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THE STRUCTURE OF ACRYLONITRILE-BUTADIENE RUBBERS: PARAMAGNETIC-PROBE STUDY

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Abstract. Chain microstructures and supramolecular structures of nitrile-butadiene rubbers are studied by ESR spectroscopy. On the temperature dependences of the rotational mobility (correlation time τ_c) of paramagnetic probe 2,2,6,6-tetramethylpiperidine-1-oxyl, relaxation transitions are observed. It is shown that there is a correlation between the Arrhenius parameters of rotational mobility of radical and the copolymer composition and that different brands of rubbers differ in microstructure and supramolecular structure.

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

1. Introduction

Nitrile-butadiene rubbers (NBRs) are the products of high-temperature (303–323 K) or low-temperature (278 K) emulsion copolymerization of butadiene with acrylonitrile (AN) in the presence of emulsifiers (Necal emulsifiers for SKN rubber and ecologically friendly paraffinates for BNKS rubber) and have different chain microstructures and types of supramolecular organization [1-3].

WAXS and SAXS studies [1, 2] revealed that statistical-average intermolecular distances L nonlinearly increase with the content of AN units in NBR. In this case, the value of L for BNKS is higher than that for SKN on condition that the content of AN units is the same (Table 1). The annealing of BNKS and SKN rubbers at different temperatures in a press results in dissimilar changes in L values for these rubbers.

The sequences of alternating *trans*-1,4-butadiene and AN units and microblocks of *trans*-1,4-butadiene units selectively segregate and form ordered structures of two types [1, 2]. BNKS macromolecules contain longer sequences of alternating *trans*-1,4-butadiene and AN units than SKN macromolecules, in which the content of

individual AN units is increased. Accordingly, at equal contents of AN units, the dimensions of ordered structures formed by these units in BNKS are higher than those in SKN.

Table 1

**Isomeric composition of butadiene units
in different AN-butadiene copolymers [6, 11]**

Copolymer	Content of units, %		
	<i>trans</i> -1,4	1,2	<i>cis</i> -1,4
SKN -18	83.2	10.1	6.7
SKN -26	86.9	7.1	6.0
SKN -40	78.8	5.0	16.2
BNKS -18	82.0	8.2	9.8
BNKS -28	76.4	14.4	9.2
BNKS -40	93.0	4.4	2.6

The aim of this study was to compare the chain microstructures and supramolecular structures of SKN and BNKS with the use of IR spectroscopy and the paramagnetic-probe method [4, 5]. In our experiments were used the nitroxyl radical TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl). Our task was to determine differences in the microstructures of chains: the distribution of polar AN units and disruptions of stereoregularity of butadiene units mainly occurring in the *trans*-1,4 configuration [6]. *Trans*-1,4 units form ordered structures, and the size distribution of these structures depends on the number of disruptions of the geometric similarity of butadiene chain fragments [6-8]. It was of interest to study the differences in the structures of block samples, in the sizes of ordered structures of butadiene units.

2. Experimental

BNKS and SKN elastomers containing 18, 28, 26, and 40 wt % AN units (BNKS-18, BNKS-28, BNKS-40,

and SKN-18, SKN-26, SKN-40) were used as research objects. The contents of *trans*-1,4-, *cis*-1,4-, and 1,2-butadiene units in films prepared from solutions in CCl₄ or chloroform were determined *via* IR spectroscopy from bands at 967, 730, and 911 cm⁻¹, respectively [9]; the extinction coefficients were taken from [10] (Table 1).

The temperature dependence of the rotational mobility of TEMPO radical in elastomers, which is characterized by correlation time τ_c , was studied *via* EPR spectroscopy on an EPR-V radiospectrometer [4, 5]. The elastomers were saturated with the TEMPO radical from the gas phase at room temperature for three days. Then, the samples were kept at room temperature for another three days in order to desorb radicals from large defect areas (pores, cavities). For BNKS-18 and SKN-18 at room temperature, the EPR spectrum of the TEMPO probe is a classical triplet; for BNKS-28 and BMKS-40, the spectral pattern is characteristic of the heterogeneous structure; and, for SKN-26 and SKN-40, the spectral pattern is typical of the homogeneous structure with retarded motion.

