Reports of the Academy of Sciences of the USSR

P. V. KOZLOV, A. A. FROLOVA, and L. F. SLESAREVA

1962

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1962. Volume 145, No. 1

PHYSICAL CHEMISTRY

P. V. KOZLOV, A. A. FROLOVA, and L. F. SLESAREVA

THE EFFECT OF MECHANICAL ACTIONS ON THE ACCELERATION OF STRUCTURAL TRANSFORMATIONS IN CRYSTALLIZING POLYMERS

(Presented by Academician V. A. Kargin on 21 II 1962)

In recent years the need to study the physicomechanical properties of polymers has become especially evident in connection with the peculiarities of their structures, which arise in the processes of synthesis and processing of polymers and which to a considerable extent determine the valuable complex of their properties. From this follows the task of investigating the influence of mechanical actions on processes that cause structural changes in polymers, which may either improve or worsen their properties.

In the present work we studied the influence of periodically acting forces on changes in the structure of crystallizing polymers. As the object of investigation we used polycarbonate with a molecular weight of 75,000, obtained in a homogeneous medium by phosgenation of 2,2-bis-(4′-oxyphenyl)-propane; it is considerably less contaminated with low-molecular fractions than products obtained under heterogeneous phosgenation conditions (^1). The choice for this investigation of polycarbonate—a polymer with bulky chains and strong intermolecular interaction—is due to the very slow course of crystallization processes, which makes it possible to separate processes occurring directly under the influence of thermal action from phenomena arising as a result of the imposition of a mechanical field. Moreover, the high retardation of relaxation processes in polycarbonates, even at high temperatures, makes it possible, by cooling the specimen, to fix readily all the structural changes in it.

In studying phenomena accompanying structural change under conditions of dynamic loading, the Alexandrov–Gaev frequency apparatus was used (^2). The investigations were carried out in the temperature range from 20 to 230° and in the frequency range from 1400 to 0.14 oscillations/min. Specimens for the investigation were prepared in the form of tablets 10 mm in diameter and 3.15-3.4 mm thick by pressing on a laboratory press, with allowance for the conditions

Fig. 1. Dependence of deformation (arbitrary units) on temperature for polycarbonate at different frequencies of force action (oscillations per minute): I –1400; II –14; III –0.14

Figure 1: Fig. 1. Dependence of deformation (arbitrary units) on temperature for polycarbonate at different frequencies of force action (oscillations per minute): I –1400; II –14; III –0.14

of true pressing (⌒3, ⌒4), and were then subjected to vibrational compressive deformation by a force varying according to a sinusoidal law with a prescribed amplitude. The rate of temperature rise in the thermomechanical tests was 1° per minute; the holding time of the specimen at the measuring temperature was 10 min. An X-ray diffraction pattern obtained from a specimen prepared for the investigation reveals a diffuse halo characteristic of an amorphous polymer.

Figure 1 presents the results of thermomechanical tests under the action of a load of 0.7 kg/cm^2. It is seen that, with change in the frequency of action of the force, the character of the dependence of deformation (in arbitrary units) on temperature changes sharply.

Thermomechanical curve *I* shows that over a wide temperature interval the specimen remains practically undeformed under the experimental conditions and only in the interval 190–220° passes into a visco-flow state.

The result obtained is well explained by relaxation phenomena in the polymer. It corresponds to the case when the frequency of the action on the specimen is so high that the chain molecules or secondary structural formations do not have time to exhibit the mobility required under the influence of such action.

In order to establish the character of the structure of polycarbonate, one of these repeated experiments was interrupted at 180°, and the specimen was subjected to X-ray examination. Its X-ray pattern proved analogous to that of the initial amorphous polymer. This indicates that, at the specified frequency, thermomechanical action, up to the transition of the polymer into the viscous-flow state, does not lead to noticeable changes in the structure of polycarbonate, since the duration of the experiment is comparatively short and the rate of temperature rise is too great for crystallization processes to occur. An analogous character of the X-ray pattern was also obtained for a specimen subjected only to thermal treatment up to 200° under the experimental conditions (the same rate of temperature rise and specimen holding time). Consequently, at high frequencies of action, high-molecular-weight amorphous polycarbonate, in its thermomechanical properties, corresponds to low-molecular-weight glass-forming substances, since it does not exhibit high-elastic properties and has only one temperature interval of transition—from the glassy to the viscous-flow state. This temperature interval of transition coincides with the region of the viscous-flow state of high-molecular-weight polycarbonates ($T_{\mathrm{t}} = 220$—$268°$).

