

Structural characterization of low molecular weight polybutadiene synthesized using cationic initiation system

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The microstructure of polymer chain of low molecular weight polybutadienes synthesized with cationic initiating systems has been investigated using one-dimensional (^{13}C , ^{13}C with a T_2 -filter, and ^{13}C DEPT-135°) and two-dimensional ^1H – ^{13}C (HSQC and HMBC) NMR spectroscopy. It was found that the unsaturated part of main polymer chain consists of 1,4-*trans*- and 1,2-structures with different combination of units. For the first time, structures of the head groups of polymers were identified, which are dimethylpropane fragments of the initiator (2-chloro-2-methyl-butane) connected with 1,4-*trans*- or 1,2-units of polybutadiene. Structures of two types (1,4-*trans*- and 1,2-) of chlorine-containing end groups were found. Methods for the calculation of the content of head and end groups, unsaturation and functionality of polybutadiene macromolecules on the terminal groups were developed.

Key words: cationic polymerization, structure of polymeric chain, low molecular weight polybutadiene, terminal units of macromolecules.

Low molecular weight polymers of conjugated dienes (*e.g.*, butadiene or isoprene) are widely used in industry as plasticizers for rubber mixtures, components of varnishes and paints, sealing, and polymer anticorrosion compositions.^{1–4} Currently, such polymers are produced by radical, anionic, or stereospecific polymerization.^{5,6} The disadvantages of these methods are the low rate of the process and complexity of the manufacturing technology related to special methods used for regulating the molecular characteristics of the polymer, as well as high costs of the initiators and catalytic systems.^{1–5} Low molecular weight polymers can also be obtained by cationic polymerization of 1,3-dienes.^{5–11} For instance, we have previously proposed^{12–15} efficient methods for the preparation of low molecular weight butadiene polymers (LMBPs) using cationic initiating systems based on TiCl_4 or organoaluminum compounds. The advantages of cationic polymerization of butadiene include relatively low cost of initiating systems, high rate of the process, and easy control of the molecu-

lar characteristics of polymer. The synthesized "cationic" LMBPs are promising components of paint, varnish, and roofing compositions.^{13,15}

Our previous work¹⁵ disclosed an efficient method for the preparation of LMPB using the cationic initiating systems consisting of Lewis acids in combination with tertiary aliphatic alkyl halides. Thus, cationic polymerization of butadiene using the initiating system diethylaluminum chloride (AlEt_2Cl)–2-chloro-2-methyl-butane (CMB) proceeds at high rate yielding completely soluble LMPB. However, there are no data in that work¹⁵ on the structures of the macromolecular chain and terminal units of synthesized LMPB. Meanwhile, such information is important for predicting the physicochemical properties of the polymer, estimation the detailed mechanism of cationic polymerization, and developing the possible methods of polybutadiene modification.

The purpose of this work is to establish the structure of polymer chain and terminal groups in LMPB macromolecules obtained using cationic

initiating systems consisting of Lewis acids and 2-chloro-2-methyl-butane, as well as the development of methods for quantitative calculation of the content of head and end groups in polybutadiene.

Experimental

Samples of low molecular weight polybutadiene were obtained by cationic polymerization of butadiene in methylene chloride according to the procedure reported previously.¹⁵

Sample of LMPB-1 was synthesized using the initiating system TiCl_4 —CMB system under the following conditions: $-78\text{ }^\circ\text{C}$; $[\text{C}_4\text{H}_6] = 4.0\text{ mol L}^{-1}$; $[\text{TiCl}_4] = 1.5 \cdot 10^{-2}\text{ mol L}^{-1}$; $[\text{CMB}] = 1.5\text{ mol L}^{-1}$; reaction time of 5 min. The yield of polymer was 30.5 wt.%, $M_n = 2270\text{ g mol}^{-1}$, $M_w = 4760\text{ g mol}^{-1}$, $M_w/M_n = 2.1$, and the polymer unsaturation was 88 mol.% from the theoretical value.

Sample of LMPB-2 was synthesized using the initiating system AlEt_2Cl —CMB under the following conditions: temperature of $-78\text{ }^\circ\text{C}$, $[\text{C}_4\text{H}_6] = 4.0\text{ mol L}^{-1}$, $[\text{AlEt}_2\text{Cl}] = 5.0 \cdot 10^{-3}\text{ mol L}^{-1}$, $[\text{CMB}] = 0.5\text{ mol L}^{-1}$, and reaction time of 5 min. The yield of polymer was 79.6 wt.%, $M_n = 4340\text{ g mol}^{-1}$, $M_w = 28800\text{ g mol}^{-1}$, $M_w/M_n = 6.6$, and the polymer unsaturation was 77 mol.% from the theoretical value.

Sample of LMPB-3 was synthesized using the initiating system AlEt_2Cl —CMB under the following conditions: temperature of $20\text{ }^\circ\text{C}$, $[\text{C}_4\text{H}_6] = 4.0\text{ mol L}^{-1}$, $[\text{AlEt}_2\text{Cl}] = 5.0 \cdot 10^{-3}\text{ mol L}^{-1}$, $[\text{CMB}] = 0.5\text{ mol L}^{-1}$, and reaction time of 1 min. The yield of polymer was 70.1 wt.%, $M_n = 1820\text{ g mol}^{-1}$, $M_w = 4600\text{ g mol}^{-1}$, $M_w/M_n = 2.5$, and the polymer unsaturation was 61 mol.% from the theoretical value.

