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## THE STRUCTURE OF POLYBUTADIENES AND BUTADIENE-ACRYLONITRILE COPOLYMERS

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**Abstract.** The paramagnetic probe method with the use of free radicals of different dimensions (2,2,6,6-tetramethyl-1-piperidinyloxy and 4-benzoate-2,2,6,6-tetramethyl-1-piperidinyloxy) has been employed to study the effect of the isomeric composition of butadiene units in polybutadienes and butadiene–acrylonitrile copolymers on the number and dimensions of ordered structures. The nature of density fluctuations and defective regions, that is, the regions in which the radicals are sorbed, has been ascertained. It has been shown that the ordered regions are composed of stereoregular chain fragments, while defective regions are enriched with butadiene isomers different from those present in prevailing amounts.

**Keywords:** polybutadiene, butadiene-acrylonitrile rubber, electron paramagnetic resonance, effective activation energy, isomerism, ordered structure, random structure.

### 1. Introduction

In [1], the micro- and supramolecular structure of ethylene-propylene-diene ternary copolymers was studied by IR and EPR spectroscopy. Paramagnetic probe measurements showed that the temperature dependences of correlation time  $t_c$  plotted in Arrhenius coordinates for microblock copolymers with high degrees of isotacticity of propylene units demonstrate transitions relevant to the breakdown of supramolecular structures composed of not only ethylene sequences but also propylene sequences [1]. Later on, the existence of these transitions was confirmed by the thermomechanical analysis of the copolymers [2]. Under the assumption that the radical solubility and distribution over rotation frequencies are the same in amorphous regions of homo- and copolymers, the correlation time of a probe in ethylene-propylene-diene copolymers was calculated with a high accuracy on the

basis of the additive contribution of each component corresponding to its weight fraction after deduction of the amounts of ordered structures. The latter were determined as the contents of fractions insoluble in toluene at room temperature. Thus, the paramagnetic probe method is a delicate instrument for investigating the molecular and supramolecular organization of elastomers.

Here, this method was applied for studying the molecular mobility in butadiene elastomers with different stereoisomerisms of units and in butadiene-acrylonitrile copolymers (acrylonitrile-butadiene rubbers (NBRs)). In most cases, they were mostly composed of isomeric butadiene units of one kind (*cis*-1,4 in PBs or *trans*-1,4 in NBRs) (Table 1). The temperature dependence of the rotational mobility of free-radical probes with different dimensions (2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and 4-benzoate-2,2,6,6-tetramethyl-1-piperidinyloxy (BZONO)) in these elastomers was investigated [3, 4].

### 2. Experimental

The objects of investigation were polybutadienes, such as *cis*-PB, SKD PB, and SKDL PB (a rubber synthesized in the presence of a lithium catalyst), with different stereoregularities of macromolecules and butadiene-acrylonitrile copolymers of the BNKS-18, BNKS-28, and BNKS-40 brands (acrylonitrile contents of 18, 28, and 40 wt %, respectively). The isomeric composition of butadiene units, that is, the contents of *trans*-1,4, *cis*-1,4, and 1,2-isomers, was determined by IR spectroscopy from bands at 967, 730, and 911  $\text{cm}^{-1}$ , respectively [5] through the use of film samples cast from solutions in  $\text{CCl}_4$  or chloroform. The calculations were performed with the extinction ratios reported in [6]; the results are listed in Table 1.

**Isomeric composition of butadiene units in PBs of different brands and butadiene–acrylonitrile copolymers**

Elastomer	Isomer content*, wt %		
	<i>trans</i> -1,4	1,2-units	<i>cis</i> -1,4
<i>cis</i> -1,4-PB	0.89	0.6	98.5
SKD	3.8	2.5	93.7
SKDL	47	8.8	44.2
BNKS-18	82.0	8.2	9.8
BNKS-28	76.4	14.4	9.2
BNKS-40	93.0	4.4	2.6

