1156 Russian Chemical Bulletin, International Edition, Vol. 56, No. 6, pp. 1156—1161, June, 2007

Microstructure of 1,2-*trans*- and 1,4-*trans*-poly(penta-1,3-dienes)

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Microstructures of 1,2-*trans*- and 1,4-*trans*-poly(penta-1,3-dienes) synthesized using different catalysts were determined by high resolution ^{13}C NMR spectroscopy. The content of dyad combinations of the 1,4- and 1,2-structures was quantitatively determined in hydrogenated poly(penta-1,3-dienes) from the ratio of intensities of the characteristic signals of the carbon atoms of the methylene groups in the ^{13}C NMR spectra.

Key words: poly(penta-1,3-diene), polymers, hydrogenation, microstructure, ^{13}C NMR spectroscopy.

The determination of the microstructure of poly(penta-1,3-diene) (polypiperilene) is a complicated task, because its monomer can exist in the polymeric chain as five possible structures: 1,4-*trans*-, 1,4-*cis*-, 1,2-*cis*-, 1,2-*trans*-, and 3,4-units and their combinations. The most informative method for studying the structure of poly(penta-1,3-diene) is ^{13}C NMR spectroscopy. It should be mentioned that the data given in the known publications[1—4] and devoted to the use of the ^{13}C NMR method for investigation of the structure of this polydiene are not unambiguous and uncontradictory. For instance, the calculation of elements of the microstructure of poly(penta-1,3-dienes) prepared by the stereoregular and cationic syntheses from the signal intensities of the carbon atoms of the methyl groups in the ^{13}C NMR spectrum is presented.[5] However, this approach provides no complete pattern of the microstructure of the polymer samples. In particular, information on homo- and mixed dyad combinations of the units is lacking, while these data are important for predicting the main physicomechanical properties of the synthesized polymers. In addition, all the five signals from the carbon nuclei of the 3,4-unit have not earlier been observed in the spectra. When determining the position of the signals, the parameters of the system of additive substitution increments were used in the calculation. However, when this approach is applied to unsaturated polymer, an empirical correction to the influence of a double bond of different configuration in the chemical shift of the carbon atom signal in the spectrum should be introduced. This correction, as a rule, contributes substantially and often can be the major one. Therefore, the expected positions of signals in the spectrum cannot be considered as absolutely reliable. In aliphatic compounds, the calculated values of chemical shifts correlate well with the line positions in the spectra. Due to this, the problem of elucidation of the corresponding signals in the spectrum becomes more definite.

This work is devoted to investigation of the microstructures of 1,2-*trans*- and 1,4-*trans*-poly(pentadienes), including the determination of their dyad combinations of the units, by high resolution ^{13}C NMR spectroscopy.

The relatively mild method for polymer hydrogenation with the degree of hydrogenation close to unity was used for the unambiguous assignment of signals in the ^{13}C NMR spectrum to fragments of the poly(penta-1,3-diene) macrochain. In addition, heteronuclear 2D NMR spectroscopy was used to identify the signals for protons and carbon atoms.

Experimental

Poly(penta-1,3-diene) **A** with the predominant content of the 1,2-*trans*-units was synthesized from *trans*-penta-1,3-diene in a hexane solution on the $Co(acac)_3$—$AlEt_2Cl$ catalytic system.[6] The mole ratio was $Co(acac)_3/AlEt_2Cl = 1 : 50$. Polymerization conditions: 20 °C, 16 h, $[Co(acac)_3] = 2.4 \cdot 10^{-3}$ mol L^{-1}, $[C_5H_8] = 2$ mol L^{-1}, polymer yield 93 wt.%, $M_n = 1.02 \cdot 10^3$, $M_w = 3.84 \cdot 10^3$.