Molecular characteristics of the polymers (M_n and M_w are number-average and weight-average molecular weights, respectively; M_w/M_n is the polydispersity) were determined by gel permeation chromatography using a Waters-Alliance GPCV-2000 liquid chromatograph equipped with refractometric and viscometric detectors, and a set of four Waters styrogel columns with pore sizes of 500 (HR-2), $1 \cdot 10^3$ (HR-3), $1 \cdot 10^4$ (HR-4), and $1 \cdot 10^5$ (HR-5) Å. The eluent was toluene, the elution rate was 0.5 ml min^{-1} , and the temperature was $30\text{ }^\circ\text{C}$.

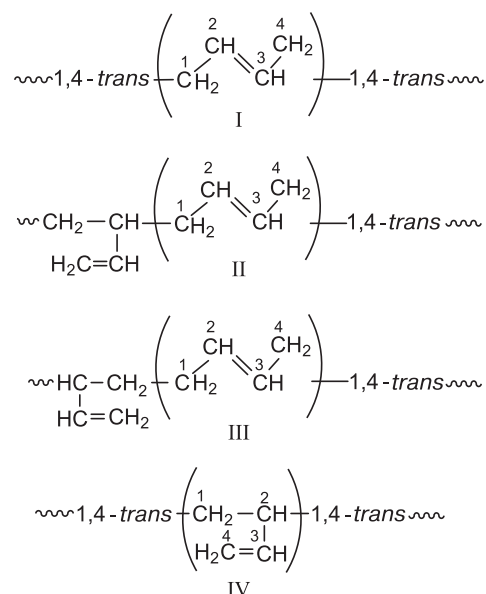
^1H and ^{13}C NMR spectra, as well as two-dimensional (2D) HSQC and HMBC ^1H — ^{13}C NMR spectra, were recorded for polybutadiene (solvent CDCl_3) at Center for Magnetic Resonance, St. Petersburg State University Research Park, using Bruker Avance III 400 spectrometer operating the frequencies of 400.13 (^1H) and 100.62 (^{13}C) MHz according to the methods reported previously.^{16,17} In ^{13}C NMR experiments with a T_2 -filter, the CPMG pulse sequences with 1522 quantitative repetitions of

impulses of spin echo and delay between impulses 320 μs were used.^{13,17} The calculation of chemical shifts for carbon atoms in ^{13}C NMR spectrum was made using prediction parameters of Grant and Paul.¹⁸

Results and Discussion

Figures 1 and 2 show aliphatic and olefinic regions of the ^{13}C NMR spectrum (Figs. 1, *b* and 2, *b*) and the ^{13}C NMR spectrum with a T_2 -filter (Figs. 1, *a* and 2, *a*) for a sample of the low molecular weight polybutadiene LMPB-1. This sample of polybutadiene is characterized by the highest unsaturation (88 mol.%), therefore it is the most convenient and informative for studying the structure of unsaturated part of the polymer chain.

A comparative analysis of literature data^{14–16} and the presented NMR spectra (see Figs 1, *b* and 2, *b*) allowed us to conclude that the unsaturated part of the main polymer chain consists in 1,4-*trans*- and 1,2-structures with different combination of units (structures I—IV).



As can be seen from Figures 1, *b* and 2, *b*, the most intense spectral signals belong to the methylene and methine carbon atoms of 1,4-*trans*-unit in structure I, exhibiting chemical shifts (δ_{C}) 32.6 and 129.8, respectively. Weaker signals at δ_{C} 38.0, 128.2, 131.1, and 32.6 belong to carbon atoms of the 1,4-*trans*-unit connected to the methine carbon atom of 1,2-unit (structure II). Signals at δ_{C} 30.0, 130.3, 129.6, and 32.6 correspond to carbon atoms of the 1,4-*trans*-unit connected to methylene carbon atom of 1,2-unit

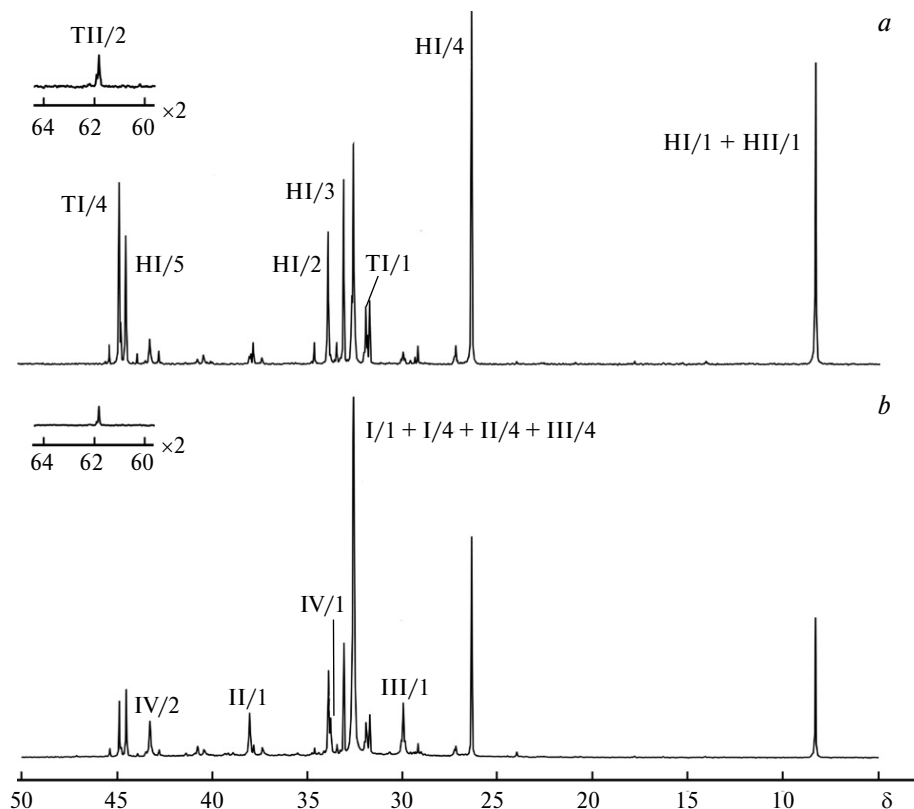


Fig. 1. Aliphatic regions of the ^{13}C NMR spectra of polybutadiene LMPB-1 recorded with a T_2 -filter (*a*) and without a T_2 -filter (*b*). Figure 1, *b* shows the signals of carbon atoms in the structural units of the main polymer chain. Figure 1, *a* shows the signals of carbon atoms in the terminal groups of the polymer.

