# Physical Chemistry

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Figure 1

Figure 1: Figure 1

## Abstract

## Full Text

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# A Comprehensive Study of the Crystallization of Polychloroprene Rubber–Nairit

*(Presented by Academician B. A. Arbuzov, January 7, 1962)*

Previously, by the method of recording thermomechanical curves (*TM* curves), crystallization phenomena in natural rubber were studied (^1). The object of the present investigation is synthetic polychloroprene rubber–nairit, a characteristic representative of crystallizing elastomers (^2). It is known that its crystallization has an optimum rate at about 0°, but also proceeds rather rapidly at room temperature. This could be verified by observing the deformability of freshly heated (to 50°) nairit under isothermal conditions with alternating loading. For this purpose we used an apparatus for recording *TM* curves (^3), in which the thermal block operated in a thermostating mode. Deformation was recorded in the usual manner. Instead of a thermocouple, a source of linearly increasing voltage (a rheochord) was connected to the recorder input, thereby providing a sweep of the deformation record with time. A load of 0.64 kg/cm$^2$ constantly pressed on the specimen; every 4 minutes a weight automatically imposed for a period of 2 minutes was applied, increasing the stress to 7.04 kg/cm$^2$.

**Fig. 1.** Deformability under loads of 7.04 and 0.64 kg/cm$^2$, alternating every 2 minutes, of freshly heated (to 50°) nairit under isothermal conditions: *a*–at 0°; *b*–at room temperature

Figure 1 shows the periodic curves obtained. As a result of crystallization of nairit under the experimental conditions, the oscillations of the curve decay: at 0° practically in 15 minutes, at room temperature–in 2 hours.

There are known studies in which the crystallization kinetics of neoprenes in vulcanized and unvulcanized mixtures was investigated by the increase in hardness (^4). The formation and melting of the crystalline phase in polychloroprene rubber was also studied by optical methods ([5,6]).

We set ourselves the task of following the process of crystallization of nairit by the method of *TM* curves, comparing it with data from X-ray and thermographic methods. Incidentally, the latter method was apparently also applied to the

Fig. 2

Figure 2: Fig. 2

study of elastomers for the first time. The recording of *TM* curves was carried out by us according to the previously described procedure (ˆ3).

Tablets of the required size were cut from a nairit specimen. For one of them a *TM* curve was recorded, while all the others were heated to 50°, as a result of which a completely amorphous polymer was obtained. One of the heated tablets was immediately used for recording a *TM* curve; the rest were kept at room temperature ($22 \pm 2°$). After definite intervals of time, one tablet at a time was taken and a *TM* curve was recorded for it. In this procedure, the specimen was cooled in the thermal block of the apparatus below the glass-transition temperature at a rate of about 1 degree/min, after which the actual experiment of recording the *TM* curve began. The possibility of some crystallization of nairit during these

procedures, which may be reflected, to some extent, in the $TM$-curves of specimens with a low content of the crystalline phase. Some of the results obtained are shown in Fig. 2. Curve 1 for unheated nairit exhibits a small rise at a temperature of $-40°$, corresponding to vitrification of the amorphous phase, after which a horizontal plateau is observed, extending to $+30°$. This plateau characterizes the high-elastic state of the amorphous phase, along with which there is a considerable amount of crystalline phase. At about 30° the latter melts; on the curve a rather sharp rise is observed, after which the course of the curve does not differ from the usual $TM$-curves of amorphous polymers, in which high-elastic deformations are accompanied by plastic deformations. On curve 2, recorded for freshly heated nairit, in which the crystalline phase is practically absent, the rise corresponding to the transition of the glassy phase into the high-elastic one is many times greater than for curve 1. This is quite understandable, since here there is no crystalline phase reinforcing the elastic polymer. At the same time, the curve also lacks the plateau caused by this phase, as a result of which there is no noticeable jump at the melting temperature of the latter. Curves 1 and 2 represent limiting cases, corresponding to the maximum and zero amounts of crystalline phase. Between them lie the curves for nairit heated and held at room temperature. The longer the specimen was held, the closer its curve is to curve 1, which indicates an increase in the amount of crystalline phase.

**Fig. 2.** Thermomechanical curves (at a load of 3.2 kg/cm$^2$) of the initial (1) and nairit heated to 50°, held at room temperature for: 2 –1 hour; 3 –6 hours; 4 –24 hours

Considering the curves in Fig. 2, it is not difficult to notice that each of them can be characterized by the magnitude of the rise $\Delta h_c$ at $T_c$ (it can be found, as shown for curve 2, and measured in percent relative deformation)*. As the crystallinity of the specimen increases, $\Delta h_c$ decreases, and the curve becomes

Fig. 3

Figure 3: Fig. 3

Fig. 4. X-ray scattering intensity curves for a nairit sample: 1 –freshly heated (amorphous); 2 –the same sample after 4 h; 3 –after 6 h; 4 –after 24 h; 5 – after 76 h; 6 –initial unheated sample

Figure 4: Fig. 4. X-ray scattering intensity curves for a nairit sample: 1 – freshly heated (amorphous); 2 –the same sample after 4 h; 3 –after 6 h; 4 – after 24 h; 5 –after 76 h; 6 –initial unheated sample

increasingly flatter. The value of $\Delta h_c$ approaches the value characteristic of unheated nairit, in which the content of the crystalline phase is limiting–equilibrium for the given temperature. Already after 1-2 days they practically reach the limiting value.