\* in the butadiene part of the polymer

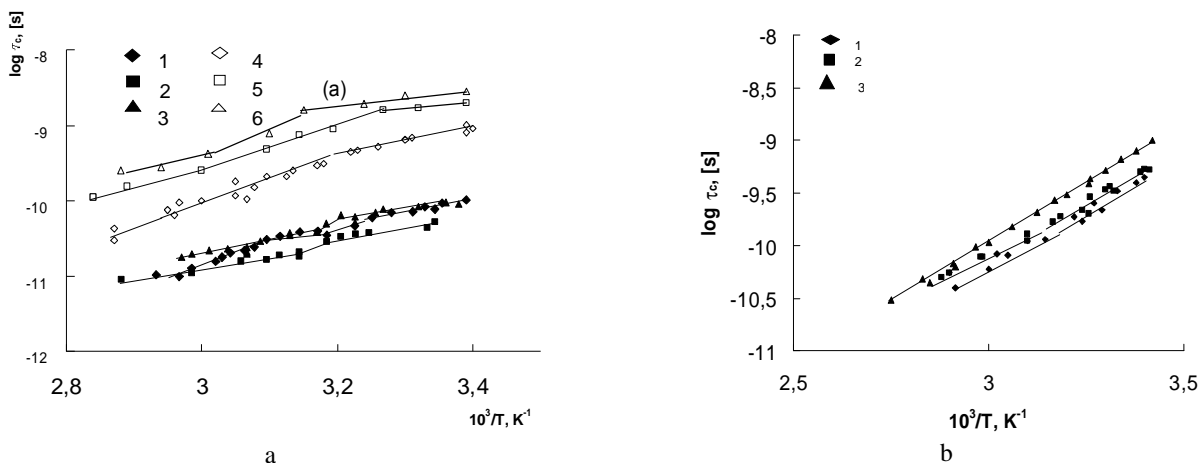
EPR spectroscopy was used to study the rotational mobility, which is characterized by correlation time  $t_c$  of TEMPO and BZONO radicals [3, 4], in the temperature range of 293–363 K with an EPR-V radiospectrometer. The elastomers were saturated with TEMPO from the gas phase at room temperature for three days. Then, the samples were stored at room temperature for a few days. During storage, the radical was desorbed from large defective regions of the samples (pores, cavities, etc.), in which polymers have almost no effect on the rotational mobility of the radical. BZONO was incorporated into PB from solutions in acetone with a concentration of  $10^{-3}$  mol/l with subsequent evaporation of the solvents at room temperature. The EPR spectra of the TEMPO probe in PBs and BNKS-18 show the classical triplet pattern. The

**Table 2**

**Arrhenius parameters of probe rotation in polymers and  $t_c$  values at 297.5 K**

Elastomer	$t_c \cdot 10^{-10}$ , s (297.5 K)	$E_1$	$E_2$	$t_o^{(1)}$ , s	$t_o^{(2)}$ , s	Temperature of the transition onset, K
		kJ/mol				
TEMPO						
<i>cis</i> -1,4-PB	0.89	33.5	56	$1.1 \cdot 10^{-16}$	$2.5 \cdot 10^{-20}$	323
SKD	0.5	24.4	54.1	$2.7 \cdot 10^{-15}$	$2.8 \cdot 10^{-20}$	314
SKDL	0.9	17.2	48.5	$8.5 \cdot 10^{-14}$	$4.4 \cdot 10^{-19}$	308
BNKS-18	7.4	33.8	54.6	$9.3 \cdot 10^{-16}$	$1.5 \cdot 10^{-19}$	311
BNKS-28	17.8	14.4	65.2	$5.6 \cdot 10^{-12}$	$1.2 \cdot 10^{-20}$	306
BNKS-40	23.4	20.1	76.4	$7.8 \cdot 10^{-13}$	$3.8 \cdot 10^{-22}$	317
BZONO						
<i>cis</i> -1,4-PB	4.0	44.3	33.0	$5.8 \cdot 10^{-18}$	$4.5 \cdot 10^{-16}$	313
SKD	5.0	44.0	35.8	$8.0 \cdot 10^{-18}$	$2.0 \cdot 10^{-16}$	309
SKDL	7.9	46.5	43.3	$5.0 \cdot 10^{-18}$	$1.7 \cdot 10^{-17}$	308

Note:  $E_i$  and  $\tau_o^{(i)}$  are the effective activation energies and preexponential factors at temperatures below ( $i = 1$ ) and above ( $i = 2$ ) the temperature of the transition onset.