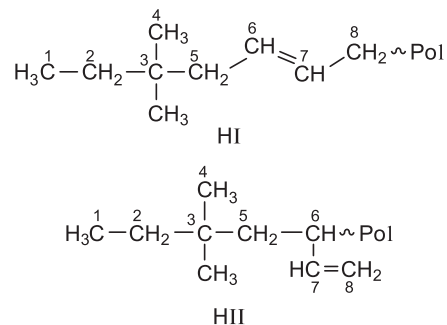
(structure III). Carbon atoms of the 1,2-unit located between the 1,4-*trans*-units (structure IV) demonstrated signals at δ_{C} 33.8, 43.3, 142.5, and 114.1. The signals of carbon atoms of 1,4-*cis*-units¹⁶ are absent in the polymer chain of LMPB-1.¹⁶ The quantitative calculation of the content of structural units in LMPB-1 performed based on the methodology of work¹⁶ gives the following results: 80 mol.% of 1,4-*trans*- and 20 mol.% of 1,2-units.

The identification of the structure of head groups in polybutadiene macromolecules synthesized with the initiating system TiCl_4 -2-chloro-2-methylbutane is performed in this work for the first time, using ^{13}C NMR spectra with a T_2 -filter (see Figs 1, *a* and 2, *a*) and DEPT-135° ^{13}C NMR spectra (Fig. 3, *b*), as well as 2D ^1H - ^{13}C HSQC (Fig. 4) and HMBC (Fig. 5) NMR spectra.

It is known that the use of NMR spectroscopy with a T_2 -filter allows to significantly increase intensities of the spectral signals of carbon atoms in the more mobile head and end groups of polydiene macromolecules.^{13,19–22} Indeed, a significantly increased intensity was observed for some spectral

signals of LMPB-1 in aliphatic and olefinic regions of the ^{13}C NMR spectrum recorded with a T_2 -filter is observed (see Figs 1, *a* and 2, *a*), as compared to their intensities in the "standard" ^{13}C NMR spectrum (see Figs 1, *b* and 2, *b*). It can be assumed that these signals belong to the carbon atoms located in the most mobile terminal units of polybutadiene macromolecules.

Expected structures of the head groups, which is formed during the initiation of the cationic polymerization of butadiene with TiCl_4 -2-chloro-2-methylbutane initiating system are shown below (HI and HII).



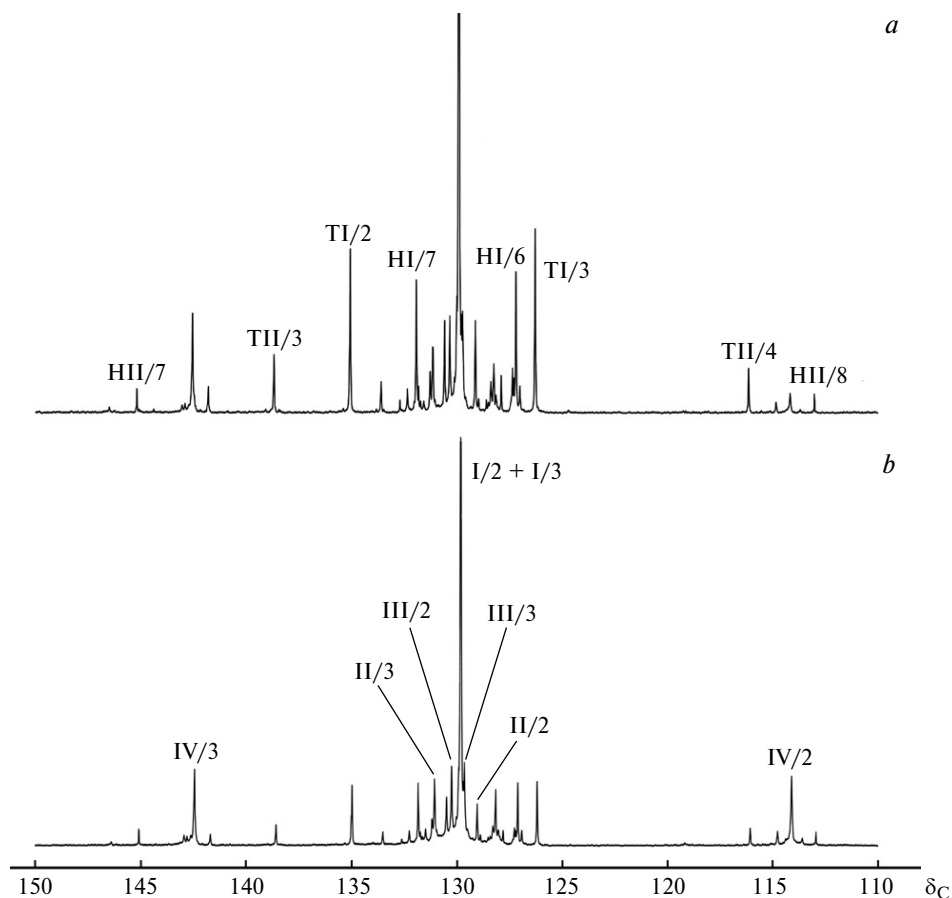


Fig. 2. Olefinic regions of the ^{13}C NMR spectra of polybutadiene LMPB-1 recorded with a T_2 -filter (*a*) and without a T_2 -filter (*b*). Figure 2, *b* shows the signals of carbon atoms in the structural units of the main polymer chain. Figure 2, *a* shows the signals of carbon atoms in the terminal groups of the polymer.

