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Abstract

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CIS-TRANS ISOMERIZATION OF NATURAL RUBBER UNDER THE INFLUENCE OF ORGANOALUMINUM COMPOUNDS AND TITANIUM TETRACHLORIDE

As is known, Ziegler catalysts have recently acquired considerable importance for the synthesis of polymers of regular structure, in particular cis-polyisoprene ($^{1-4}$). Disruption of the chain structure through the formation of trans units has hitherto been associated only with the influence of the physical and chemical characteristics of the catalysts on the nature of the addition of the monomer (diene) during the polymerization process. In the present work it is shown that disruption of structural regularity may be caused by isomerization of cis units in the finished polymer chain into trans units under the influence of components used to initiate the polymerization process. Attempts to isomerize natural rubber in gutta-percha under the influence of ultraviolet light and under the influence of iodine (^{5}) did not give the expected effect. Ferri (^{7}) was the first to establish that, under the influence of zinc chloride and titanium tetrachloride, natural rubber undergoes changes which, according to X-ray structural analysis, are accompanied by the disappearance of crystallization effects upon stretching of the rubbers.

On the basis of the results obtained, the authors suppose that, under the influence of the indicated agents, isomerization of cis units of the polymer chain of natural rubber into trans units occurs.

The isomerization of cis-1,4 units into trans units in polybutadiene under the influence of ultraviolet rays in the presence of organic compounds of bromine or sulfur was first carried out and demonstrated by Golub (^{7}). In natural rubber, under analogous conditions, the formation of trans units was not observed.

The study of the isomerizing influence of $TiCl_4$ and organoaluminum compounds was carried out by us in solutions of milled natural rubber (NR) in benzene, in sealed glass ampoules. Before use, the benzene was dried and distilled over sodium. All work was conducted in a dry argon atmosphere. For each sample, the unsaturation and the microstructure of the chain were determined.

The microstructure of the polyisoprenes was investigated from infrared spectra; the relative content of the different configurations of units of the polymer chain was determined from absorption in the region 800–1000 cm^{-1}. In doing so, the method previously developed by one of us was used (^{8}). The results of a quantitative investigation of the microstructure of the initial NR sample and of samples subjected to the action of isomerizing agents are contained in Table 1, where the contents of the cis-1,4; trans-1,4-, 1,2- and 3,4-configurations are given, calculated relative to the concentration of units with a C=C double bond.

From the data presented it follows that the components of the Ziegler catalyst used to carry out the polymerization process ($TiCl_4$,

Table 1

Isomerization of natural rubber under the influence of $TiCl_4$ and organoaluminum compounds at 90° and a rubber concentration in solution of 2%

Sample No.	Isomerizing agent	Content of isomerizing agent, wt. % relative to rubber	Reaction duration, h	Unsaturation, % of theory	Structure by infrared spectra, %, cis-1,4	Structure by infrared spectra, %, trans-1,4	Structure by infrared spectra, %, 3,4	Structure by infrared spectra, %, 1,2
1	–	–	–	99; 99.5	95	3	2	0
2	$TiCl_4$	10	10	86.5; 87	65	33	2	0
3	$TiCl_4$	10	10	84; 85	67	32	1	0
4	$TiCl_4$	10	10	not determined	68	29	2	1
5	$TiCl_4$	50	10	61.5; 65.1	13	78	6	3
6	$TiCl_4$	10	1	75.4; 72.8	74	21	4	1
7	$TiCl_4$	10	20	68.5; 64.5	44	51	4	1

Sample No.	Isomerizing agent	Content of isomerizing agent, wt. % relative to rubber	Reaction duration, h	Unsaturation, % of theory	Structure by infrared spectra, %, cis-1,4	Structure by infrared spectra, %, trans-1,4	Structure by infrared spectra, %, 3,4	Structure by infrared spectra, %, 1,2
8	$AlEt_2Cl$	10	10	65; 65.5	58	40	2	0
9	$AlEt_3$	10	10	89; 85.4	49	47	2	2
10	Aluminum ethyl-di-(2-phenylbutyl)	10	10	83; 81	69	30	1	0
11	Triisobutylaluminum	10	10	70; 74	43	54	2	1

AlR_3, AlR_2Cl, exert an isomerizing action on the polymer chain of natural rubber.

Using titanium tetrachloride as an example, it was shown that the amount of trans units increases with an increase in the concentration of the isomerizing agent and the duration of interaction.

Fig. 1. Absorption bands of infrared radiation at different contents of cis-trans configurations in the polymer chains. 1 —natural rubber (NR): cis 95%, trans 3%; 2 —isomerized NR: cis 65%, trans 33%; 3 —isomerized NR: cis 44%, trans 51%; 4 —isomerized NR: cis 13%, trans 78%.

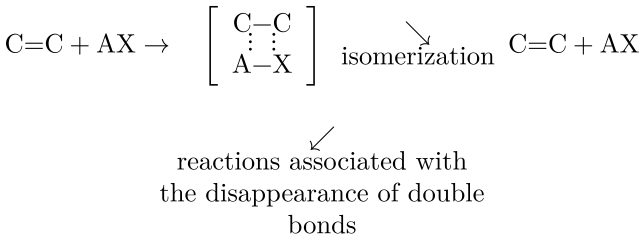
The phenomenon of polyisoprene isomerization observed by us is clearly illustrated by the curves in Fig. 1, which show the absorption bands of infrared radiation corresponding to different contents of cis- and trans-units.

Since the molar absorption coefficient K for the cis units of polyisoprene at $\nu = 839$ cm^{-1} is 52, and for trans units at the same point of the spectrum is 28, the relative decrease in the intensity of the absorption bands caused by the cis-trans configurations and reduced to one and the same concentration of units with the double bond C=C unambiguously characterizes a decrease in the content of cis units in the polymer chains and, accordingly, an increase in trans configurations.

The isomerization processes occurring under the influence of the indicated agents are accompanied by a substantial decrease in the unsaturation of the polymer.

The considerable decrease in unsaturation, while the solubility of the polymer is retained, is apparently due mainly to cyclization processes within the chain, as was discussed in one of our papers.

The decrease in unsaturation is associated with the ability of the above-mentioned compounds to add to the C=C bond. This is apparently preceded by the stage of formation of an unstable complex capable of decomposing with regeneration of the starting substances. Isomerization may proceed at this intermediate stage:



We have established that, in the case of aluminum ethyl dichloride, natural rubber undergoes deeper secondary changes: the process proceeds toward the formation of insoluble, high-melting amorphous powders. An analogous effect is observed in those cases in which large amounts of $TiCl_4$ are used (100 wt.% relative to the rubber).

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