**Fig. 1.** Temperature dependences of correlation times of the rotational mobility plotted for TEMPO (a) and BZONO (b) radicals in Arrhenius coordinates: *cis*-PB (1); SKD (2); SKDL (3); BNKS-18 (4); BNKS-28 (5) and BNKS-40 (6)

spectra of both radicals measured in BNKS-28 and BNKS-40 at room temperature attest to a heterogeneous structure, that is, to the existence of fast and slow components. In the case of BZONO, the pattern of the spectra is typical of anisotropic rotation characterized by different frequencies of rotation about different molecular axes. The  $t_c$  values determined at 297.5 K are listed in Table 2. The error in the measurements of  $t_c$  is 5 %.

### 3. Results and Discussion

The effective activation energy  $E_{ef}$  was calculated for the rotation of the radicals (Table 2) from the temperature dependences of correlation time  $t_c$  of TEMPO and BZONO in PBs and TEMPO in butadiene-acrylonitrile copolymers (Fig. 1). The calculations were performed for different parts of the curves plotted in Arrhenius coordinates. These parts corresponded to different relaxation processes relevant to supramolecular structures. During approximation of the linear parts of the curves in Fig. 1, correlation coefficients  $R^2$  were 0.82–0.97.

For stereoregular polybutadienes (SKD rubbers) and NBRs, in the region of the high-elasticity plateau, relaxation spectrometry data indicate as many as three  $I$ -relaxation processes relevant to the molecular mobility of structural elements that are larger than segments, that is, microblocks whose activation energy is equal to that of the viscous flow of the elastomers [7]. Hence, segments play the role of kinetic units of slow relaxation  $I$  processes. The mechanism governing the molecular mobility of the microblocks consists in their formation and decomposition through the fluctuation attachment and detachment of segments as individual kinetic units [7]. Moreover, the thermomechanical analysis, the energy parameters of dissolution and diffusion of low-molecular-mass substances, and IR spectroscopy data suggest the existence of fluctuation structures in elastomers [8–12].

The presence of ordered microscopic regions and their size distribution is, as is shown below (and in [13]), governed by the microtacticity (the geometric similarity of chain fragments) and temperature. The molecular dynamics of polymer chain fragments located in a structural defect depends on the mobility of regular chain fragments comprising ordered structures. The transitions are explained by the unfreezing of the molecular mobility in fluctuation structures composed of units occurring in the prevailing configuration and by their rearrangements [7–13].

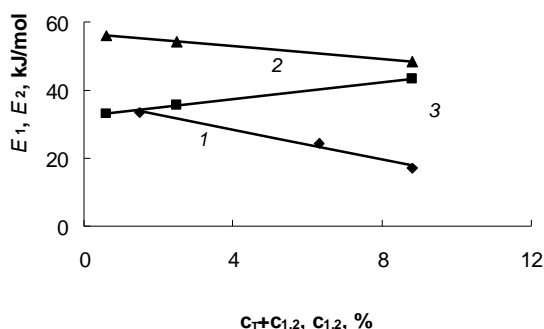
Like any other low-molecular-mass substance, radicals are sorbed in the polymer regions with subsequent deteriorations of short-range order in the arrangement of chains [14]. Such regions most probably appear at the joints of different isomers of butadiene units, because

there is no geometric similarity between them [13, 15]. When the samples are stored for a few days at room temperature, TEMPO remains in the regions in which its desorption is hindered, that is, in the regions with rather dense macromolecular packing but free volume sufficient for accommodation of the radical. Defects in the chain stereoregularity may give rise to the appearance of such a free volume. The radical cannot penetrate regions with ordered structure and hindered molecular mobility.

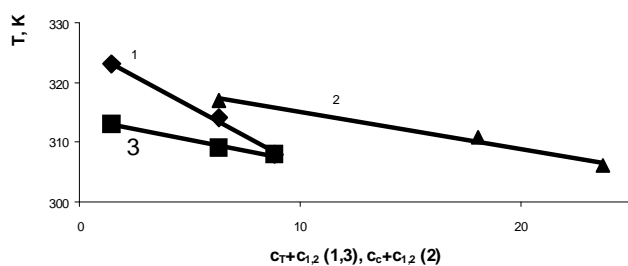
Stereoregular PBs containing more than 99 % *cis*-1,4-units form crystals with a maximum melting temperature of 285.5 K. When the content of *cis*-1,4-isomer is 98 %, the melting temperature of the polymers is 273 K; at room temperature, their ordered structures are preserved [16]. At a *cis*-1,4-unit content of 90 %, the maximum crystallinity of SKD is 55 % (236 K), while at 81 %, the crystallinity is insignificant. It was shown that, during photochemical isomerization, crystallization occurs when the content of *trans*-1,4-units is higher than 75 % [17]. However, when the content of *trans*-1,4-isomers is lower than 20 %, *cis*-1,4-structures undergo low-temperature crystallization [18].