As one can see, the head group with HI structure is a dimethylpropane fragment of the initiator (CMB) connected to the 1,4-*trans*- unit of polybutadiene, whereas the head group with HII structure is the same fragment of the initiator connected to the 1,2-unit of polybutadiene. Table 1 shows both calculated and experimentally found values of the chemical shifts of the signals of carbon atoms in HI and HII structures.

The data listed in Table 1 shows a good correlation between the calculated and experimental ones found in the ^{13}C NMR spectra the values of the chemical shifts of the signals of carbon atoms in HI and HII structures. It is important to note that intensities of all experimentally found signals of carbon atoms in the head groups increased significantly in the ^{13}C NMR spectrum with a T_2 -filter, as compared to their intensities in the "standard" ^{13}C NMR spectrum (see Figs 1 and 2). This is one of the proofs that these signals belong to the carbon atoms in the head groups.

Another confirmation of the correct identification of the structure of the head groups is the data acquired by the ^{13}C DEPT-135° NMR. For example, one can see from Figure 3, *b* that there are signals in the aliphatic region at δ_{C} 26.4 and 27.2, which exhibit positive increments and may belong to carbon atoms of the methyl groups. Signals at δ_{C} 33.9, 34.4, 44.5, and 45.4 demonstrate negative increments and belong to methylene carbon atoms, whereas signals at δ_{C} 33.1 and 33.4 are absent in the spectrum and therefore, they belong to quaternary carbon atoms.

The correctness of identification of the structure of the HI and HII head groups is also confirmed by the data acquired by two-dimensional NMR spectra. According to the 2D ^1H – ^{13}C HSQC NMR spectrum, signals of the carbon atoms HI/1 (δ_{C} 8.3) and HI/5 (δ_{C} 44.5) on the carbon scale of spectrum are located in the regions of δ_{H} 0.87 and 1.92 on the proton scale, respectively (see Fig. 4). As one can see from Figure 5, *a*, on a vertical line with a signal

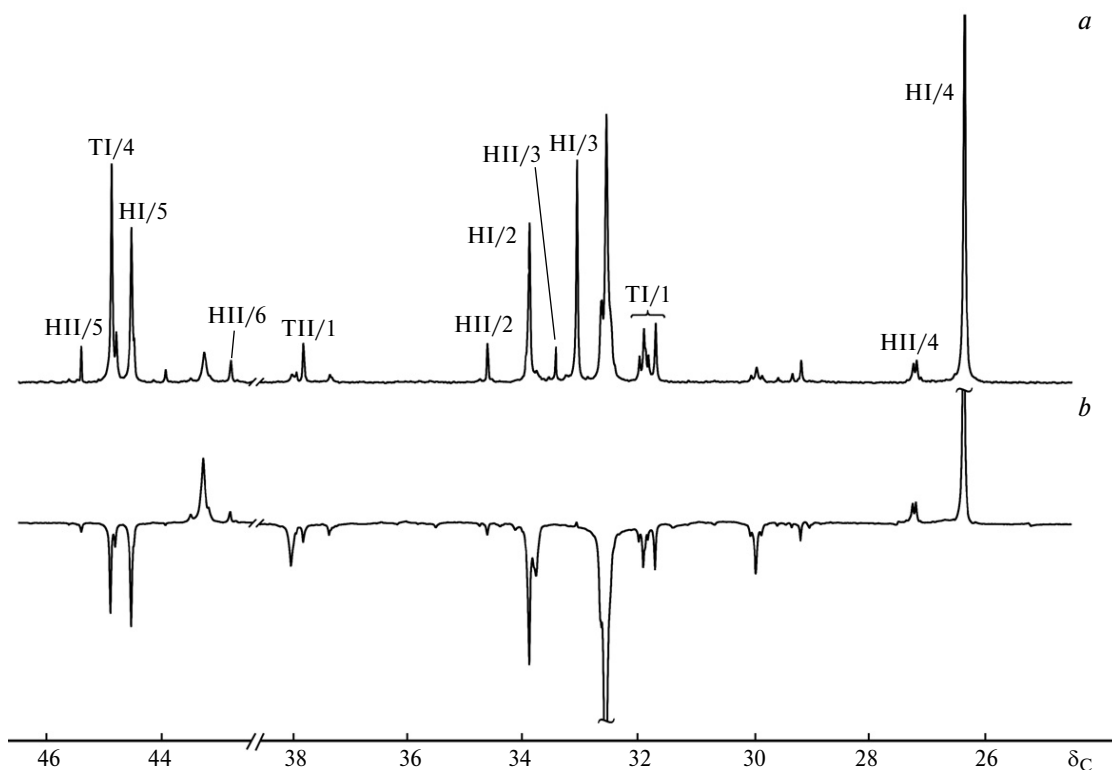


Fig. 3. Fragments of aliphatic regions of the ^{13}C NMR spectrum of polybutadiene LMPB-1 recorded with a T_2 -filter (a) and DEPT- 135° ^{13}C NMR spectrum (b). Figures 3, a shows the signals of carbon atoms in the head and end groups.

