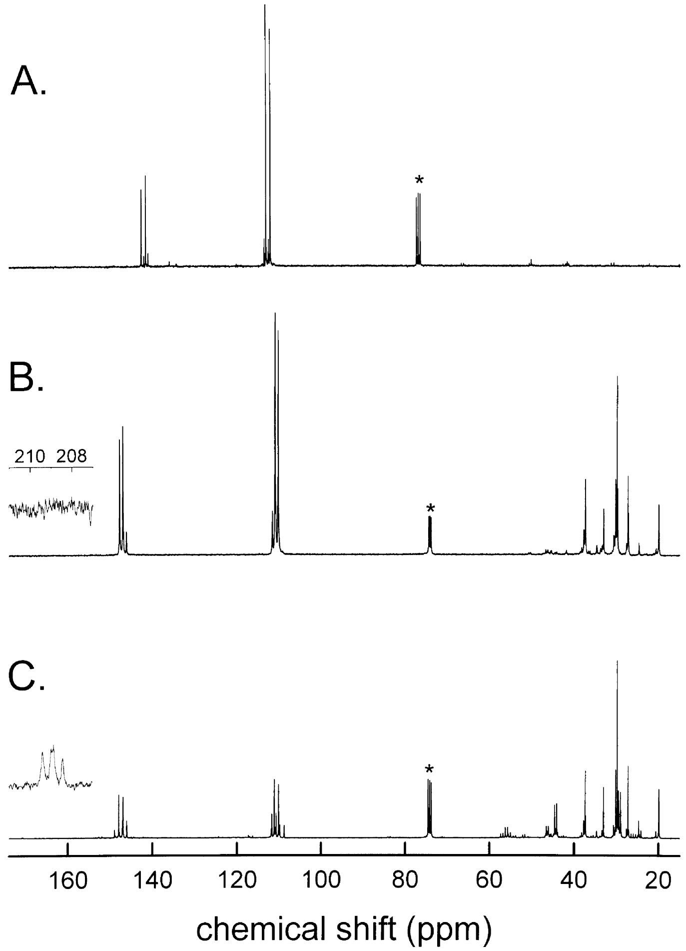

Fig. 3. ^{13}C NMR spectra of: A. [2,8-$^{13}C_2$] ENB (recorded at 300 Mhz), B. [2,8-$^{13}C_2$]ENB-EPDM (recorded at 400 MHz) and C. oxidized [2,8-$^{13}C_2$] ENB–EPDM (recorded at 300 MHz). The inset traces show the magnified carbonyl part of the EPDM spectra. Asterisks denote the solvent signals.

a large number of homo- and hetero-nuclear *J*-couplings over one and more bonds. This makes the NMR spectra more complex and, therefore, complete elucidation of spectra and the determination of all *J*-couplings was not attempted.

The assignment of the signals in the spectra of the labelled norbornenes was facilitated by the availability of the NMR spectra of the corresponding unlabelled compounds and by the abundant literature data. [10–12, 17–26]. For example, from literature it is known that generally 7-*anti* protons in norbornenes are more shielded, and resonate at higher field than the 7-*syn* protons [22,24]. The NMR data are summarized in the experimental section.

The ^1H NMR spectra of both the unlabelled and the labelled ethyl ester compound **5** show very complex responses of the OCH_2 moieties (data not shown). This phenomenon can be explained as being due to the occurrence of diastereotopy due to the asymmetric centre C(3) three C–C bonds away [28]. However, it can also be attributed to long-range *J*-couplings, as has been shown to occur in the corresponding unlabelled methyl ester compound [12]. The assignment of the NMR spectra of the alcohol compound **6** and the aldehyde **7** is in agreement with published data [11,19,29]. From the NMR data it is determined that in the product mixtures of the norbornene compounds **5**, **6** and **7** the ratio of isomers *endo*: *exo* is similar and approximately 3:1.