Fig. 1. Dependence of deformation (arbitrary units) on temperature for poly-

carbonate at different frequencies of force action (oscillations per minute): I –1400; II –14; III –0.14

With a decrease in the frequency of the force action, polycarbonate already exhibits properties typical of high-molecular-weight amorphous polymers. On the thermomechanical curve (curve II in Fig. 1) all three regions appear, corresponding to the three physical states of an amorphous polymer. At the same time, the temperature interval of transition into the viscous-flow state is strongly shifted into the region of lower temperatures. A further decrease in frequency (curve III in Fig. 1) promotes the manifestation in polycarbonate of thermomechanical properties characteristic of an amorphized polymer crystallizing during its testing, as was shown earlier for isotactic polystyrene (^{5}), isotactic polypropylene (^{6}), and low-molecular-weight polycarbonate (^{7}). From curve III in Fig. 1 it follows that, at a temperature of 140°, the transition from the glassy to the high-elastic state begins to occur in polycarbonate. However, a further increase in temperature leads to hardening of the specimen as a result of crystallization processes. The appearance on the X-ray photograph of diffraction rings, although not sufficiently sharp, in the structural examination of polycarbonate subjected to thermomechanical treatment up to 175° at a frequency of 0.14 oscillations/min, indicates the formation of a structure of a higher order than the initial one.

Consequently, such treatment of polycarbonate led not only to a narrowing of the interval between the glass-transition temperature (T_c) and the flow temperature (T_t), owing to a strong decrease in T_t, but also to substantial changes in its structure, which were not observed at higher frequencies.

It therefore seemed of interest to carry out a special X-ray structural and thermomechanical study of polycarbonate specimens that had previously been subjected only to thermal and thermomechanical treatments. Such treatment was carried out at 140 and 170°, i.e., at temperatures close to and above the glass-transition temperature ($T_c = 150°$), but far below the flow temperature ($T_t = 220–268°$). Tests showed that the X-ray pattern of polycarbonate heated for 1 hour at 170° has a diffuse halo, whereas the X-ray pattern of a specimen subjected, for the same time and at the same temperature, to vibrational compressive deformation with a frequency of 0.14 oscillations/min has diffraction rings, indicating the appearance of crystalline-type ordering, while even 5-hour heating at 170° without the application of a mechanical field did not lead to any change in the character of the X-ray pattern compared with the initial one.

Fig. 2. Dependence of deformation on temperature (frequency 0.14 oscillations/min) for a polycarbonate specimen: 1 –heated for 1 hour at 170°; 2 –deformed at a frequency of 0.14 oscillations/min for 1 hour at 170°.

A sharp difference is also manifested in the character of the thermomechanical curves for specimens prepared in exactly the same way and tested at a frequency of 0.14 oscillations/min (Fig. 2). As can be seen from the figure, after heating (curve 1) the polycarbonate still retains the ability to exhibit high-elastic prop-

Fig. 2. Dependence of deformation on temperature (frequency 0.14 oscillations/min) for a polycarbonate specimen: 1 –heated for 1 hour at 170°; 2 –deformed at a frequency of 0.14 oscillations/min for 1 hour at 170°

Figure 2: Fig. 2. Dependence of deformation on temperature (frequency 0.14 oscillations/min) for a polycarbonate specimen: 1 –heated for 1 hour at 170°; 2 –deformed at a frequency of 0.14 oscillations/min for 1 hour at 170°