Stereoregular 1,4-*trans*-polypentadiene **B** was synthesized from *trans*-penta-1,3-diene in a toluene solution in the presence of the $VOCl_3$—$TiCl_4$—$AlBu^i_3$ system.[7] Triisobutylaluminum was added to a $VOCl_3$—$TiCl_4$ mixture by two portions. Mole ratios of the catalyst components: $VOCl_3 : TiCl_4 = 2 : 1$, $AlBu^i_3 : VOCl_3 = 6 : 1$. Polymerization conditions: 80 °C, 2 h, $[VOCl_3] = 5 \cdot 10^{-3}$ mol L^{-1}, $[C_5H_8] = 2.0$ mol L^{-1}, polymer yield 65 wt.%, $M_n = 56 \cdot 10^3$, $M_w = 353 \cdot 10^3$.

Poly(penta-1,3-diene) **C** was prepared by the cationic polymerization of *trans*-penta-1,3-diene in a toluene solution on the

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1113—1118, June, 2007.

$TiCl_4$—H_2O catalytic system.[8] Polymerization conditions: 20 °C, 0.5 h, $[TiCl_4]$ = 0.033 mol L^{-1}, $[H_2O]$ = 0.008 mol L^{-1}, $[C_5H_8]$ = 4.0 mol L^{-1}, polymer yield 87 wt.%, $M_n = 3.68 \cdot 10^3$, $M_w = 7.57 \cdot 10^3$.

All polymers were hydrogenated using *p*-toluenesulfonylhydrazide in xylene.[9]

Molecular characteristics of the polymer samples were determined by gel permeation liquid chromatography on a Waters GPCV-2000 instrument with a set of HR-2, HR-4, and HR-6 columns equipped with two detectors (viscosimeter and refractometer). Toluene was used as the eluent, and the elution rate was 1.0 mL min^{-1}.

NMR spectra were recorded on a Bruker AM-500 high resolution spectrometer with a working frequency of 500 and 125 MHz for the ^1H and ^{13}C nuclei, respectively. Samples were prepared as solutions in $CDCl_3$ (3—10 wt.%) using 5-mm tubes. The spectra were recorded at ~20 °C with 4000—6000 transients and pulse delay 8—12 s. To minimize the Overhauser effect, the ^{13}C NMR spectra were recorded in the inverse gated decoupling mode. The position of overlapped components of the NMR signals was localized by the mathematical processing of the spectra. The DEPT-135° mode and heteronuclear correlation 2D $^{13}C\{^1H\}$ NMR spectroscopy were used for the detailed assignment of signals. The latter was performed with a 5-mm $^{13}C\{^1H\}$ sensor using the XHCORR.AU standard program. The main parameters of 2D spectra detection: power of transmitters 38 (^{13}C) and 20 (^1H) kHz, 16 repetitions with a relaxation delay of 3 s, data matrix 4096/1024 points for $^{13}C/^1H$; digital resolution in the spectrum 14/5 Hz point ($^{13}C/^1H$), repetition time ~17 h.

Positions of signals in the spectra of the hydrogenated samples were calculated using the system of additive substituent increments for the ^{13}C NMR chemical shifts.[10]

The use of modern NMR procedures, comparison (predominantly of the signal intensities of carbon nuclei with the same hybridization), and multiple processing of the FID files followed by measuring the signal intensities of the same polymer make it possible to achieve good accuracy of quantitative measurements. At the same time, the measurement accuracy depends on the signal-to-noise ratio in the spectrum. This is especially substantial for the determination of the content of minor structures in an amount of 1—5%. Therefore, one can speak about the 5% relative measurement error for the intense signals and a more significant error (up to 30%) for the structures present in the polymer in a minimum amount. As for the samples obtained by cationic polymerization, the measurement accuracy for their composition can be lower in several cases, because the signals are arranged on a broad "pedestal" (Fig. 1, sample **C**), distorting the base line correction.