at δ_{H} 0.87 on the proton scale of the 2D ^1H – ^{13}C HMBC NMR spectrum, the cross-peaks with signals at δ_{C} 26.4, 33.1, 33.9, and 44.5 are observed on the

carbon scale of spectrum. At the same time on a vertical line with a signal at δ_{H} 1.92 on the proton scale of the 2D ^1H – ^{13}C HMBC NMR spectrum the cross-

Table 1. Calculated and experimentally found chemical shifts of the signals of carbon and hydrogen atoms in the head groups with HI and HII structures in polybutadiene LMPB-1

Structure	Signal designation on Figs 1–5	δ		
		^{13}C NMR		^1H NMR
		calculated	experimental	experimental
HI	HI/1	8.2	8.3	0.87
	HI/2	34.5	33.9	1.28
	HI/3	33.4	33.1	—
	HI/4	27.8	26.4	0.87
	HI/5	45.4	44.5	1.92
	HI/6	126.7	127.1	5.43
	HI/7	130.9	131.8	5.41
HII	HII/1	8.3	8.3	0.87
	HII/2	34.7	34.4	1.26
	HII/3	33.9	33.4	—
	HII/4	28.5	27.2	0.88
	HII/5	46.7	45.4	1.32
	HII/6	41.3	42.8	2.31
	HII/7	144.6	145.1	5.65
	HII/8	113.2	112.9	4.94–5.00

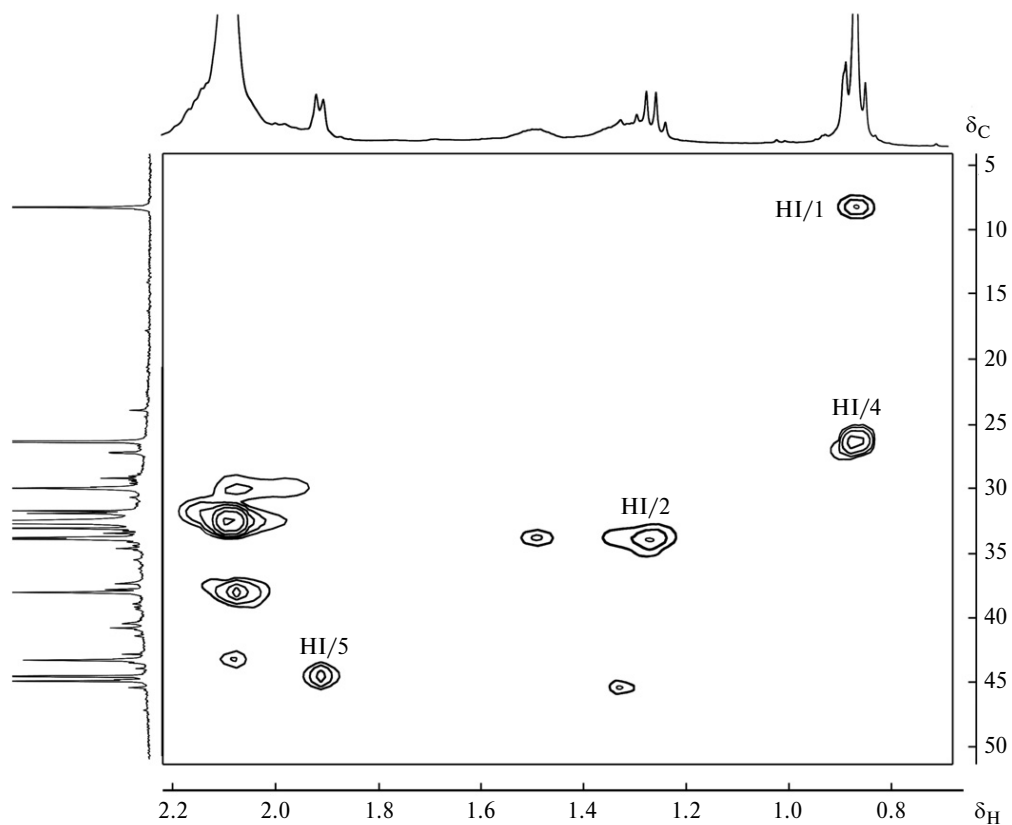


Fig. 4. Aliphatic region of the 2D ^1H - ^{13}C HSQC NMR spectrum of polybutadiene LMPB-1.

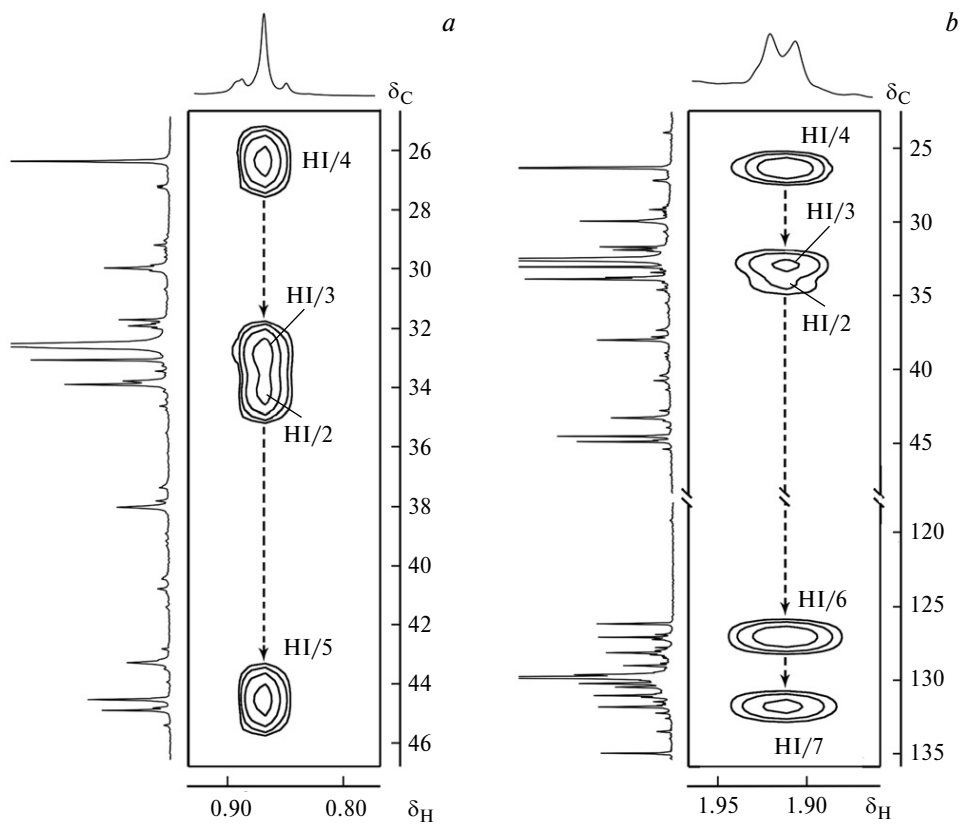
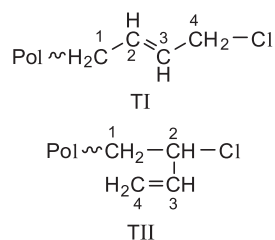


