Chemistry

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Abstract

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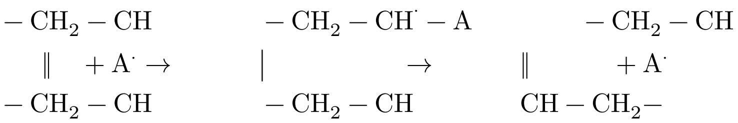
Cis-Trans Isomerization of 1,4-Polybutadiene Units under the Influence of Nitrogen Dioxide

It is known that, under the influence of various catalytic agents of ionic character, cis-trans isomerization of the units of natural rubber occurs. A similar action is exerted by SO_2 ([1]-[4]), organoaluminum compounds, titanium halides ([5], [6]), anhydrous hydrogen chloride, and others ([6]). The possibility has also been established of isomerizing the cis units of natural rubber at elevated temperatures under the influence of selenium ([7]), thiocarboxylic acids, and certain compounds that decompose by a radical mechanism, for example dibenzoyl disulfide ([1]-[4]). For 1,4-cis-polybutadiene, the possibility of isomerization under the influence of ultraviolet rays and γ-radiation in the presence of sensitizers has been shown ([8], [9]), as well as under the influence of thiocarboxylic acids and certain organic disulfides ([1]-[4]). It is assumed that the isomerization is caused by successive reactions of addition of free radicals to the double bond and decomposition of the products formed:



$$\begin{array}{lclcl} -\mathrm{CH_2}-\mathrm{CH} & & -\mathrm{CH_2}-\mathrm{CH}^{\cdot}-\mathrm{A} & & -\mathrm{CH_2}-\mathrm{CH} \\ \quad \| \quad +\mathrm{A}^{\cdot} & \rightarrow & | & \rightarrow & \| \qquad +\mathrm{A}^{\cdot} \\ -\mathrm{CH_2}-\mathrm{CH} & & -\mathrm{CH_2}-\mathrm{CH} & & \mathrm{CH}-\mathrm{CH_2}- \end{array}$$

We investigated the isomerization of cis-1,4-polybutadiene and cis-butene-2 (a hydrocarbon modeling the polybutadiene unit) under the influence of nitrogen dioxide. As is known, nitrogen dioxide is an active catalyst of the cis-trans transformation in a series of fatty acids and their esters ([10]-[12]).

The study of the isomerizing influence of nitrogen dioxide was carried out by us in 2% solutions of cis-1,4-polybutadiene and cis-butene-2 in benzene. The experiments were conducted in glass ampoules with a partition; one part of the ampoule was filled with a calculated amount of gaseous nitrogen dioxide, and the other with a solution of the product being isomerized. The sealed ampoule was thermostated, and, when the required temperature was reached, the partition was broken with a "striker." All work was carried out in a dry argon atmosphere. At the end of the experiment the polymer was treated with alcohol and dried, and butene-2 was distilled off from the reaction mass. For each polymer sample the microstructure of the chain and the content of added nitrogen were determined. The microstructure of the polybutadienes was studied from infrared absorption spectra. On the basis of the absorption intensity at the maxima of the bands 909 and 967 cm^{-1}, the contents of 1,2- and trans-1,4 units, respectively, were calculated. The change in the cis-trans forms of butenes in the course of the process was determined by a chromatographic method.* Nitrogen dioxide was obtained by thermal decomposition of a ground, dried lead nitrate salt ([13]).

We showed that, upon interaction of cis-1,4-polybutadiene with nitrogen dioxide, isomerization of the cis units of the polymer chain occurs

into trans units. Figure 1 shows the absorption bands of polybutadiene obtained by interaction with 6, 11.7, and 23.5 mol.% nitrogen dioxide at a temperature of 96° for 2.5 hours.

As can be seen from Fig. 1, the depth of isomerization increases with increasing concentration of NO_2; at 23.5 mol.% nitrogen dioxide under these conditions, a polymer containing about 60% trans units was obtained. Figure 2 shows the absorption bands for polybutadiene after its interaction with NO_2 at temperatures of −50° and +96°. As can be seen from Fig. 2, at a temperature of −50° the isomerization process does not occur. It is known that nitrogen dioxide has a strong tendency toward dimerization, and at temperatures below 0° it exists in the dimeric form N_2O_4. With increasing temperature, the concentration of the monomeric form increases; the acts of isomerization are apparently associated with this form. In all the cases listed above, both at +96° and at −50°, quantitative addition of nitrogen dioxide to the double bonds of the polymer chain takes place. The products formed in this process are insoluble in a hydrocarbon medium.

Fig. 1 Fig. 2

Fig. 1. IR spectra of polybutadiene treated at 96° for 2.5 hours with NO_2: **1** –6 mol.%, **2** –11.7 mol.%; **3** –23.5 mol.%

Fig. 2. IR spectra of polybutadiene treated with 23.5 mol.% NO_2 for 2.5 hours: **a** –at −50°, **b** –at +96°

Similar results were obtained in the interaction of NO_2 with cis-butene-2. At an NO_2 concentration of 6.0 mol.% at 90° for 2.5 hours, 40% of cis-butene-2 is converted into trans-butene-2. It should be noted that the content of the trans form in the polymer and in the butenes is lower than corresponds to equilibrium at 90°. This is apparently due to the fact that the reaction does not reach the state of equilibrium because nitrogen dioxide is consumed in the addition reaction.

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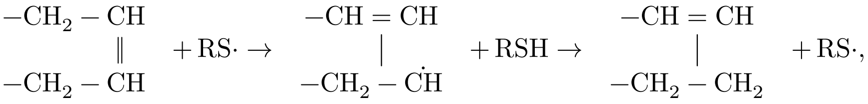
* Spectroscopic analyses of the polybutadiene samples were performed by Z. D. Stepanova; chromatographic analyses of mixtures of cis-trans-butenes-2 were performed by A. N. Genkin.

The experiments we carried out showed that hexaphenylethane at temperatures of 96–130° and diphenylpicrylhydrazyl at 20 and 60° do not cause structural changes in the chain of cis-1,4-polybutadiene. Disulfides (tetramethylthiuram disulfide, diisopropylxanthogen disulfide, and mercaptobenzothiazole disulfide), which decompose at 120° with formation of free radicals, lead only to gel formation due to addition of the radical to the double bond, without an isomerization effect.

It seems to us that the isomerization effects noted above under the influence of RS· radicals are observed only in those cases where the main reaction is not addition of the radical to the double bond, but abstraction of an H atom from the chain:



$$\begin{array}{r}\mathrm{-CH_2-CH}\\ \|\\ \mathrm{-CH_2-CH}\end{array} + \mathrm{RS}\cdot \rightarrow \begin{array}{c}\mathrm{-CH=CH}\\ |\\ \mathrm{-CH_2-\dot{C}H}\end{array} + \mathrm{RSH} \rightarrow \begin{array}{c}\mathrm{-CH=CH}\\ |\\ \mathrm{-CH_2-CH_2}\end{array} + \mathrm{RS}\cdot,$$

The mercaptan formed in stage 1 participates in chain-transfer events, which leads to regeneration of the RS· radical. Such isomerization should be accompanied by migration of the double bond.

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