Results and Discussion

The ^{13}C NMR spectra of poly(penta-1,3-dienes) **A**, **B**, and **C** are presented in Fig. 1. The data on the polymer composition calculated from the ratio of intensities of the ^{13}C NMR signals of the methyl groups[5] are given in Table 1. The structures containing the quaternary carbon atoms, which are presumably formed due to secondary reactions (isomerization or polymer chain cyclization) are discussed in the works[3,4] devoted to the study of the microstructure of poly(penta-1,3-dienes) synthesized by cationic polymerization. In this case, the amount of these structures is estimated[3,4] to be up to 30%. The authors attribute the loss of unsaturation of the polymers just to the presence of these structures. The unsaturation character of poly(penta-1,3-diene) is determined, as a rule, by the ^1H NMR spectra. The residual unsaturation in the "cationic" sample **C** under study was 80.2 mol.%.

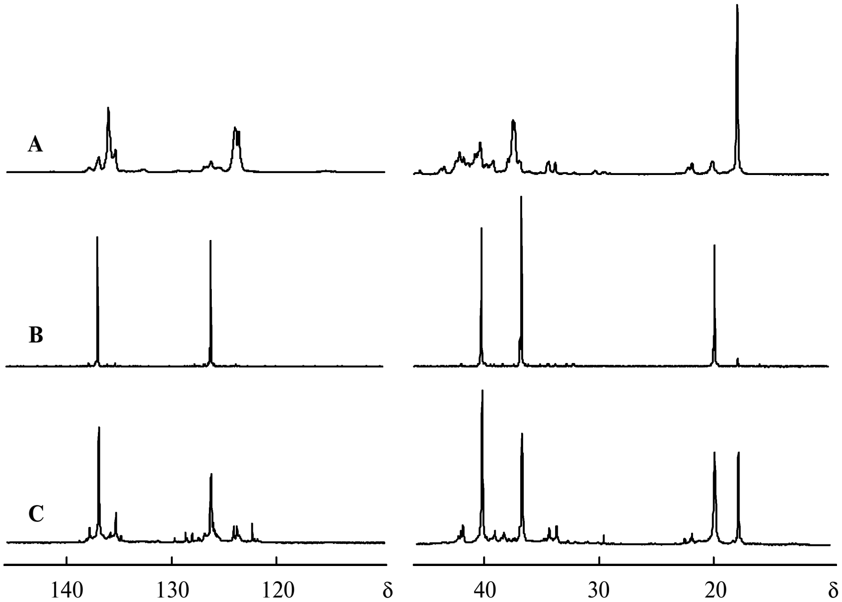

Fig. 1. ^{13}C NMR spectra of the poly(penta-1,3-diene) samples with the predominant content of the 1,2- (**A**) and 1,4-*trans*-units (**B**) and the sample obtained using the cationic catalyst (**C**).

Table 1. Relative content of the units of the unsaturated part of the samples of poly(penta-1,3-dienes) **A**—**C** determined from the signal intensities of the carbon atoms of the methyl group in the ^{13}C NMR spectra

Chain fragment	Content of fragment (mol.%)		
	A	**B**	**C**
1,2-*cis**	Traces	0.2	2.6
1,2-*trans**	77.8	6.8	22.1
1,4-*cis*	0	0	0
1,4-*trans* (head-to-tail)	13.0	92.7	54.9
1,4—4,1-*trans* (tail-to-tail), *dl*	Traces	0	3.8
1,4—4,1-*trans* (tail-to-tail), *meso*	Traces	0	3.0
1,4-*trans* (1,2)	9.2	0.3	13.6
3,4-Units	0	0	0

* The total content of the 1,2- and 2,1-units is given, because the chemical shifts of the carbon atoms of the methyl groups in various triad combinations involving these units are poorly sensitive to the environment and give an unresolved signal due to their remoteness from the joint carbon atoms per four bonds.