In the ^1H NMR spectrum of labelled ENB **9** (Fig. 2A) the signal at $\delta \sim 0.9$ ppm is attributed to some residual petroleum ether from the eluent which was used for the column chromatographic purification. The olefinic region of the ^1H NMR spectrum contains the complex responses from the H-atoms attached to C(5), C(6) and C(8). The signal between δ 4.7 and 5.9 ppm consists of a small doublet of multiplets and a more intense doublet, which are attributed to the hydrogen atom attached to C(8) of the *Z* and the *E* isomer, respectively. The averages of the chemical shifts of the doublets are 5.18 and 5.41 ppm and match the chemical shifts of the corresponding unlabelled compound well (δ 5.22 and 5.45 ppm). The observed large splittings are evidently due to the large one-bond C–H *J*-couplings of 152 and 153 Hz for the *Z* and the *E* isomer, respectively.

The ^{13}C NMR spectrum of **9** (Fig. 3A) is dominated by the very large doublets at δ 112.7 and 142.2 ppm, each with

Table 1
One bond *J*-coupling constants in norbornene compounds

Compound		*J*-coupling (Hz)		
		$^{13}C(2)-^{13}C(8)$	$^{13}C(2)-^{1}H$	$^{13}C(8)-^{1}H$
Endo 2-carbethoxy [2,8-$^{13}C_2$] bicyclo [2.2.1] hept-5-ene	**5** *endo*	61.1	135	–
Exo 2-carbethoxy [2,8-$^{13}C_2$] bicyclo [2.2.1] hept-5-ene	**5** *exo*	57.7	∽ 130	–
Endo 2-methanol[2,8-$^{13}C_2$] bicyclo [2.2.1] hept-5-ene	**6** *endo*	40.0	131	141
Exo 2-methanol[2,8-$^{13}C_2$] bicyclo [2.2.1] hept-5-ene	**6** *exo*	39.0	[a]	140
Endo 2-carboxaldehyde[2,8-$^{13}C_2$] bicyclo [2.2.1] hept-5-ene	**7** *endo*	43.1	[a]	170
Exo 2-carboxaldehyde[2,8-$^{13}C_2$] bicyclo [2.2.1] hept-5-ene	**7** *exo*	39.5	[a]	180
E [2,8-$^{13}C_2$] ethylidenebicyclo [2.2.1] hept-5-ene	**9** *E*	77.0	–	153
Z[2,8-$^{13}C_2$] ethylidenebicyclo [2.2.1] hept-5-ene	**9** *Z*	77.4	–	152
[2,8-$^{13}C_2$] ENB-EPDM		76	–	∽ 151

[a] Could not be accurately determined.

a splitting of ∼ 77 Hz. Further, smaller doublets with a splitting of ∼ 77 Hz are present at δ 113.1 and 141.6 ppm. These signals are attributed to the C(8) and C(2) atoms of the *E* and *Z* isomers of **9**, respectively. The splittings are caused by the prominent one-bond *J*-coupling between the ^{13}C isotopes.

From the ^{1}H and ^{13}C NMR spectra it is determined that for the ENB mixture of isomers (**9**) the *E* to *Z* ratio is ∼ 9:1. From the NMR and the MS data it is evident that ENB is labelled at the desired C(2) and C(8) sites and that no scrambling of the labels has occurred. Further, since no singlet ^{13}C NMR signals are found for the C(2) and C(8) atoms, it is concluded that no dilution of the labels has occurred and that the enrichment of ^{13}C labels at the desired sites is as good as complete.