Experimental melting temperatures  $T_m$  depend on the contents of units occurring in different configurations and on the duration and temperature of crystallization and the rate of melting [16]. At a *cis*-1,4-unit content of 96.4 %, the DTA method demonstrated the appearance of two overlapping endothermic peaks during rapid cooling and slow heating [19]. The DTA and dilatometry data depend on the frequency and randomness of the repetition of units with a structure different from the *cis*-1,4-configuration along a polymer chain [16]. Thus, the capability of ordering or crystallization is predetermined by the stereoregularity of elastomer chains. This conclusion is confirmed below by the EPR data.

For *cis*-PB and SKD and SKDL with different isomeric butadiene unit ratios, the effective activation energy  $E_1$  of TEMPO radical rotation at temperatures below the transition linearly diminishes with an increase in the content of isomers present in small amounts, that is, *trans*-1,4- and 1,2-units (Fig. 2). The total amount of *trans*-1,4- and 1,2-units in *cis*-PB and SKD is small (less than 10 %) (Table 1). Therefore, it is assumed that they are randomly distributed over polymer chains. According to [20], SKDL, which is synthesized in the presence of *n*-BuLi as a catalyst, contains blocks of *cis*- and *trans*-isomers connected by vinyl units. Hence, only *cis*-1,4-unit–1,2-unit–*trans*-1,4-unit joints are present in it. *cis*-1,4 and *trans*-1,4-isomers form fluctuation structures [11]. Thus, the regions with the lowest order are enriched with 1,2-units located between *cis*-1,4- and *trans*-1,4-isomers. Hence, the  $E_1$  value of SKDL falls on the linear dependence of  $E_1$  on the isomeric composition of butadiene units (Fig. 2) if the content of 1,2-units (8.8 %) (Table 1) is plotted on the abscissa axis.



**Fig. 2.** Effective activation energies  $E_1$  (1) and  $E_2$  (2, 3) of the rotational mobility of radicals as functions of the content of *trans*-1,4 and 1,2-units ( $c_T + c_{1,2}$ ) (1) and 1,2-conformers ( $c_{1,2}$ ) (2, 3) for TEMPO (1, 2) and BZONO (3)



**Fig. 3.** Transition temperatures of PBs (1, 3) and NBRs (2) vs. the contents of *trans*-1,4- and 1,2-units ( $c_T + c_{1,2}$ ) (1, 3); *cis*-1,4- and 1,2-butadiene units ( $c_C + c_{1,2}$ ) (2): TEMPO (1, 2) and BZONO (3)

The effective activation energy of probe rotation decreases in proportion to reduction in the stereoregularity of chains and the dimensions of ordered structures (Tables 1 and 2; Fig. 2). This fact agrees with the data reported in [16], where a PB sample synthesized in the presence of an  $ALR_3/TiCl_4$ -type catalyst was separated into fractions with different contents of *cis*-1,4-units by selective extraction.

In the case of *cis*-PB containing 98.5 % *cis*-1,4-units and a content of *trans*-1,4- and 1,2-isomers of ~15 %, the activation energy of the probe rotation in the initial region of the  $t_c(T)$  curve (293–323 K) is 33.5 kJ/mol (Table 2). This result agrees with the data from [7], where the activation energy of the low-frequency relaxation processes, which are relevant to the mobility of microblocks of supramolecular structures and  $\lambda$  processes, for monodisperse PBs was found to be 34 kJ/mol.

In SKD containing 93.7 % *cis*-1,4-units, structures composed of sequences of these units are found; however, because of a higher content of *trans*-1,4- and 1,2-units than that in *cis*-PB and, accordingly, a lower chain stereoregularity, the amount and dimensions of these structures are smaller than those in *cis*-PB. Therefore, the temperature of transition is lower (Table 2). The effective

activation energy of TEMPO rotation in SKD (22.5 kJ/mol) is close to the activation energy of viscous flow determined for PB with a *cis*-1,4-unit content of 92 % (23.5 kJ/mol) and the activation energy of sulfur diffusion in SKD (23.1 kJ/mol) [7, 10, 21].