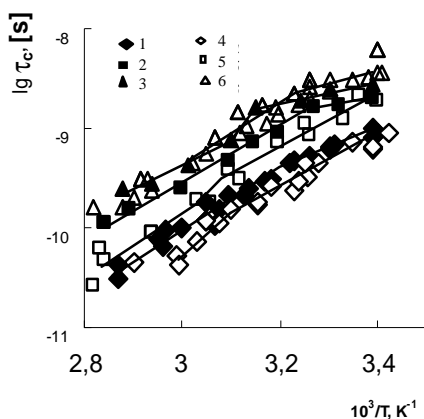


Fig. 1. Temperature dependence of the correlation time of rotational mobility for TEMPO radical in Arrhenius coordinates for BNKS-18 (1); BNKS-28 (2); BNKS-40 (3); SKN-18 (4); SKN-26 (5) and SKN-40 (6)

Table 2
Arrhenius parameters of probe rotation in polymers and τ_c at 297.5 K

Polymer	$t_c \cdot 10^{10}$, s	Effective activation energy, kJ/mol		Preexponential factor, s		Temperature of the outset of transition, K
		E_1	E_2	t_0^1	t_0^2	
SKN -18	4.0	45.0	52.9	$7.62 \cdot 10^{-18}$	$4.50 \cdot 10^{-19}$	323
SKN -26	12.6	43.2	57.7	$4.42 \cdot 10^{-17}$	$1.31 \cdot 10^{-19}$	327
SKN -40	31.6	39.4	68.7	$4.17 \cdot 10^{-16}$	$5.98 \cdot 10^{-21}$	319
BNKS -18	7.4	33.8	56.2	$9.25 \cdot 10^{-16}$	$1.45 \cdot 10^{-19}$	311
BNKS -28	17.8	14.4	65.2	$5.55 \cdot 10^{-12}$	$1.18 \cdot 10^{-20}$	306
BNKS -40	23.4	20.1	76.4	$7.83 \cdot 10^{-13}$	$3.84 \cdot 10^{-22}$	317

The Arrhenius dependences of τ_c demonstrate relaxation transitions in the range of 293–343 K [6, 7, 11]. The activation energy for the rotational mobility of radicals was calculated from different portions of the curves (Fig. 1), and the temperature ranges of transitions were determined (Table 2). The measurement error for τ_c was 5 %.

3. Results and Discussion

In PB and BNKS, TEMPO is adsorbed by random portions of the matrix with a high molecular mobility [6]. These portions are formed by butadiene units enriched in isomers, that are present in small amounts and are randomly distributed along the chain. The mobility of polymer chain segments in the defect zones is influenced by macromolecular fragments of the ordered structures connected with the above segments via chemical bonds. The intensity of the molecular mobility of a polymer (the rotational mobility of radicals) with temperature is related to the gradual decomposition of fluctuation structures whose size constantly increases until disappearance of the initial ordered structures [6, 11, 12]. This conclusion is evident (as will be shown below) from the linear dependences of E_1 and the temperature of relaxation transition on the stereoregularity of butadiene units.

Thus, the existence of relaxation transitions is related to the heterogeneous elastomer structure due to the presence of supramolecular entities [6-8, 11-13]. Their positions on the temperature scale and the effective activation energy in portions of the curves before and after the relaxation transition are different for different rubbers with the same content of AN units and even with similar contents of *trans*-1,4 isomers of butadiene (Table 2). The associates of AN units that undergo dissociation at a high temperature (>90°C) are disregarded in this case [12].

For BNKS and SKN elastomers, effective activation energy E_1 in the portions of the Arrhenius dependences obtained for the rotational mobility of TEMPO before the transition depends on the total number of disruptions of butadiene comonomer regularity, that is, *cis*-1,4 isomers, 1,2 structures, and AN units (Table 1, Fig. 2). The effective activation energy of the molecular mobility is affected by side CN groups and their distribution along the chain.

In the case of BNKS elastomers, effective activation energy E_1 declines as the stereoregularity of butadiene units decreases (Fig. 2). For SKN samples, E_1 is significantly higher and remains practically unchanged as the geometric similarity of butadiene chain fragments decreases, *i.e.*, as the content of *trans*-1,4 butadiene units decreases (Fig. 2).

