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INVESTIGATION OF THE STRUCTURE OF MOLECULAR CHAINS OF POLYISOPRENES BY INFRARED ABSORPTION SPECTRA

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In the general problem of synthesizing rubbers with specified properties, an essential place is occupied by the study of the influence of polymerization conditions on the structure and spatial configuration of the main unit of molecular chains. In the present work, the microstructure of a number of polyisoprene rubbers was studied by the method of infrared spectra. Polyisoprenes obtained by catalytic polymerization (SKI), which in their principal physicomechanical properties approach natural rubber (ˆ1), and emulsion polyisoprenes (SEI), obtained by polymerization under the influence of free radicals (ˆ2), were investigated.

During the polymerization of isoprene, four different structures of macromolecular units may be formed, differing both in the position of the double bond relative to the main chain and in the spatial configuration of the atoms relative to the double bond: 1,2; 3,4; cis-1,4 and trans-1,4. Quantitative determination of the content in the polymer chain of each of the indicated structures, the totality of which is called the microstructure of the polymer, was carried out from absorption spectra in the infrared region (800 cm^{-1}–1000 cm^{-1}) by the method described earlier (ˆ3).

The following were used as reference substances: natural rubber (band 841 cm^{-1}) and gutta-percha (band 845 cm^{-1}), for determining the content in the polymer chain of cis-1,4- and trans-1,4-configurations; heptene-1 (band 909 cm^{-1}) and 2,3,3-trimethylbutene-1 (band 887 cm^{-1}).

The microstructure of SKI rubber was investigated on a series of samples obtained at a definite polymerization temperature. For emulsion polyisoprene SEI, the effect of polymerization temperature (T_p) on the microstructure was studied; in this connection, samples of this polymer obtained at temperatures from $-47°$ to $+50°$ were investigated (see Table 1).

From the data of Table 1 it follows, first, that all the SKI rubber samples we investigated are characterized by a high content of cis-1,4-configurations, reaching 75% of the total number of 1,4-units of the molecular chains. The data presented show, furthermore, that the presence of small side branches in this

polymer is due mainly to additions in the 3,4-position (isopropenyl groups); the number of units built in the 1,2-position in this polymer is small (1–1.5%).

The results we obtained in studying the structure of emulsion isoprene rubbers synthesized at different temperatures indicate that the polymerization temperature has a certain influence on the microstructure of these polymers. Thus, in rubbers obtained at temperatures from −47° to 0°, the 1,4 units of the molecular chain are constructed entirely in the trans-position; a further increase in the polymerization temperature leads to the appearance of a certain amount of cis-1,4 units, increasing monotonically with increasing polymerization temperature and reaching 8% at a process temperature of +50°. At the same time, in all the investi-

in the investigated polymerization-temperature interval, the content of 1,2 and 3,4 units in the polymer chains remains practically constant.

On the basis of the data on the microstructure of samples of emulsion isoprene rubber, obtained at various temperatures and given in Table 1, and using the Arrhenius-Eyring equation ([4]), we obtained a general analytical expression that makes it possible to calculate the relative content of the corresponding microstructure elements for any polymerization temperatures.

In the case under consideration, the Arrhenius-Eyring equation for the specific rates of formation of the corresponding microstructure components may be written as:

$$K_{1,2} = \frac{RT}{Nh} \exp\left[\frac{\Delta S_{1,2}}{R}\right] \exp\left[-\frac{\Delta H_{1,2}}{RT}\right]; \tag{1}$$

$$K_{3,4} = \frac{RT}{Nh} \exp\left[\frac{\Delta S_{3,4}}{R}\right] \exp\left[-\frac{\Delta H_{3,4}}{RT}\right]; \tag{2}$$

$$K_{\text{cis}} = \frac{RT}{Nh} \exp\left[\frac{\Delta S_{\text{c}}}{R}\right] \exp\left[-\frac{\Delta H_{\text{c}}}{RT}\right]; \tag{3}$$

$$K_{\text{trans}} = \frac{RT}{Nh} \exp\left[\frac{\Delta S_{\text{t}}}{R}\right] \exp\left[-\frac{\Delta H_{\text{t}}}{RT}\right]. \tag{4}$$

Here ΔH and ΔS_1 are, respectively, the heat and entropy of activation, and h is Planck' s constant.

