Physical Chemistry

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1961

SovietRxiv

Abstract

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On the Crystallization of Cellulose Tribenzoate

(Presented by Academician V. A. Kargin, March 16, 1961)

As was shown in work (^{1}), cellulose itself in the condensed phase is always in an amorphous state, since the temperatures of its transitions from one physical state to another are substantially higher than the temperature of chemical decomposition. Therefore cellulose by itself does not crystallize, for, as is known, any low-molecular or high-molecular compounds in the glassy state are not capable of forming crystalline structures.

However, if we are dealing with products of polymer-analogous transformations of cellulose, for example with its triesters, then among them substances are possible for which the basic conditions for the crystallization of polymers are fulfilled, i.e., regularity of the structure of the molecular chains, a definite conformation of the molecules necessary for achieving the densest packing, and the corresponding mobility of the chain molecules. The latter is realized in the temperature interval of the highly elastic state of the polymer.

It was of interest, using as an example some cellulose triester for which all three conditions indicated above are fulfilled, to determine the possibility of crystallization of such a product. As the sample for the investigation we used cellulose tribenzoate.

Attempts to obtain a completely esterified high-molecular cellulose benzoate were undertaken long ago; however, apart from the mono- and diester, and also a comparatively low-molecular triester, better results could not be obtained ($^{2-4}$).

The synthesis of cellulose tribenzoate was carried out by the action of benzoyl chloride on purified cotton linters in pyridine medium in a nitrogen atmosphere. The product was purified by filtering its solutions in methylene chloride, followed by repeated reprecipitation with methanol. The reprecipitated product was thoroughly washed first with hot water, then with methyl alcohol, and finally with diethyl ether. All the obtained samples of cellulose tribenzoate had a similar elemental composition.

The content of bound benzoic acid was determined by saponification of the ester with an alcoholic NaOH solution. It varied within the limits 75.9–77.0%, whereas for the triester the calculation gave 77.2%. The intrinsic viscosity of solutions

Fig. 1. Thermomechanical curves of cellulose tribenzoate: 1 —amorphous; 2 —crystallizing during the tests; 3 —crystallized

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of various samples of cellulose tribenzoate in dichloroethane varied from 4.5 to 5.2. The product obtained gave sufficiently strong films, which indicated that it was undoubtedly a high-molecular substance.

First of all we investigated the temperatures of transition of this cellulose ester from one physical state to another. For this purpose tablets were prepared from the previously dried product at a pressure from 50 to 100 kg/cm^2, at a temperature from 100 to 190°, and with holding under the indicated temperature regimes for 20 min. These tablets were used to determine the thermomechanical properties of cellulose tribenzoate on a dina-

···on momentometric balances with variable load (5). The temperature was raised at rates from 2° over 1 min to 1° over 2 min. The results of the thermomechanical tests are given in Fig. 1.

The very form of the three thermomechanical curves obtained already characterizes cellulose tribenzoate as a crystallizing polymer. Indeed, for one and the same rate of deformation of the polymer, depending on the time and temperature of preliminary heating of the specimen during pressing of the tablet and on the rate of temperature increase during the thermomechanical tests, cellulose tribenzoate exhibits thermomechanical properties typical of an amorphous polymer, an amorphized but crystallizing polymer, and a crystallized product. Curve 1 in Fig. 1 shows a typical thermomechanical curve for amorphous polymers and requires no special explanation. It is true that on it there is already observed a certain decrease in the deformation values in the middle part of the high-elastic region of the thermomechanical characteristic of the product. This curve corresponds to the lowest-temperature treatment of the specimen. Curve 2 in Fig. 1 characterizes, as was first shown by V. A. Kargin, V. A. Kabanov, and I. Yu. Marchenko using isotactic polystyrene (6) as an example and in work (7) on polycarbonates, the typical change in the thermomechanical properties of an amorphized polymer crystallizing in the course of thermomechanical tests. A certain slight stiffening of the product as a result of its crystallization on curve 1 already reaches, on curve 2 (with corresponding increases in the time of heat treatment), considerable degrees, and the curve shows a sharp drop in deformation in the region above the glass-transition point of cellulose tribenzoate. Finally, curve 3 is typical of any crystallized polymer under comparatively small loads during thermomechanical tests. This curve was obtained for a specimen subjected to the longest heating time at temperatures above the glass-transition point of the product.

Fig. 1. Thermomechanical curves of cellulose tribenzoate: 1 —amorphous; 2 —

Fig. 2. Spherulites of cellulose tribenzoate (650×): a, b—in a polarization microscope; c, d—the same, with crossed nicols

Figure 2: Fig. 2. Spherulites of cellulose tribenzoate (650×): a, b—in a polarization microscope; c, d—the same, with crossed nicols

crystallizing during the tests; 3 —crystallized.

Thus, already from the very character of the three thermomechanical curves shown in Fig. 1, obtained on one and the same product as a function of the conditions of heat treatment, it may be concluded that the cellulose triester under study is a crystallizing polymer. Another conclusion following from consideration of the thermomechanical curves is that, at the heating rates of the product used, the optimum conditions for the course of crystallization processes in cellulose tribenzoate apparently correspond to the temperature range from 200 to 220°. It is in this temperature region that the stiffening of the polymer begins and passes through its maximum, characterized by a minimum on the deformation curve in the high-elastic region. Consequently, to effect crystallization of cellulose tribenzoate it is necessary to use the indicated temperature interval···

for heating the product. The X-ray diffraction pattern obtained upon heating in this temperature interval of a cellulose tribenzoate film is characterized by a fairly rich set of interference rings.

Finally, an attempt was made to obtain more complex forms of the crystalline structures of cellulose tribenzoate. For this purpose cellulose tribenzoate was dissolved with heating in dimethyl phthalate, and its 1% solution was dried

Fig. 2. Spherulites of cellulose tribenzoate (650×): *a*, *b*—in a polarization microscope; *c*, *d*—the same, with crossed nicols

at 200° with rapid evaporation of the solvent (over 10 min) and with slow evaporation (over 2 hours).

The spherulitic structures obtained in this way are shown in Fig. 2. The figures show two morphological types of cellulose tribenzoate spherulites in a polarization microscope under ordinary observation (*a*, *b*) and with crossed nicols (*c*, *d*), with the characteristic dark Maltese cross in the latter case. It is noteworthy that the two morphological types of cellulose tribenzoate spherulites obtained —with radial (*a*, *c*) and ringed (*b*, *d*) characteristics, caused by specific optical effects of different structural elements, as was also observed for the spherulites of some synthetic polymers (8, 9)—are due

to their occurrence by the kinetic conditions of crystallization. Rapid evaporation of the solvent leads to the appearance of spherulites of the radial type (*a, v*); slow evaporation—to the formation of spherulites of the ring type (*b, g*).

Thus, on the basis of studies of thermomechanical properties, X-ray structural analysis, and direct observations of spherulitic structures, it has been shown that cellulose tribenzoate is a typical crystallizing polymer, apparently capable of forming all forms of crystalline structures. Two of them have been obtained and described in the present study.

In conclusion, we express our gratitude to Academician V. A. Kargin for his interest in this work, and to N. F. Bakeev for fruitful discussion of the results.

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Received
10 III 1961

CITED LITERATURE

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