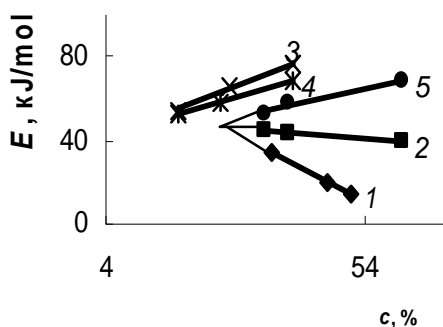


Fig. 2. Effective activation energy E_1 of rotational mobility of TEMPO vs. content of AN+*cis*-1,4 and 1,2 units in BNKS (1) and SKN (2); E_2 content of AN units in BNKS (3) and SKN (4); content of AN+*cis*-1,4+1,2 units in SKN (5). C is units content here and in Fig. 3.

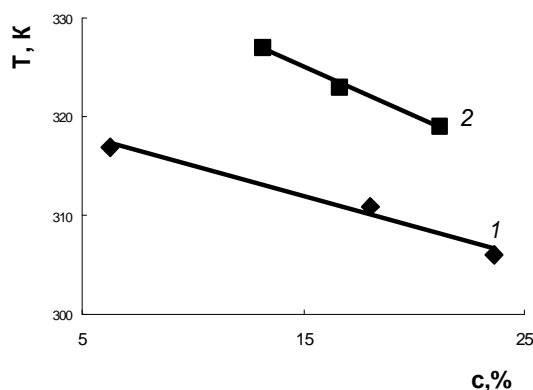


Fig. 3. Temperature of relaxation transition in BNKS (1) and SKN (2) vs. the total content of *cis*-1,4 and 1,2 units

A higher value of E_1 for SKNs of different polarities and its insignificant drop with the number of disruptions of *trans*-1,4 butadiene units can be interpreted as the same wide range of the ordered structure size (Fig. 2). This result implies that, in SKN, along with high density fluctuations, a significant fraction of small structures is present.

For BNKS, a decrease in the length of *trans*-1,4-butadiene units results in a significant drop in E_1 , *i.e.*, in a weak change of τ_c with temperature. This finding may be explained by narrowing of the range of the ordered structure size in elastomers in the following sequence: BNKS-18, BNKS-40, BNKS-28. As is evident from the temperatures of relaxation transitions (Table 2, Fig. 3), the maximum size of the ordered structures in BNKS-18 and BNKS-28 is significantly smaller than that for analogous SKN brands.

The temperatures of relaxation transitions in BNKS and SKN linearly decrease with the content of *cis*-1,4 and 1,2 units and the maximum size of fluctuation structures decreases (Fig. 3).

At the temperature higher than the temperature of the relaxation transition, chains with the unfrozen

molecular mobility are separated to a distance corresponding to the maximum effect of AN units imparting enhanced rigidity to chains on the frequency of probe rotation. In the case of SKN and BNKS, the effective activation energy in the second portion of the curve, E_2 , grows with the content of AN units (Fig. 2, curves 3, 4). Note that E_2 is higher for BNKS than for SKN. At almost identical total contents of AN units in these elastomers, a higher value of effective activation energy E_2 for BNKS may be explained by different characters of distribution of AN units along the chain.

The latter assumption is confirmed by the linear dependence of E_2 on the total content of AN and *cis*-1,4- and 1,2-butadiene units in SKN. The value of E_2 increases owing to reduction in the molecular mobility during the action of CN side groups, as evidenced by parallel patterns of the dependences (Fig. 2, curves 4, 5). The dependence of the effective activation energy in the second portion on the stereoregularity of butadiene units in SKN suggests that, after the decay of fluctuations in the first portion the structure rearranged to form larger supramolecular structures (the temperature of the second transition is significantly higher than that for the first transition, Fig. 1) and with a decrease in the number of long sequences of *trans*-1,4 units, the size spread grows.

For BNKS, there is no similar dependence. This circumstance evidences that there is hindrance to rearrangement of the initial structure because of the presence of AN microblocks whose associates can decay at a higher temperature [12]. These data lead us to conclusion that the random distribution of AN units is more probable for SKN than for BNKS. This feature of the SKN chain microstructure determines higher values of E_1 and T and lower values of E_2 (Fig. 2, curves 3, 4). The formation of even short sequences of AN units and the strong dipole-dipole interaction of nitrile groups cause a decrease in the molecular mobility of BNKS chains, an increase in E_2 , and a decline in E_1 owing to hindered formation of fluctuation structures and a greater size uniformity of these structures.