**Fig. 3.** Curve of accumulation of the crystalline phase at room temperature in amorphous nairit (according to quantitative thermographic analysis)

From what has been said it is clear that the $TM$-curve can serve for estimating the degree

* The steepness of the rise of the plateau in the interval from the vitrification point of the amorphous phase to the melting point of the crystalline phase also proves characteristic.

crystallinity of nairit. However, it is also clear that the indices found from the $TM$-curve are not directly proportional to the amount of the crystalline phase.

Consequently, it is important to know the dependence of these indices on the degree of crystallinity, as determined by some independent method. For this purpose we used X-ray and thermographic methods.

For the thermographic study, samples weighing about 0.5 g, in the form of cylinders 7 mm in diameter, were prepared in exactly the same way as for recording the $TM$-curves. Heating of the sample during recording of the thermograms was carried out in a block analogous to that used for recording $TM$-curves, and under the same conditions. The curves were recorded on a PK-52 pyrometer. On the thermograms of nairit, in the region of 30–40°, a peak is observed on the differential curve corresponding to melting of the crystalline phase. After heating to 50° and holding the samples at room temperature, the magnitude of the peak successively increases, approaching its value for the unheated (maximally crystallized) sample.

Fig. 4. X-ray scattering intensity curves for a nairit sample: 1 –freshly heated (amorphous); 2 –the same sample after 4 h; 3 –after 6 h; 4 –after 24 h; 5 – after 76 h; 6 –initial unheated sample

As shown by L. G. Berg and V. Ya. Anosov ([7]), the area of the peak formed

by the differential recording is proportional to the magnitude of the thermal effect. In our case it is equivalent to the heat of fusion, whose magnitude is proportional to the amount of crystalline phase. By planimetering the peaks on the thermograms, using known procedures for delimiting these areas ([8]), and relating them to the exact weighed portion of nairit, one can find a value proportional to the amount of crystalline phase. Taking the area on the thermogram of the initial sample as corresponding to the limiting degree of crystallinity at the given temperature, one can express, relative to it (in percent), the degree of crystallinity of all the samples studied and construct a kinetic curve. The graph obtained in this way is shown in Fig. 3. It is evident from the figure that the limiting crystallinity of nairit under the conditions indicated is reached in approximately one week.

The peak areas on thermograms recorded under identical conditions are proportional to the mass of crystalline material and do not depend on other causes. Therefore the data obtained can be used to construct a calibration plot that makes it possible to determine the degree of crystallinity from the results of thermomechanical studies. However, the thermographic method naturally cannot give the absolute amount of the crystalline phase, which can be calculated only on the basis of knowledge of the mass ratio of the crystalline and amorphous phases in the maximally crystallized sample. Such a possibility is provided by the X-ray method, in which the intensity of the scattered radiation consists of scattering by the crystalline and amorphous phases. By comparing on the X-ray diagram the area of the peaks corresponding to the crystalline phase with the halo area for a completely amorphous sample, one can estimate the absolute fraction of the crystalline phase. In view of the known conventionality of delimiting the areas, an accuracy on the order of $±$10% should be considered quite satisfactory.

The content of the crystalline phase in nairite was determined by us by the X-ray diffraction method on a URS-50I apparatus. A specimen with a flat cut was mounted in the goniometer holder, and the curve of the intensity of X-ray reflection was recorded for it in the usual manner. Then, there on the goniometer, the specimen was heated with a stream of hot air to 50°. In this process the crystalline maxima disappeared completely, and the intensity of the amorphous halo increased at their expense. After this, for the same specimen, without changing its mounting, recording was carried out at room temperature at specified time intervals. The results obtained are shown in Fig. 4. Successive diffractograms show the accumulation of the crystalline phase in the specimen and an approach to the pattern of unheated nairite. By comparing the areas of the peaks characteristic of crystalline nairite, one can investigate the kinetics of crystallization. As a result of planimetry it was found that, within the accuracy limits of the method, the kinetic curve constructed on the basis of thermographic data is reproduced completely. In this case the limiting degree of crystallinity was found to be $50 \pm 10\%$.

On the basis of all the data presented, a graph can be constructed of the depen-

dence of $\Delta h_c$ on the thermomechanical curve on the degree of crystallization, found by the thermographic method and recalculated into the absolute percentage content of the crystalline phase from the results of the X-ray method. It is not difficult to see that the thermomechanical method is especially sensitive at a low degree of crystallinity and can be effectively used to investigate the initial stages of the crystallization process.

Thus, a comprehensive investigation using thermomechanical, X-ray, and thermographic methods made it possible to study the crystallization kinetics of nairite and to compare the capabilities of these methods in the investigation of crystallization of elastomers.

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