Taking into account that $\frac{K_i}{K_j} = \frac{C_i}{C_j}$ (where K_i and K_j are the reaction-rate constants, and C_i and C_j are the concentrations of the corresponding configurations), we obtain:

$$\frac{C_{3,4}}{C_{1,2}} = \exp\left[\frac{1}{R}(\Delta S_{3,4} - \Delta S_{1,2}) + \frac{1}{RT}(\Delta H_{1,2} - \Delta H_{3,4})\right]; \tag{5}$$

$$\frac{C_{\text{c}}}{C_{1,2}} = \exp\left[\frac{1}{R}(\Delta S_{\text{c}} - \Delta S_{1,2}) + \frac{1}{RT}(\Delta H_{1,2} - \Delta H_{\text{c}})\right]; \tag{6}$$

$$\frac{C_{\text{t}}}{C_{1,2}} = \exp\left[\frac{1}{R}(\Delta S_{\text{t}} - \Delta S_{1,2}) + \frac{1}{RT}(\Delta H_{1,2} - \Delta H_{\text{t}})\right]. \tag{7}$$

Introducing the notation: $\Delta S_i - \Delta S_j = {}^{i}S_j$, $\Delta H_i - \Delta H_j = {}^{i}H_j$, it is easy to obtain a general expression for the concentrations of any microstructure components as a function of the polymerization temperature:

$$C = 100\left[1 + \sum \exp\left(\frac{{}^{j}S_i}{R} + \frac{{}^{i}H_j}{RT}\right)\right]^{-1}. \tag{8}$$

The differences in entropy and heat of activation, determined by us from the experimental data (from the plot of $\ln\frac{C_i}{C_j} = f(T_{\text{p}})$–Table 1), have the following values:

$$\Delta H_{\text{t}} - \Delta H_{\text{c}} = -5000\ \frac{\text{cal}}{\text{mol}}, \qquad \Delta S_{\text{t}} - \Delta S_{\text{c}} = -11.0 \text{ entropy units}\left[\frac{\text{cal}}{\text{mol}\cdot\text{deg}}\right];$$

$$\Delta H_{\text{t}} - \Delta H_{1,2} = -400\ \frac{\text{cal}}{\text{mol}}, \qquad \Delta S_{\text{t}} - \Delta S_{1,2} = 3.6 \text{ entropy units};$$

$$\Delta H_{\text{t}} - \Delta H_{3,4} = -600\ \frac{\text{cal}}{\text{mol}}, \qquad \Delta S_{\text{t}} - \Delta S_{3,4} = 3.6 \text{ entropy units};$$

$$\Delta H_{1,4} - \Delta H_{1,2} = -150\ \frac{\text{cal}}{\text{mol}}, \qquad \Delta S_{1,4} - \Delta S_{1,2} = 4.6 \text{ entropy units}.$$

Thus, in the polymerization-temperature interval under consideration (from −47 to +50°), the formation of trans configurations is energetically

more favorable than the cis configuration. As regards chain growth in the 1,4 position in comparison with 1,2 additions, the values of the heat and entropy of activation favor the formation of a main chain with internal double bonds C=C.

A very essential characteristic of the structure of a polymer chain from the standpoint of its regularity is the type of connection of 1,4 units according to the "head-to-tail" or "head-to-head" feature. Spectroscopic data on the relative content of 1,2 and 3,4 components of the microstructure in the macromolecule made it possible to clarify this question for the isoprene rubbers we studied. In doing so, the natural assumption was made that, upon addition of monomer

units in the 1,4 position, the opening of the "tail" double bonds (between the 3rd and 4th carbon atoms) or the "head" double bonds (between the 1st and 2nd atoms) occurs with the same probability as in the growth process accompanied by the formation of side groups. Consequently, from the relative content of 1,2 and 3,4 additions one can judge the regularity of the molecular chains from the standpoint of their construction according to the "head-to-tail" and "head-to-head" type.

As follows from the experimental results presented in Table 1, the content of 1,2 and 3,4 additions in emulsion isoprene rubbers proved to be approximately the same, while in SKI rubbers it was, respectively, 1% and 6%. This leads to the conclusion that, whereas the molecular chains of emulsion polyisoprenes consist of randomly alternating trans-1,4 units connected with equal probability in the "head-to-tail"

Table 1

Microstructure of SKI and SEI polyisoprenes of different types of addition

Type of rubber	Sample No.	Polymerization temp., °C	1,2, percent	3,4, percent	cis-1,4, percent	trans-1,4, percent	Type of rubber	Sample No.	Polymerization temp., °C	1,2, percent	3,4, percent	cis-1,4, percent	trans-1,4, percent
SKI	1	–	1	6	65	28	SEI	–	−47	8	6	0	86
SKI	2	–	1.5	6	64.5	28	SEI	–	−35	8	5	0	87
SKI	3	–	2	6	66	26	SEI	–	−25	7	4	0	89
SKI	4	–	1	6	70	23	SEI	–	+5	7	5	1	87
SKI	5	–	1.5	6.5	65	27	SEI	–	+30	7	5	5	83
SKI	6	–	2	5.5	66	26.5	SEI	–	+40	7	5	6	82
SKI	7	–	1	7	68	24	SEI	–	+50	7	5	8	80
SKI	8	–	1	6	70	23							

and "head-to-head" positions, the macromolecules of SKI rubber are predominantly regular chains consisting mainly of cis-1,4 units connected in the "head-to-tail" position. The latter accounts for the ability of SKI isoprene rubbers to crystallize upon stretching.

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Note: Figure translations are in progress. See original paper for figures.