This circumstance is confirmed by the values of τ_c for SKN-18 and SKN-26. Throughout the temperature range, these values are lower than those for corresponding BNKS samples because of a higher segmental mobility (Fig. 1, Table 2).

For high-polarity SKN-40, the mobility of macromolecules at room temperature is lower (the correlation time is longer) than that for BNKS-40, while E_1 (the scatter in the fluctuation-structure size) is significantly higher than that for BNKS-40 (Table 2). The maximum dimensions of the ordered structures in these samples are close, as corroborated by almost equal temperatures of relaxation transitions in these structures (Fig. 3).

The extended linear dependences of E_1 (for SKN and BNKS) and E_2 (for SKN) on the total content of AN, *cis*-1,4 and 1,2 units intersect at the point with a coordinate corresponding to a quantity of disruptions in the regularity of *trans*-1,4 isomers of 25 % (Fig. 2). As was shown in [14], at the content of *trans*-1,4 units above 75 %, crystallinity manifests itself at room temperature. Thus, at the intersection of the curves, where for SKN, $E_1 = E_2$, the crystallization of the elastomer should occur. Equal effective activation energies for different temperature ranges imply the absence of the transition, a result that is due to formation of thermodynamically stable species, *i.e.*, microcrystallites with a significantly higher melting temperature. As follows from the above dependences, the ordered structures are the nuclei of crystallization of *trans*-1,4-PB.

The intersection of curves (Fig. 2) corresponds to $E_{eff} = 44\text{--}45$ kJ/mol. The same value of E_{eff} was determined at the intersection of dependences of E_2 values for SKN and BNKS on the content of AN units at their zero content, that is, for *trans*-1,4-PB. This value of E_{eff} is close to activation energy of viscous flow for all three rubbers above 353 K (46 kJ/mol), at which the dipole–dipole bonds of CN groups are broken [7].

This result indicates that the observed processes are correctly assigned to λ relaxations related to formation of fluctuation structures involving butadiene units [7, 11, 12]. The fact that the values of E_1 for SKN are similar to E_{eff} suggests that they are related to the structure of *trans*-1,4-PB. BNKS elastomers characterized by very low E_1 values because smaller ordered structures with a low spread in size predominate in them. The above data confirm that in the case of SKN AN units have a significantly weaker effect on the molecular dynamics because of their random distribution along the chain.

4. Conclusions

Thus, the microstructures and supramolecular structures of rubbers polymerized under various conditions with the use of different emulsifiers are different. This difference manifests itself as a dissimilar character of distribution of AN units, as the isomeric composition of butadiene units, and as the size of their ordered structures. The SKN elastomers are random copolymers, whereas BNKS, along with the randomly distributed units, contains AN microblocks.

The above described data are of interest for forecasting the processes of NBR compatibilization with other rubbers and sorption and diffusion of low-molecular mass compounds in them that are used for crosslinking of macromolecules. For example, it was shown *via* the stress relaxation method in an ozone containing medium that

there is a difference in the degrees of crosslinking of rubbers and the rates of their ozone degradation [3].

Thus, the distribution of AN units along chains of SKN and BNKS elastomers affects not only formation of a network of supramolecular structures of AN units but also formation of *trans*-1,4-butadiene isomers.

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СТРУКТУРА БУТАДІЄН-НІТРИЛЬНИХ КАУЧУКІВ: ДОСЛІДЖЕННЯ ПАРАМАГНІТНОГО ЗОНДУ

Анотація. *Методом ЕСР-спектроскопії досліджено мікроструктуру та надмолекулярну структуру бутадієн-нітрильних каучуків. На температурних залежностях обертової рухомості (часу кореляції (τ_c)) парамагнітного зонду 2,2,6,6-тетраметилпіперидин-1-оксид спостерігаються релаксаційні переходи. Встановлено зв'язок між арреніусовськими параметрами обертової рухомості радикала і складом кополімерів та показано, що різні марки каучуків відрізняються мікро- та надмолекулярною структурою.*

Ключові слова: *полібутадієн, бутадієн-нітрильний каучук, електронний парамагнітний резонанс, ефективна енергія активації, ізомеризація, впорядкована структура, невпорядкована структура.*