Fig. 5. Fragments of the 2D ^1H - ^{13}C HMBC NMR spectrum of polybutadiene LMPB-1 in regions of δ_{H} 0.8–0.9 (a) and 1.85–1.95 (b) on a proton scale of spectrum.

peaks with signals at δ_C 26.4, 33.1, 33.9, 127.1, and 131.8 are observed. Consequently, the signals at δ_C 8.3, 26.4, 33.1, 33.9, 44.5, 127.1, and 131.8 belong to the same structure of the head group HI, whose structure was confirmed by a combination of 2D ^1H – ^{13}C HSQC and HMBC NMR spectra. Similar methods were used to prove the structure of the head group with HII structure.

As concerning the structure of end groups of macromolecules LMPB-1, the ^{13}C NMR spectra revealed pronounced signals of carbon atoms located in two types of chlorine-containing end groups with 1,4-*trans*- and 1,2-structures (TI and TII, respectively).



As was demonstrated previously,¹² chlorine-containing end groups in polydienes synthesized using initiating systems comprising tertiary alkyl halides are formed due to the transfer reaction of the growing chain to tertiary alkyl halide. Position of

signals of carbon atoms in the chlorine-containing end groups TI and TII of polybutadiene in the ^{13}C NMR spectrum was determined in our previous work.¹⁶ Carbon atoms in the chlorine-containing end group with TI structure contain signals at δ_C 31.7–31.9 (TI/1), 135.1 (TI/2), 126.1 (TI/3), and 45.0 (TI/4) (see Figs 1–3). Carbon atoms in the chlorine-containing end group with TII structure demonstrate the following signals (δ_C): 37.5 (TII/1), 61.9 (TII/2), 138.5 (TII/3), and 116.1 (TII/4) (see Figs 1–3).

Thus, almost all the spectral signals appeared in the ^{13}C NMR spectra (see Figs 1–3) were assigned to the corresponding carbon atoms located in the structures of the main polymer chain or in the terminal groups of LMPB-1.

Figure 6 shows aliphatic regions in the ^{13}C NMR spectra of polybutadienes LMPB-2 and LMPB-3 synthesized with the initiating system AlEt_2Cl –CMB.

As can be seen from Figure 6, the same signals are observed in the spectra of aliphatic region of spectrum of polybutadiene LMPB-1 (see Fig. 1, *b*). This indicates the same structure for the unsaturated part of main polymer chain, the head and end groups of all three considered polybutadiene samples synthesized with different initiating systems and under different polymerization conditions. It

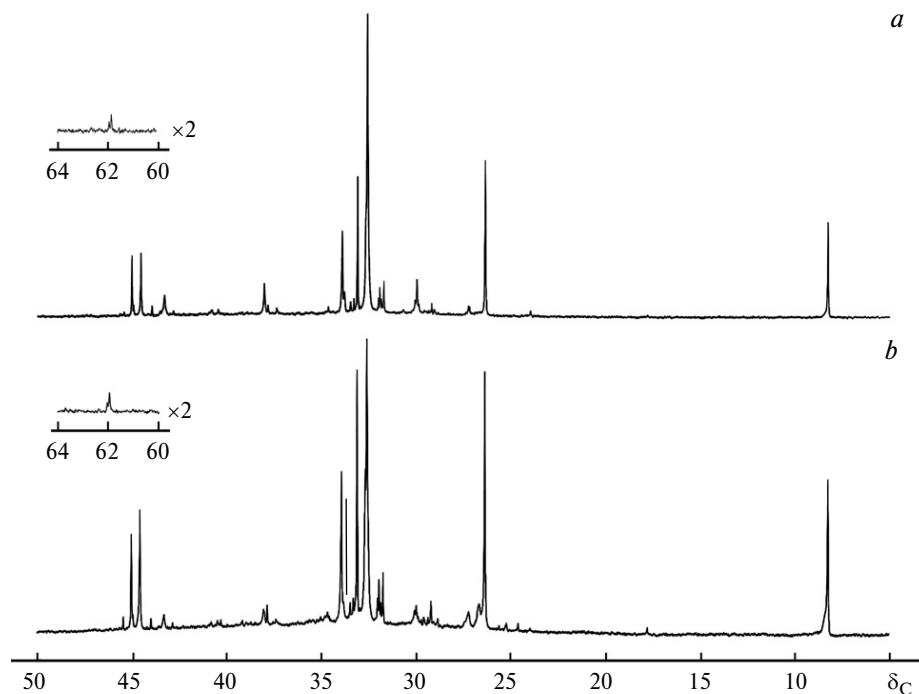


Fig. 6. Aliphatic regions of the ^{13}C NMR spectra of polybutadienes LMPB-2 (*a*) and LMPB-3 (*b*).