The incorporation of two adjacent ^{13}C labels allows the determination of some C–C and C–H *J*-couplings. The magnitudes of some one-bond scalar couplings are summarized in Table 1. They supplement the large body of data on NMR parameters of norbornene compounds that already exists [10–12,18–26]

Table 2
New signals in the ^{13}C NMR spectrum of [2,8-$^{13}C_2$] ENB–EPDM upon exposure to air at high temperature

Chemical shift (ppm)	Splitting (Hz)
25.2	40
26.3	38
29.2	35
29.3	34
44.4	34
46.3	35
46.5	35
51.9	38
54.1	39
55.3	42
56.0	41
57.1	41
109.3	75
148.5	75
208.7	43
209.1	40

3.3. Labelled EPDM — synthesis and characterization

13.8 g of transparent high molecular weight [2,8-$^{13}C_2$] ENB–EPDM of narrow molecular weight distribution ($d = 3$) has been prepared in a batch polymerization reaction. Its solution ^{1}H NMR spectrum (Fig. 2B) contains two pairs of complex shaped signals between δ 4.6 and 5.7 ppm attributable to the olefinic proton of the labelled ENB monomer unit. The signals of both pairs, which are centred at δ 5.1 and 5.0 ppm, are ∼ 151 Hz apart, the magnitude of the $^{1}J_{C(8)-H(8)}$. The ratio of the areas of the C(8)–H ^{1}H NMR signals of the *E* and *Z* isomers is approximately 4. Since no signals can be discerned between δ 6.0 and δ 6.2 ppm, the range characteristic of the C(5)– C(6) olefinic hydrogen atoms of the original ENB monomer, it is concluded that no or very little ENB has been incorporated through the exclusive polymerization of the *exo* cyclic C(2)–C(8) double bond. Hence, it is concluded that ENB has mainly or exclusively been incorporated into the polymer through the *endo* cyclic C(5)– C(6) double bond. This is corroborated by the observation that the aliphatic region of the ^{13}C NMR spectrum (Fig. 3B) of [2,8-$^{13}C_2$] ENB–EPDM recorded at 110°C closely resembles a typical EPM spectrum [31]. Significant

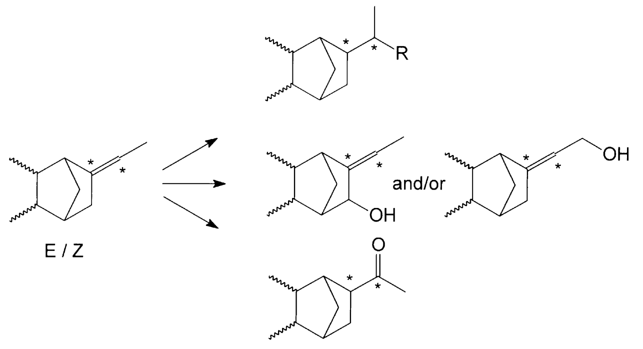

Fig. 4. Proposed structures that occur in EPDM rubber under NMR acquisition conditions and in the presence of air. R = EPDM backbone, asterisks denote the sites of the ^{13}C labels.

reaction of the labelled double bond would have given rise to new aliphatic signals in the ^{13}C spectrum.

From the olefinic peak areas of the ^{1}H NMR spectrum it is determined that the ENB content is ~ 8.1 wt.%. On the basis of the areas of typical ethene and propene unit peaks the ratio of these two monomeric units is found to be 1.75 (w/w).

Due to the labelling of C(2) and C(8), large olefinic signals dominate the ^{13}C NMR spectrum. These comprise two pairs of doublets: large doublets at δ 110.6 and 147.4 ppm from the more abundant *E* ENB unit and smaller doublets at δ 111.9 and 146.6 ppm for the *Z* isomer. For both sets the scalar coupling ($^1J_{C(2)-C(8)}$) is ~ 75 Hz, which is a typical value of a one-bond sp^2–sp^2 C–C coupling. The intensity ratio of the olefinic ^{13}C NMR signals of the isomers is approximately 5 (see Fig. 3B). From this, and from the ^{1}H NMR data, it is estimated that the *E* to *Z* ratio for the ENB monomer in the EPDM rubber is roughly 4–5. Hence, some 80–84% of the ENB units is in the *E* isomeric form. However, the *E* to *Z* ratio in the isomer mixture of the labelled ENB monomer fed to the polymerization reactor was about 9. Consequently, either the *Z* isomer is incorporated into the polymer backbone with a certain preference, or some isomerization involving the C(2)– C(8) double bond has occurred during polymerization.