To find the structures including the quaternary carbon atom, we used the DEPT-135° mode, when signals of the carbon nuclei bearing different number of hydrogen atoms are apart relative to the base line and the resonance of the quaternary carbon atom does not appear. This spectrum of polymer **C** is shown in Fig. 2. The lines characterizing the carbon atoms of the CH and CH_3 groups are directed up relative to the horizontal axis, the lines of the CH_2 groups are directed down, and all substantial signals of the carbon atoms that are detected under standard conditions

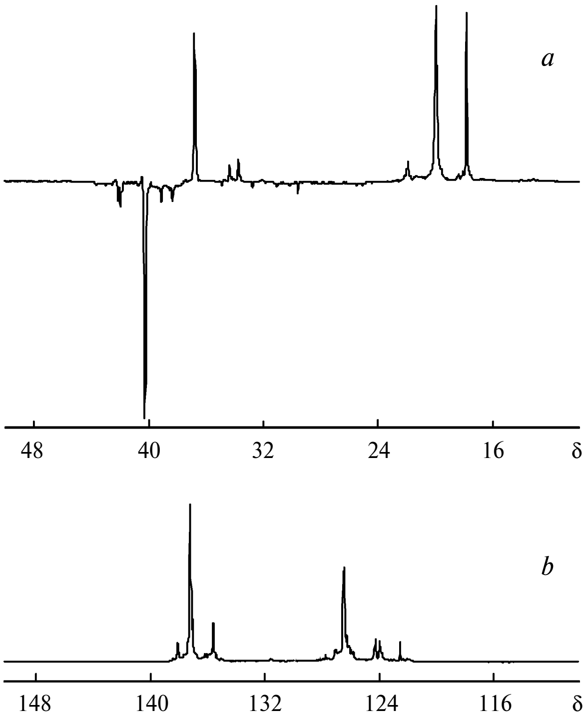

Fig. 2. ^{13}C NMR spectrum of poly(penta-1,3-diene) **C** detected in the DEPT-135° mode: aliphatic (*a*) and olefinic (*b*) regions.

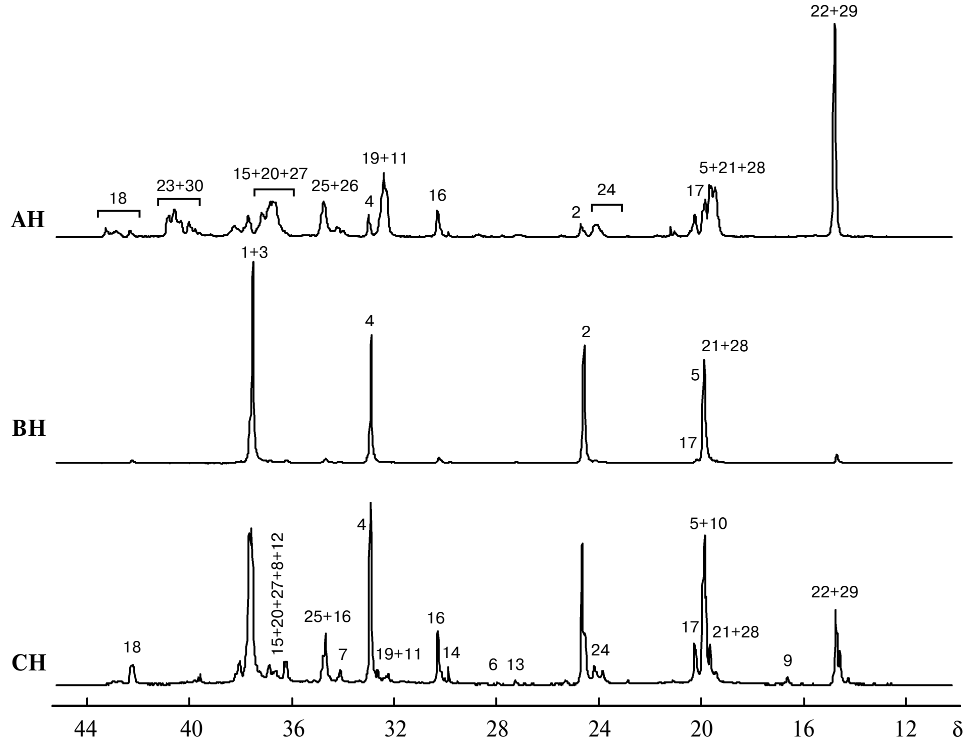

Fig. 3. ^{13}C NMR spectra of hydrogenated polymers **AH**, **BH**, and **CH**.