Table 2. Structural characteristics of the polymer chain of "cationic" low molecular weight polybutadienes

Characteristic	Polymers		
	LMPB-1	LMPB-2	LMPB-3
Unsaturation (mol.%)	88	77	61
Contents of the structural units in the unsaturated part of the main polymer chain (mol.%):			
1,4- <i>trans</i> -units	80	81	81
1,2-units	20	19	19
Content of the head groups (mol.%):			
structure HI (1,4- <i>trans</i> -)	7.8	7.4	10.9
structure HII (1,2-)	1.3	1.2	1.8
total amount	9.1	8.6	12.7
functionality of the macromolecules on the head groups	3.4	6.2	2.4
Content of the end groups (mol.%):			
structure TI (1,4- <i>trans</i> -)	6.4	5.2	7.3
structure TII (1,2-)	1.0	0.8	1.2
total amount	7.4	6.0	8.5
functionality of the macromolecules on the end groups	2.6	4.1	2.2

should be noted that the height of the so-called "pedestal" in the NMR spectrum of polybutadiene LMPB-3 increases noticeably, which is associated with a significant decrease in the unsaturation of polybutadiene, as compared to samples of LMPB-1 and LMPB-2 (Table 2). The presence of "pedestals" in the NMR spectra of "cationic" polydienes is associated with the feature of "low-mobility" carbon atoms located in the branching points of macromolecules to give broad lines of spectral signals due to their fast relaxation.^{13,21,22} In the ¹³C NMR spectra of LMPB-3 with a T₂-filter, the "pedestal" in the spectrum disappeared due to the suppression of fast relaxing signals of "low-mobility" carbon atoms located in branched and cross-linked fragments of the main polymer chain.

Methodologies and results for the content calculations of terminal units, functionality, and unsaturation of polybutadienes. Quantitative calculation of the content of the head dimethylpropane groups has to be based on the "standard" ¹³C NMR spectrum (see Fig. 1, *b*), using the intensity (*I*) of total signal of carbon atoms HI/1 and HII/1 at δ_C 8.3. At the first stage of calculation, the total intensity *I*(Σ) of all the carbon atoms in the ¹³C NMR spectrum is determined in the ranges of δ_C from 5 to 65 in the aliphatic region and from δ_C 110 to 150 in the olefinic region of the spectrum (see Figs 1, *b* and 2, *b*). Since

the head dimethylpropane (DMP) group contains 8 carbon atoms (see structures HI and HII), the total intensity for all the signals of carbon atoms in the head groups *I*(ΣDMP) is calculated by multiplying the intensity of signal at δ_C 8.3 by five. Then, the value of total intensity for all the signals of carbon atoms, related to polybutadiene *I*(ΣPB) is determined according to the following equation:

$$I(\Sigma PB) = I(\Sigma) - I(\Sigma DMP). \quad (1)$$

A value *I*^N(ΣPB) of the normalized signal intensity of carbon atoms in the polybutadiene is calculated by dividing the value *I*(ΣPB) by four (since the monomer unit of polybutadiene contains four carbon atoms) according to the equation:

$$I^N(\Sigma PB) = I(\Sigma PB)/4. \quad (2)$$

After that, a value *N*(DMP), which is the number of monomer units in the polymer chain of polybutadiene per one head dimethylpropane group, is calculated by dividing the normalized signal intensity of carbon atoms in polybutadiene *I*^N(ΣPB) by the intensity of the total signal at δ_C 8.3 of the carbon atoms HI/1 and HII/1:

$$N(\text{DMP}) = I^N(\Sigma PB)/I(\text{HI}/1 + \text{HII}/1). \quad (3)$$

The total content of the first units HI and HII is determined as mole percent *M*(DMP) and weight

percent W (DMP) according to the following equations:

$$M(\text{DMP}) = 1 \cdot 100\% / N(\text{DMP}), \quad (4)$$

$$W(\text{DMP}) = 71 \cdot 100\% / N(\text{DMP}) \cdot 54, \quad (5)$$

where 71 and 54 are the molecular weights of the head dimethylpropane group and the polybutadiene monomer unit, respectively.

The number-average molecular weight M_n (NMR DMP) of polybutadiene calculated from the ^{13}C NMR data and the functionality F_n (DMP) of polybutadiene macromolecules on the head dimethylpropane groups are determined according to the equations (6) and (7):

$$M_n(\text{NMR DMP}) = 71 + N(\text{DMP}) \cdot 54, \quad (6)$$

$$F_n(\text{DMP}) = M_n(\text{GPC}) / M_n(\text{NMR DMP}), \quad (7)$$

wherein M_n (GPC) is the number-average molecular weight experimentally determined using gel permeation chromatography (GPC).

If necessary, it is easy to calculate the individual content of the head groups with HI and HII structures using the ratio of intensities of the spectral signals of the carbon atom HI/4 at δ_{C} 26.4 and carbon atom HII/4 at δ_{C} 27.2 (see Fig. 1, *b*).

