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Abstract

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STUDY OF RUBBER CYCLIZATION BY THE METHOD OF NUCLEAR MAGNETIC RESONANCE

(Presented by Academician A. A. Balandin, 27 V 1963)

Intramolecular cyclization of polyisoprenes is the most important type of their isomeric transformations and has attracted the attention of many investigators (^{2}). We studied the process of cyclization of natural rubber in a phenol medium, using phosphorus pentoxide as catalyst at 180°C (^{3}). To obtain samples with a low degree of cyclization, the process was carried out in the binary solvent decalin–phenol (ratio 1 : 1), which made it possible to take samples of partially cyclized rubber at early stages of the reaction. The content of double bonds in cyclorubber, hereinafter called the "residual unsaturation," was determined by titration with perbenzoic acid by the method of N. Prilezhaev, improved by B. Dogadkin and A. Dobromyslova (^{4}). The unsaturation of the initial natural rubber (pale crepe) was 94% of the theoretical unsaturation. NMR spectra were recorded on the spectrometer of the Central Automation Laboratory (^{5}) in the temperature range 77–400°K. Samples in thin-walled ampoules 9 mm in diameter were kept at the measurement temperature for no less than 30 minutes. Second moments were determined by numerical integration with allowance for corrections for the modulation amplitude and for the rate of passage through the resonance region.

Fig. 1. Dependence of the NMR line width of cyclorubber on residual unsaturation: *1*—at 293°K, *2*—at 77°K

At room temperature the initial natural rubber gives a narrow NMR line, $\delta H = 0.09$ gauss (according to (^{6}), $\delta H = 0.08$ gauss), owing to the high mobility of the molecular chains. At the initial stages of cyclization, at residual degrees of unsaturation of 80 and 60%, the line shape does not change and the width increases only slightly (Fig. 1). A further increase in the degree of cyclization (at residual unsaturation below 50%) leads to a rapid increase in the line width.

This permits the assumption that, at the early stage of cyclization, the cyclic structures that form do not reduce the mobility of the molecular groups of the macromolecule. Apparently, at this stage of cyclization, monocyclic structures

Fig. 2. Shape of the NMR line at room temperature for cyclorubber with a residual unsaturation of 36%

Figure 1: Fig. 2. Shape of the NMR line at room temperature for cyclorubber with a residual unsaturation of 36%

Fig. 3. X-ray diffraction pattern of cyclorubber with a residual unsaturation of 25% (1) and of polytetrafluoroethylene (2)

Figure 2: Fig. 3. X-ray diffraction pattern of cyclorubber with a residual unsaturation of 25% (1) and of polytetrafluoroethylene (2)

are formed that possess sufficient mobility. At a great depth of cyclization, bulky condensed polycyclic structures are formed, whose mobility is considerably lower, which leads to line broadening. A sample with a residual degree of unsaturation of 36% gives an NMR line of complex shape, consisting of two components, a broad and a narrow one (Fig. 2). Such a line shape is characteristic of systems in which there are two types of protons differing in degree of mobi-

for example, the protons of crystalline and amorphous regions in polymers (7), cured and uncured regions in epoxy resin, etc. The broad line corresponds to protons with lower mobility, and the narrow line to protons with greater mobility.

To clarify the reasons for the appearance of a complex-shaped NMR line, the phase state of cyclorubber was determined. For this purpose, an X-ray diffraction pattern of cyclorubber was obtained (Fig. 3, curve *1*)*. For comparison, the X-ray diffraction pattern of a crystalline polymer—polytetrafluoroethylene—is shown.

Fig. 2. Shape of the NMR line at room temperature for cyclorubber with a residual unsaturation of 36%

Fig. 3. X-ray diffraction pattern of cyclorubber with a residual unsaturation of 25% (*1*) and of polytetrafluoroethylene (*2*)

As can be seen, the X-ray diffraction pattern of cyclorubber is, in character, close to the X-ray diffraction pattern of amorphous polymers. The absence of sharp peaks in the X-ray diffraction pattern indicates the amorphous structure of the polymer and the absence of crystalline regions. Therefore the broad component in the NMR spectrum of cyclorubber should apparently be assigned to regions of the polymer where cyclization has occurred, and the narrow line to the mobile protons of the linear portions of the cyclorubber molecules. From the ratio of the areas of the broad and narrow components of the spectrum (when recording the derivative of the signal, from the ratio of the first moments), one can estimate the fraction of protons corresponding to both regions. The spectrum in Fig. 2 corresponds to a content of about 7% mobile protons. It should be borne in

Fig. 4

Figure 3: Fig. 4

mind, however, that the value of the "degree of cyclization" obtained in this way, as well as the "degree of crystallinity" determined by the NMR method, is a conditional quantity that changes somewhat with the temperature at which the NMR spectrum is recorded. Completely cyclized samples (residual unsaturation 25%) at room temperature give a broad NMR line, but when the temperature is raised a complex line structure also appears. At the temperature of liquid nitrogen, all samples give a simple line, the width of which increases upon cyclization from 9 to 12 gauss, which indicates an increase in the density of the structure (Figs. 1, 2). Figure 4 shows the change in the NMR line width with temperature. For all three cyclorubber samples, in the low-temperature region a slow decrease in the line width is observed, caused by the motion of methyl groups (8), and then the line narrows rapidly owing to the onset of motion of macromolecular segments. The temperature of rapid line narrowing is 210-230° K for partially cyclized rubber with a relative degree of unsaturation of 60% and 310-350° K for completely cyclized rubber (degree of unsaturation 25%). As shown

* The X-ray diffraction pattern was obtained by A. V. Ermolina, to whom the authors express their gratitude.

According to Gutowsky et al. (8), in natural rubber the transition in the line width occurs at 225°K and is almost not shifted upon vulcanization. Evidently, with partial cyclization, as with vulcanization, the mobility of sufficiently large chain segments characteristic of natural rubber is still retained. For low-molecular-weight cyclorubber the temperature interval of line narrowing lies in the region of 250—270°K, i.e., lower than for completely cyclized high-molecular-weight rubber with the same value of residual unsaturation, but higher than for high-molecular-weight partially cyclized rubber with an unsaturation of 60%.

Fig. 4. Dependence of the NMR line width on temperature.
1 —partially cyclized rubber with residual unsaturation of 60%; 2 —low-molecular-weight cyclorubber with residual unsaturation of 25%; 3 —completely cyclized rubber with residual unsaturation of 25%.

From this one may conclude that, for partially cyclized rubber, rapid line narrowing occurs as a result of the thermal motion of individual segments, whereas for low-molecular-weight rubber it occurs as a result of the thermal motion of rigid molecules as a whole. The low molecular weight of the latter sample leads to the fact that at room temperature it is in a viscous-flow state. At the same time, the greater depth of cyclization and, consequently, the rigidity of the structure lead to a shift of the interval of rapid line broadening upon freezing into the region of higher temperatures, in comparison with the high-molecular-weight partially cyclized sample, which is in a highly elastic state.

We give the values of the second moment of the NMR line at the temperature of liquid nitrogen (in gauss^2):

Natural rubber	Partially cyclized cyclorubber with unsaturation 60%	Completely cyclized cyclorubber with unsaturation 25%
17.0	19.7	20.4

The obtained value of the second moment of the NMR line of natural rubber at 77°K is close to the theoretically calculated value of 18.5 gauss^2 for a rigid structure (8). Upon cyclization, the second moment, like the line width, increases somewhat, which indicates an increase in the density of the rubber structure upon cyclization.

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