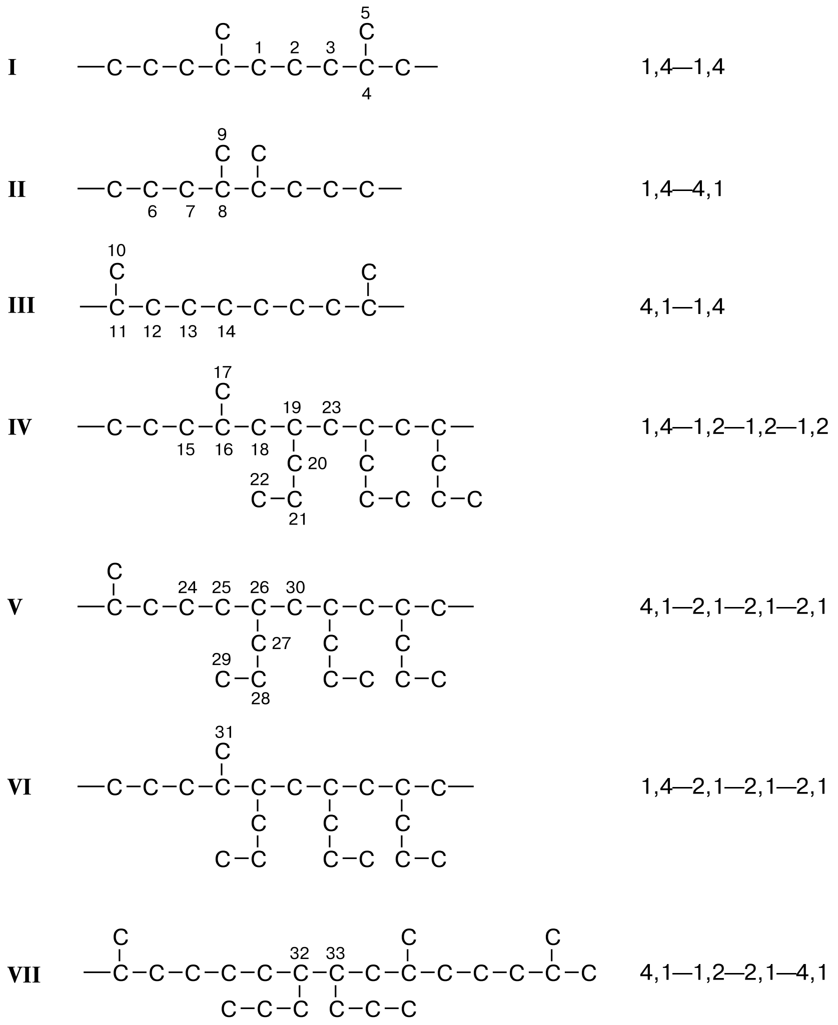

Fig. 4. Possible combinations of the 1,4- and 1,2-units (**I**—**VII**) in the hydrogenated polymers.

appear (see Fig. 1). This indicates practically complete absence of the quaternary carbon atoms in sample **C**.

The spectra of hydrogenated polymers **AH**, **BH**, and **CH** presented in Fig. 3 were used to estimate the content of dyad combinations of the units of different configuration. Possible combinations of the 1,4- and 1,2-units in the hydrogenated polymers are shown in Fig. 4. The calculated and experimental chemical shifts of the ^{13}C nuclei in these structures are given in Table 2. These values coincide rather well for the major combinations of the units. At the same time, it is difficult to determine the exact position of signals in the experimental spectra for some minor structures because of superposition of the group of signals (see Fig. 3).