The ethene, propene and ENB contents of the rubber were determined using the standardized ASTM D6047 and ASTM D3900 FT–IR methods. The IR spectrum obtained is typical of an EPDM rubber. The absorption of the C(2) = C(8) double bond of the ENB monomer, which is at 1685 cm^{-1} for unlabelled EPDM, has shifted from 58 to 1627 cm^{-1} due to the isotope substitution. If it is assumed that the extinction coefficient is not altered by the isotope enrichment it can be concluded that the labelled EPDM has an ENB content of 7.9 wt.%. Further, from the FT IR spectrum it can be derived that the ethene to propene unit ratio is 1.83 (w/w). The NMR and FT–IR data on the ENB content and the ethene to propene ratio are in very good agreement, and hence it may be concluded that the incorporation of [2, 8-^{13}C$_2$] ENB is approximately 8 wt.%, whereas the ethene to propene ratio is ~ 1.8 (w/w). This amounts to an approximate molar ratio for the monomeric units of ENB: ethene: propene of 1:32:12. Consequently, the weight fraction of ethene monomer is ~ 0.59, which is a typical value for commercial EPDM rubbers [1].

The enthalpy of melting as determined with DSC is ~ 18 J/g. The temperature at which the heat of melting is at its maximum is − 6°C. Upon cooling, ethene-rich segments of the polymer backbone crystallize from 9°C until the glass transition is reached at − 50°C. These data are consistent with those of a typical EPDM rubber of ~ 60 wt.% ethene content.

3.4. EPDM oxidation

During our investigation it was observed that when an EPDM solution in tetrachloroethane is heated to 115°C for a prolonged period to obtain the NMR spectra, and no elaborate precautions are taken to prevent contact with the air, the ^{13}C NMR spectrum of the labelled EPDM rubber changes significantly (Fig. 3C). Using the large response from the polymethylene sequences at δ 29.8 ppm [30, 32] as an internal calibration, it can be estimated that the amounts of *E* and *Z* ENB monomers have decreased by factors of 5 and 2, respectively. Clearly, the ENB double bonds are subject to some chemical reaction. The *E* ENB monomer is converted preferentially, causing the *E* to *Z* ENB ratio to decrease from 4–5 to 2. The disappearance of the signals from ^{13}C enriched olefinic carbons is accompanied by the emergence of many new aliphatic signals. These signals are all doublets of considerable intensity [$\geq$ 1% of the (CH$_2$)$_n$ signal] with a splitting of ~ 35–40 Hz (Table 2). This magnitude is typical of a *J*-coupling through a single sp^3–sp^3 C–C bond. From their chemical shifts it is inferred that these new labelled aliphatic carbon atoms bear hydrogen and/or carbon substituents. Such structures can be formed when secondary and/or tertiary EPM backbone radicals add to the ENB double bond (Fig. 4, top). The feasibility of this type of crosslinking reaction is known from the peroxide vulcanization of EPDM rubber [6]. Here, the necessary radicals may be formed by some action of oxygen or be generated by the tetrachloroethane solvent at elevated temperatures [33]. Since the spectra of Fig. 3b and c were recorded at practically identical temperatures, the generation of backbone radicals is probably due to the presence of some oxygen in the NMR sample. This demonstrates that when NMR spectra of EP(D)M rubbers in (chlorinated) solvents are recorded, strict measures must be taken to exclude air from the sample. This condition is not explicitly mentioned in most standardized NMR data acquisition methods [34,35].