Quantitative calculation of the content of chlorine-containing end groups with TI and TII structures has to be based on the "standard" ^{13}C NMR spectrum (see Fig. 1, *b*), using the signal intensities of carbon atoms TI/4 (δ_{C} 45.0) and TII/2 (δ_{C} 61.9). At the first stage, the total intensity I (ΣCEG) of signals of carbon atoms in the chlorine-containing end groups (CEG) is determined by multiplying the total intensity of signals at δ_{C} 45.0 and 61.9 by four, since the each chlorine-containing end group contains four carbon atoms.

Then, the value of $N(\text{CEG})$, which is the number of monomer units in polybutadiene chain per one chlorine-containing end group, is calculated according to the equation:

$$N(\text{CEG}) = (I(\Sigma\text{PB}) - I(\Sigma\text{CEG})) / I(\Sigma\text{CEG}), \quad (8)$$

where $I(\Sigma\text{PB})$ is the value of total intensity for the polybutadiene carbon atoms, calculated according to the formula (1). The content of chlorine-containing end groups is calculated as mole percent M

(CEG) and weight percent W (CEG) according to the following equations:

$$M(\text{CEG}) = 1 \cdot 100\% / N(\text{CEG}), \quad (9)$$

$$W(\text{CEG}) = (89.5 \cdot 100\%) / N(\text{CEG}) \cdot 54, \quad (10)$$

where 89.5 and 54 are the molecular weights of chlorine-containing end group and polybutadiene monomer unit, respectively. The number-average molecular weight M_n (NMR CEG) of polybutadiene calculated from the ^{13}C NMR data and the functionality F_n (CEG) of polybutadiene macromolecules on chlorine-containing end groups are determined according to the equations (11) and (12):

$$M_n(\text{NMR CEG}) = 71 + (N(\text{CEG}) \cdot 54) + 89.5, \quad (11)$$

$$F_n(\text{CEG}) = M_n(\text{GPC}) / M_n(\text{NMR CEG}). \quad (12)$$

If necessary, it is easy to calculate the individual content of the chlorine-containing end groups with TI and TII structures using the ratio of intensities of the spectral signals of the carbon atom TI/4 at δ_{C} 45.0 and carbon atom TII/4 at δ_{C} 61.9.

Unsaturation (U , mol.%) of polybutadiene is calculated using formula (13):

$$U = I(110-150) / I(\Sigma\text{PB}) \cdot 0.5, \quad (13),$$

where $I(110-150)$ is the experimentally determined signal intensity of carbon atoms in the olefinic region of ^{13}C NMR spectrum in the range δ_{C} from 110 to 150, and the coefficient 0.5 reflects the theoretical signal intensity value of olefinic carbon atoms in the polybutadiene unit at 100 mol.% unsaturation of polymer.

Table 2 summarizes the results of calculations performed for the structural characteristics of polybutadienes LMPB-1, LMPB-2, and LMPB-3 according to the equations (1)–(13). As can be seen from the data of Table 2, polybutadienes LMPB-2 and LMPB-3, synthesized using AlEt_2Cl –CMB initiating system, are characterized by significantly lower unsaturation, as compared to polybutadiene LMPB-1 obtained using a TiCl_4 –CMB system.

The content of 1,4-*trans*- and 1,2-units in the main polymer chain for all the three samples is almost at the same level. The highest content of the head and end groups in polymers is observed in the case of LMPB-3 sample synthesized at the temperature

of 20 °C and characterized by the lowest average molecular weights of the polymer. For all polybutadienes, the functionality of macromolecules on the head and end groups is in the range from 2.2 to 6.2 (see Table 2). The values of polymer functionality above unity indicated the occurrence of transfer reaction of a growing chain to the double bond of polybutadiene with the formation of branched macromolecules containing several head and end groups. Similar results were obtained in our previous works^{23,24} devoted to studying the structure of the polymer chain of polyisoprene synthesized using various cationic initiating systems.

It is interesting to note that the content of the head and end groups with 1,2-structure (HII and TII) is about 13–15 mol.% of their total amount, while the rest corresponded to the end groups with 1,4-*trans*- structure (HI and TI) (see Table 2). The content of 1,2-units in the main polymer chain of polybutadiene is noticeably higher, about 19–20 mol.%. As can be seen from the data of Table 2, all the polybutadiene samples contain a significant amount of end chlorine-containing groups (6.0–8.5 mol.%), which expands opportunities for targeted modification of macromolecules of low molecular weight polybutadiene obtained using cationic initiating systems.

In summary, for the first time the structure of the polymer chain of low molecular weight polybutadienes synthesized using highly efficient initiating systems consisting of TiCl_4 or AlEt_2Cl with 2-chloro-2-methyl-butane was investigated using various methods of NMR spectroscopy. It was demonstrated that the unsaturated part of main polymer chain consists of 1,4-*trans*- and 1,2-structures with different combination of units. For the first time spectral signals of carbon and hydrogen atoms of two types of the head groups in a polymer chain, which are dimethylpropane fragments of the initiator (2-chloro-2-methyl-butane) connected to the 1,4-*trans*- or 1,2- units of polybutadiene, were identified. Structures of the head groups were confirmed using one-dimensional ^{13}C NMR with a T_2 -filter and ^{13}C DEPT-135° NMR spectroscopy, as well as two-dimensional ^1H – ^{13}C HSQC and HMBC NMR spectroscopy. The structures of two types of chlorine-containing end groups of polybutadiene with 1,4-*trans*- and 1,2-structure were also established.

The methods were developed for the quantitative calculation of content of the head and end groups,

unsaturation, and functionality of polybutadiene macromolecules on the terminal units. These methods can be used in the future to study the kinetics and mechanism of cationic polymerization of butadiene, as well as subsequent modification of the polymer.

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Animal Testing and Ethics

No human or animal subjects were used in this research.

Conflict of Interest

The authors declare no competing interests.

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