The data presented in Table 2 and Fig. 3 made it possible to reveal the following dyad combinations of the units in hydrogenated polypentadienes **AH**, **BH**, and **CH**: 1,4—1,4; 1,2—1,2; 1,4—1,2; 4,1—2,1. In addition, the signals of inversion additions 1,4—4,1 and 4,1—1,4 were determined in the spectrum of polymer **CH**. No structures corresponding to the 1,4—2,1 and 1,2—2,1 inversion sequences were observed, which is caused, most likely, by steric hindrance for the connection of the monomeric units with the closely arranged substituted carbon atoms during polymerization. In addition, no lines of the C atoms corresponding to the structure of the 3,4-units in hydrogenated poly(penta-1,3-diene) are observed (including no intrinsic signals of the carbon atom of the methyl group with the chemical shift 17.1 ppm). This confirms the published data**[5]** on the absence of the 3,4-units in the composition of poly(penta-1,3-dienes) under study.

Information obtained from the DEPT-135° spectra (Fig. 5) was also used to refine the line assignment in the ^{13}C NMR spectra of the hydrogenated poly(penta-1,3-diene) samples **AH** and **CH**. The data of these experiments showed that the literature method for the calculation of the polymer structure from the signals of the carbon atoms of the methyl groups cannot be applied to hydrogenated poly(penta-1,3-dienes), because the chemi-

Table 2. Calculated and experimental chemical shifts of signals in the ^{13}C NMR spectra (δ) at different combinations of the monomeric units of hydrogenated poly(penta-1,3-diene) (see Fig. 4)

Structure	Number of C atom	Type of C atom	δ	
			Calculation	Experiment
I	1	CH_2	37.16	37.5
	2	CH_2	24.58	24.5
	3	CH_2	37.16	37.5
	4	CH	32.54	32.8
	5	CH_3	19.63	19.8
II	6	CH_2	27.80	27.8
	7	CH_2	33.80	33.9*
	8	CH	37.30	37.4*
	9	CH_3	16.84	16.5
III	10	CH_3	19.60	19.7*
	11	CH	32.54	32.5*
	12	CH_2	36.90	36.7*
	13	CH_2	27.14	27.1
	14	CH_2	30.20	29.7
IV	15	CH_2	37.41	36.7*
	16	CH	30.45	30.1
	17	CH_3	20.12	20.1
	18	CH_2	41.67	42.1*
	19	CH	32.91	32.6*
	20	CH_2	37.41	37.6*
	21	CH_2	20.21	20.2
	22	CH_3	14.35	14.4
	23	CH_2	39.48	39.5*
V	24	CH_2	24.83	23.7*
	25	CH_2	34.97	34.7*
	26	CH	34.98	34.5
	27	CH_2	37.16	37.4*
	28	CH_2	20.21	20.2
	29	CH_3	14.35	14.4*
	30	CH_2	39.23	39.5*
VI	31	CH_3	17.13	—
VII	32	CH	39.78	—
	33	CH	37.71	—

* Superposition of several signals.

cal shift region of the Me groups also contains the signal of the methylene carbon atoms of the 1,2-addition unit (see Fig. 4, atoms 21 and 28). This is additionally confirmed by the data presented in the map of heteronuclear proton—carbon correlation 2D NMR spectroscopy for poly(penta-1,3-diene) **CH** (Fig. 6). It can be seen from this map that the signals at δ_C ~19.8 include the resonance lines of both the methylene and methyl groups (δ_H ~1.3 and ~0.9, respectively). Therefore, we propose to use intensities of the characteristic lines or groups of lines of the methylene carbon atoms comprising these dyads enumerated according to Fig. 4 and presented in Table 3 for the determination of the content of dyad combinations of the units in the macrochain. Table 3 also contains the results of estimation of the content of dyad combinations of the units in hydrogenated polymers **AH**, **BH**, and **CH** from the intensities of signals of the methylene groups in the chosen spectral regions. Comparative analysis of the structures of hydrogenated poly(penta-1,3-dienes) (**AH**, **BH**, and **CH**) shows the tendency to microblock formation in the synthesis of these polymers, including those from the units present in the polymer samples in insignificant amounts compared to the prevailing content of other structures (**AH** and **BH**).