Thus, the  $E_{ef}$  value of SKD is equal to the activation energy of the viscous flow of PB with a close isomeric composition. In SKD, the radical is sorbed by regions with defective chain microtacticity that are composed of the same sequences of isomers as those in *cis*-1,4-PB.

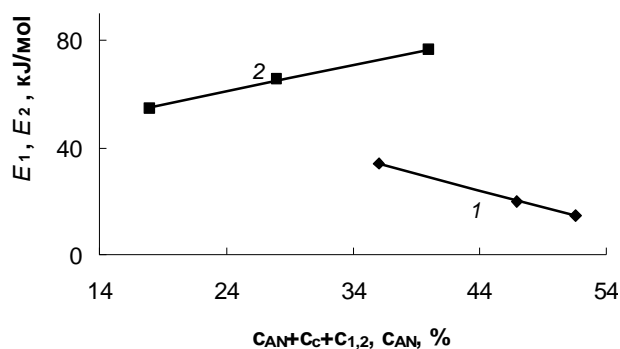
In SKDL containing almost equal amounts of *cis*-1,4- and *trans*-1,4-isomers, the effective activation energy of radical rotation is 17.5 kJ/mol at temperatures below the transition temperature (308 K). The obtained transition temperature agrees with [11].

Hence, if the regular parts of chains are composed of ordered structures, polymer chains located in unordered regions (the regions of radical sorption) are enriched with butadiene isomers that are present in smaller amounts.

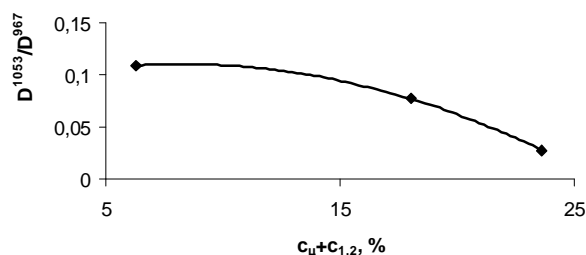
Similarly to  $E_1$ , the transition temperature linearly decreases with an increase in the content of *trans*-1,4- and 1,2-isomers in PBs (Fig. 3). This fact testifies to the conclusion that, at low temperatures, the temperature dependence of the radical mobility is governed by the dimensions of stereoregular fragments of chains and related ordered structures.

The effective activation energy of TEMPO radical rotation,  $E_2$ , corresponding to the region above the transition temperature is higher than  $E_1$  and slightly declines according to a linear relationship with an increase in the 1,2-isomer content (Fig. 2). Hence, the transition is associated with the breakdown of primary structures and separation of chains related to an increase in segmental mobility; as a result, only vinyl units containing side double bonds influence the radical rotation.

In butadiene-acrylonitrile copolymers with different contents of polar units and isomer ratios of the butadiene comonomer (Tables 1 and 2), the effective activation energies of TEMPO probe rotation that correspond to the initial part of Arrhenius dependence  $t_c(T)$  likewise linearly decrease with an increase in the amount of all defects in the regularity of the butadiene component ( $\sum AN\text{-units} + cis\text{-1,4-units} + 1,2\text{-units}$ ) (Fig. 4). Energy  $E_2$  corresponding to the region above the transition temperature linearly increases with the content of acrylonitrile units in the copolymers, that is, with the concentration of polar units exhibiting a high cohesion energy, because of a strong dipole–dipole interaction of nitrile groups, which noticeably increase chain rigidity. Thus, the transition improves the segmental mobility so much that chains are separated and the effect of butadiene unit isomers becomes unnoticeable against the background of the strong interaction between the polar groups, which strongly reduce chain flexibility.



**Fig. 4.** Effective activation energies  $E_1$  (1) and  $E_2$  (2) of radical TEMPO rotation vs. total contents of acrylonitrile + *cis*-1,4- + 1,2-units ( $c_{AN} + c_c + c_{1,2}$ ) (1) and  $c_{AN}$  (2)



**Fig. 5.** Optical density ratio for bands at 1053 and 967  $\text{cm}^{-1}$  characterizing the fraction of ordered structures in NBRs vs. total content of *cis*-1,4- and 1,2-units ( $c_c + c_{1,2}$ )

Above the transition temperature, the mobility of TEMPO in PBs and NBRs is influenced by side vinyl or nitrile groups. In both cases, the larger the amount of defects in the stereostructure of the butadiene part of a chain, the lower the effective energy of radical rotation.