Figure 3

Figure 3: Figure 3

erties, although the deformations are comparatively smaller in magnitude than those occurring in the previously unheated specimen. The thermomechanical curve looks quite different when the specimen has previously been subjected to mechanical action. In this case (curve 2), up to T_t practically no deformability is observed. Thermal and mechanical treatment even at 140°, i.e., at a temperature somewhat below T_c, already has a strong effect on the capacity for deformation (Fig. 3). Preliminary heating of the specimen (for 1 hour at 140°) almost did not change the magnitude of the deformation in comparison with the unheated specimen, whereas in the specimen subjected to mechanical action (for 1 hour at 140° with a frequency of 0.14 oscillations/min) the deformability decreased sharply.

From comparison of the curves presented and the corresponding X-ray structural data, it is clearly seen to what extent periodic mechanical actions change the structure of polycarbonate. By increasing the mobility of chains or of secondary structural formations, these actions, in the case of a difficultly crystallizing polymer, using polycarbonate as an example, lead in particular to acceleration of the processes of ordering of structural elements and formation of a crystalline-type structure, i.e., to acceleration of the crystallization process of polymers. This is also confirmed by the interesting phenomena that were observed quite recently for polyamides (8), when, under the influence of the periodic action of bending forces at a temperature above T_c, growth occurred in the polymer block of spherulites already present earlier in the polymer substance, which, however, did not take place in the absence of mechanical actions. Of substantial importance is the dependence

deformation on the frequency of the acting force in the region T_c—T_t, where, in the crystallizing polymer, using polycarbonate as an example, a broad relaxation spectrum is manifested, considerably broader than in ordinary amorphous irregular polymers. Broadening of the relaxation-spectrum region has also been found for certain other crystallizing polymers (^{9}).

Fig. 3. Dependence of deformation on temperature (frequency 0.14 oscillations/min) for a polycarbonate specimen: **1** –heated for 1 hour at 140°; **2** –deformed at a frequency of 0.14 oscillations/min for 1 hour at 140°.

Thus, in the present work, by means of thermomechanical and X-ray structural methods, it has been shown that mechanical periodically acting forces lead to an increase in the orderliness of structural elements and to an acceleration of the process of structural transformations in a crystallizing polymer. The use of a difficultly crystallizing polymer with a high T_c made it possible to separate processes caused directly by temperature factors from those caused by mechanical action. By applying different frequencies of the periodically acting force, it was possible to find the optimal conditions for the occurrence of the indicated transformations, to reveal a broad relaxation spectrum throughout the entire interval T_c—T_t, and to show the dependence of the character of the thermomechanical curves on frequency.

It should be especially noted that, when articles made of crystallizing polymers are used, it is necessary to take into account the structural changes occurring under mechanical actions, which lead to crystallization of the polymer, as well as relaxation processes.

Moscow State University
named after M. V. Lomonosov

Received
19 II 1962

CITED LITERATURE

1. N. I. Shirokova, E. F. Russkova et al., *Vysokomolek. soed.*, **3**, 642 (1961).
2. Yu. S. Lazurkin, *ZhTF*, **9**, 1261 (1939).
3. L. A. Igonin, Yu. A. Ovchinnikov, S. A. Arzhakov, *DAN*, **120**, 1062 (1958).
4. S. A. Arzhakov, E. E. Rylov, B. P. Shtarkman, *Vysokomolek. soed.*, **1**, 1351, 1357 (1959).
5. V. A. Kargin, V. A. Kabanov, I. Yu. Marchenko, *Vysokomolek. soed.*, **1**, 94 (1959).
6. V. A. Kargin, I. Yu. Marchenko, *Vysokomolek. soed.*, **2**, 549 (1960).
7. P. V. Kozlov, L. Makaruuk et al., *Vysokomolek. soed.*, **2**, 770 (1960).
8. V. A. Kargin, P. V. Kozlov et al., *DAN*, **142**, No. 5 (1962).
9. V. A. Kargin, T. I. Sogolova, N. P. Pavlichenko, *Vysokomolek. soed.*, **4**, 738 (1962).

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