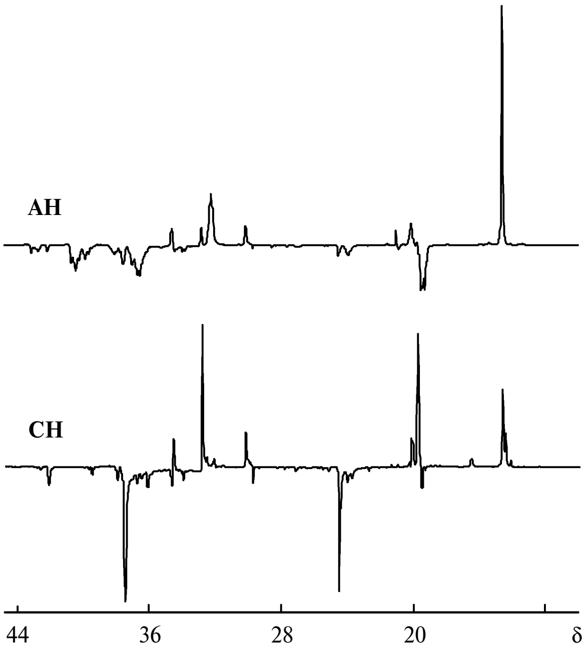

Fig. 5. ^{13}C NMR spectra of hydrogenated polymers **AH** and **CH** detected in the DEPT-135° mode.

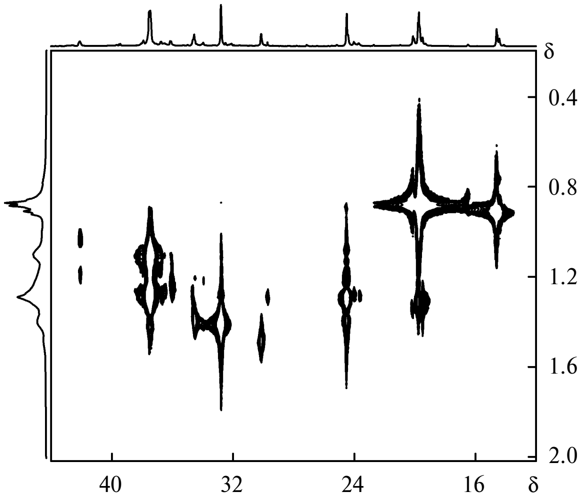

Fig. 6. Map of proton—carbon heteronuclear correlation 2D NMR spectroscopy for the hydrogenated sample of "cationic" poly(penta-1,3-diene) (**CH**).

Table 3. Content of dyad combinations of the 1,4- and 1,2-addition units in the hydrogenated samples of poly(penta-1,3-diene) **AH**, **BH**, and **CH** (see Fig. 4)

Structure	Type of dyad	Number of C atom*	δ	Content of dyads (mol.%)		
				AH	**BH**	**CH**
I	1,4—1,4	2	24.5	8	85	43
II	1,4—4,1	6	27.8	0	0	1
III	4,1—1,4	13	27.1	0	0	2
IV	1,4—1,2	18	41.8—43.3**	16	5	20
V	4,1—2,1	24	23.5—24.2**	16	8	18
IV, **V**	1,2—1,2	23, 30	39.0—40.8**	60	2	16

* Characteristic signal of the C atom used in the calculation.

** The effect of closely arranged neighbors of the 1,2-unit (at a distance of only two bonds) is observed, resulting in the appearance of a group of lines.

Thus, the calculation of the chemical shifts of signals in the ^{13}C NMR spectra of the hydrogenated samples using the approach of additive substitution increments in the NMR chemical shifts and comparison of these data with the experimental spectral parameters in poly(penta-1,3-dienes) under study revealed the following dyad combinations of the units: 1,4—1,4; 1,4—4,1; 4,1—1,4; 1,4—1,2; 4,1—1,2; 1,2—1,2.

The authors are grateful to I. S. Podkorytov and L. V. Osetrova for performing NMR experiments.

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Received September 12, 2006;
in revised form April 17, 2007