Upon exposure to air at high temperatures not only the unsaturation of the ENB moiety is converted to saturated crosslinked structures, but also new structures with intact unsaturations are formed. A new pair of doublets at δ 109.3 and 148.5 ppm arises in the olefinic region. The doublets are of approximately equal intensity and have a splitting of ~75 Hz. Clearly, the signals are subject to a one-bond C=C sp^2–sp^2 *J*-coupling. This proves that the double bond is intact, but that carbon atoms near the double bond have changed with respect to their functionality. In view of the small chemical shift difference it is likely that carbon atoms at γ and δ positions relative to C(2), i.e. C(4) through C(7) have undergone some chemical changes through action of oxygen radicals (Fig. 4, centre). In the spectrum of Fig. 3c a smaller pair of doublets of approximately equal intensity is present at δ 116.8 and 152.3 ppm. On the basis of the chemical shift change relative to the unmodified units it can be assumed that these signals are from the labelled olefinic carbon atoms of an ENB unit that has undergone some reaction at the allylic positions [36–38].

Further, upon exposure to air at high temperatures a small signal arises around δ 209 ppm (see inset Fig. 3b and c). In view of the chemical shift, this signal is most likely to originate from a ketonic carbonyl moiety. The signal appears to consist of two doublets, each with a splitting of ~ 42 Hz. An acetyl norbornane structure may be formed when the $^{13}C = {}^{13}C$ double bond reacts with oxygen (Fig. 4, bottom). Indeed, the chemical shift of δ 209 ppm closely matches that of the carbonyl of 2-acetyl-5-norbornene (δ 208 ppm)[39]. The occurrence of *endo* and *exo* isomerism in the structure thus produced may explain the presence of two doublets. The magnitude of the observed splitting of ~ 42 Hz is as expected for the $^{13}C(2)–{}^{13}C(8) = O$ one bond *J*-coupling. No estimate can be made of the relative abundance of this structure since the low intensity of the signal at δ 209 ppm could be explained by insufficiently long recycle times during NMR data acquisition. Transformation of the ^{13}C(8) into a carbonyl implies that ^{13}C(2) will become an aliphatic carbon atom. Therefore, one or two of the new aliphatic signals (Table 2) have to be attributed to the C(2) in the acetyl norbornane structure. Finally, it is unlikely that the double bond is split under the conditions present during the acquisition of the spectrum of Fig. 3C. This would yield singly labelled monomeric units, which should give rise to singlet signals in the ^{13}C NMR spectrum. However, no new singlets of appreciable intensity ($\geq$ 1% of the large $(CH_2)_x$ signal at δ 29.8) are present in the spectrum of the altered EPDM.

4. Conclusions

A scheme for the preparation of isotopically labelled 2-ethylidene-5-norbornene has been developed. [2,8-$^{13}C_2$] ENB was prepared from doubly labelled acetic acid in an overall yield of 29%. The labelled ENB was terpolymerized with ethene and propene to form high molecular weight EPDM rubber with a [2,8-$^{13}C_2$] ENB content of approximately 8 wt.% and an ethene to propene ratio of ~ 1.8 (w/w). Apparently, the presence of some air during the lengthy acquisition of the ^{13}C NMR spectra causes the amount of C(2)– C(8) double bonds to decrease. The dominant mode of conversion is the addition of EPDM backbone radicals to the ENB double bond. The *E* ENB unit is more susceptible to chemical conversion than the *Z* isomeric unit. Some oxidation of the double bond appears to occur, giving rise to acetyl norbornene units. No significant cleavage of the C(2)–C(8) double bond takes place.

Clearly, labelling the appropriate sites in EPDM and subsequent NMR spectroscopy provides an excellent tool for studying (minor) chemical conversions in the actual polymer.

Acknowledgements

The authors gratefully acknowledge a gift of 20 g of [$^{13}C_2$]acetic acid from Cambridge Isotope Laboratories, Andover, Mass., USA as CIL research grant and would like to thank Mr J.W. Beulen, Mr P.T.M. Aussems and Mr P.J.H. Windmuller of DSM Research for their contributions to this work.

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