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Abstract

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Cis-trans Isomerization of Natural Rubber under the Influence of Hydrogen Chloride and Ethylaluminum Dichloride

We have previously established that organoaluminum compounds and titanium tetrachloride cause isomerization of the cis units of natural rubber into trans units (^{1}). The process of isomerization under the influence of the indicated compounds proceeds at a noticeable rate even at room temperature. In the present communication, we set forth the results of a study on the cis-trans isomerization of natural rubber under the influence of hydrogen chloride and ethylaluminum dichloride. The isomerizing action of hydrogen chloride on unsaturated acids and stilbene has previously been covered in a number of works (^{2}-^{7}).

We studied the action of dry hydrogen chloride and ethylaluminum dichloride on a benzene solution of natural rubber under the conditions described earlier (^{1}). Hydrogen chloride was introduced in the form of a saturated benzene solution. In studying the action of hydrogen chloride, for each sample the unsaturation, the chlorine content in the polymer chain, and the microstructure were determined. The latter was characterized by means of IR absorption spectra. As in the preceding communication (^{1}), the quantitative content of the cis and trans configurations was determined from the band at 840 cm^{-1}, whose intensity and contour differ substantially in natural rubber and gutta-percha.

In addition, a qualitative check was carried out using other bands of the spectrum (1100-1150 cm^{-1} and 1300-1330 cm^{-1})*.

In view of the partial decrease in the unsaturation of the polymer due to addition of HCl, the relative content of units of either configuration was calculated as a percentage of the double bonds remaining in the polymer.

Table 1

Isomerization of a 2% solution of natural rubber in benzene

Fig. 1

Figure 1: Fig. 1

Catalyst	Catalyst, wt. % relative to polymer	Temp., °C	Duration, h	Chain structure, %	Chain structure, %	Chain structure, %	Chain structure, %
				1,4 cis-	1,4 trans-	3,4	1,2
$Al(C_2H_5)Cl_2$	1.0	30	10	91	8	1	0
Same	1.0	90	10	85	14	1	0
Same	5.0	30	10	75	24	1	0
Same	5.0	90	10	28	65	4	0
HCl (dry)	10.0	80	15	72	26	1	1
Same	50.0	80	15	19	78	1	1
Same	100.0	80	15	0	98	1	1

* The possibility of using the band 1300–1330 cm^{-1} was noted in a recently published article by M. A. Golub, who investigated the isomerization of natural rubber and gutta-percha under the influence of selenium at a temperature of 180–200° ([9]).

The experimental results of the work are given in Table 1 and in Figs. 1, 2. It should be noted that the data presented for the relative content of cis-trans units characterize only the qualitative picture of the process, since, owing to the decrease in the unsaturation of the polymer, the accuracy of spectroscopic determinations falls noticeably. Because of the limited solubility of the polymer, it was not always possible to compensate for the loss of double bonds by a corresponding increase in the concentration of the polymers in the solutions studied. From the data given in Table 1 it follows that ethylaluminum dichloride and hydrogen chloride exert an isomerizing effect on the polymer chain of natural rubber, the amount of trans units increasing with an increase in the concentration of the isomerizing agent.

Fig. 1. Degree of isomerization of the polymer and amount of added HCl as a function of process duration at $t = 30°$ and a weight ratio HCl : rubber = 1. **1** –content of double bonds as percent of theory; **2** –amount of trans units as percent of the total content of double bonds; **3** –amount of added HCl as percent of theory

Fig. 2. Effect of temperature on the processes of polymer isomerization and addition of hydrogen chloride (process duration 15 h, weight ratio HCl : rubber = 1).

Fig. 2

Figure 2: Fig. 2

1 –amount of trans units as percent of the total content; **2** –chlorine content in the polymer

In both cases the isomerization process is accompanied by a considerable decrease in the unsaturation of the polymer chain. In the case of ethylaluminum dichloride, which is an effective cationic-type catalyst in polymerization processes, the decrease in unsaturation is apparently connected mainly with the process of intramolecular cyclization (8).

In the case of hydrogen chloride, the decrease in unsaturation is connected only with acts of addition of hydrogen chloride to the double bond, as illustrated by the data given in Fig. 1. The content of added HCl corresponds to the decrease in chain unsaturation.

With increasing duration of interaction, the unsaturation continuously decreases (curve 1), the relative content of trans units increases (curves 2 and 3), and the chlorine content in the polymer continuously increases (curve 3). As can be seen from Fig. 2, the processes of chain isomerization and HCl addition begin to proceed already at a temperature of minus 70° and are strongly accelerated when the temperature is raised. At 60°, the total content of double bonds and added chlorine amounts to only 82% of theory, which is apparently due to the development of cyclization processes.

A certain parallelism between the processes of cis-trans isomerization of units and the addition of hydrogen chloride is in agreement with the scheme of the process set forth earlier (1).

The experiments carried out by us showed that, under the indicated conditions, cis-polybutadiene is not appreciably isomerized. The high sensitivity of cis-polyisoprene to isomerization under the influence of ionic catalysts, probably

probably, is connected with the isostructure of the unit. This also accounts for the fact that the stereospecific synthesis of cis-polyisoprene is carried out considerably more readily than that of cis-polybutadiene.

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of Synthetic Rubber

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