Fig. 5 shows the dependence of the intensity ratio between the band at 1053  $\text{cm}^{-1}$  attributed to the *trans*-1,4-units contained in crystallites and the band at 967  $\text{cm}^{-1}$  that characterizes the total content of *trans*-1,4-isomers [5] on the total content of 1,2- and *cis*-1,4 isomers. As their content increases, the order of *trans*-1,4-units diminishes. BNKS-28 and BNKS-40 have the least and the most ordered structures, respectively. As was shown in [16], at a *trans*-1,4-unit content above 75 %, the crystallinity is observed at room temperature. The total amorphization attests to a random distribution of *trans*-1,4-units. Hence, at a high content of acrylonitrile units, BNKS-40 contains the greatest amounts of structures formed by both strong dipole–dipole bonds between nitrile groups and *trans*-1,4-butadiene sequences [7, 12, 22].

The BZONO probe, which is characterized by a high molecular mass, an asymmetric shape, and an anisotropic rotation, was incorporated into the elastomers from solutions; therefore, the sample structure may be

different from the initial one. TEMPO molecules occupy defects that exist in a polymer. As regards BZONO, it seems the defect is formed as solvent evaporates. This fact may explain different patterns of the Arrhenius  $t_c(T)$  dependences plotted for TEMPO and BZONO radicals (Fig. 1).

When BZONO is used, relaxation transitions are distinctly observed for *cis*-PB and SKD (Fig. 1, Table 2). Linear  $t_c(T)$  dependences or small differences between  $E_{ef}$  values in the first and second regions suggest the absence of ordered structures or their insignificant effect on the radical mobility (their absence or small dimensions in SKDL).

In contrast to TEMPO, the BZONO radical occurs in the environment of long disordered defective butadiene fragments of chains. This circumstance seems to influence the  $E_{ef}$  value.

Equal  $E_1$  values, which are observed for BZONO in PBs (Fig. 2) irrespective of the stereoregularity of elastomer chains, may be interpreted as a consequence of the probe location in large defects possessing the same structure, while close temperatures of the relaxation transitions (Fig. 3), which are lower than those for TEMPO, may be considered to be due to a smaller size of ordered structures. The  $E_2$  value of BZONO slightly increases with an increase in the content of 1,2-isomers of butadiene units (similarly to TEMPO) (Fig. 2). This finding may be explained by certain hindrances to the rotational mobility of the large probe from the side units of chains.

According to data of X-ray analysis [23] the sequence of alternation *trans*-1,4-butadiene units and AN-units and *trans*-1,4-butadiene sequences, segregating selectively because of their difference in chemical and geometrical structure, form two types of regulated formations. Regulated structures, formed by alternation *trans*-1,4-butadiene units and AN-links, disintegrate under higher temperatures. However, this aspect is not considered in the present work.

## 4. Conclusions

The above results lead us to draw the following conclusions. A small TEMPO radical provides more complete information on the structure of polymers and the nature of defective regions in them. The incorporation of a probe from solutions is accompanied by changes in the initial structural organization of elastomers. For some systems, this phenomenon may be of interest. Radicals are sorbed by regions of a polymer matrix that contain butadiene units. Defective regions comprise chain fragments with alternating butadiene units of different isomeric structures. Their mobility is influenced by

regular chain fragments composing ordered structures, a fact that additionally confirms the existence of the latter.

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## СТРУКТУРА ПОЛІБУТАДІЕНІВ І БУТАДІЕН-АКРИЛОНІТРИЛЬНИХ КОПОЛІМЕРІВ

**Анотація.** *Методом парамагнітного зонду з використанням радикалів різної величини (2,2,6,6-тетраметилпіперидин-1-оксиду і 4-бензоат-2,2,6,6-тетраметилпіперидин-1-оксиду) досліджено вплив ізомерного складу бутадієнових ланок у полібутадієнах і кополімерах бутадієну з акрилонітрилом на кількість та величину впорядкованих структур. Встановлено природу флуктуацій густини і дефектних областей, в яких сорбовані радикали. Показано, що впорядковані області утворені стереорегулярними ділянками ланцюгів, а дефектні – збагачені ізомерами бутадієну.*

**Ключові слова:** *полібутадієн, бутадієн-акрилонітрильний каучук, електронно-парамагнітний резонанс, ефективна енергія активації, ізомеризм, впорядкована структура, невпорядкована структура.*