FEATURES OF THE COURSE OF RELAXATION PROCESSES IN CRYSTALLIZING POLYMERS

1965

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

A. A. Frolova, P. V. Kozlov

FEATURES OF THE COURSE OF RELAXATION PROCESSES IN CRYSTALLIZING POLYMERS

(Presented by Academician V. A. Kargin, July 20, 1964)

In recent years, especially great attention has been devoted to the study of the physicomechanical properties of crystalline polymers and to establishing the connection between their structure, arising in the processes of synthesis and processing, and their properties. From this point of view, it is of interest to study the features of the behavior of polymers in which structural transformations take place during thermomechanical tests.

In the present work, the thermomechanical properties of amorphized crystallizing polymers were investigated over a wide interval of frequencies of a periodically acting force, and the dependence of deformation magnitudes on frequency was established. Polyethylene terephthalate, isotactic polystyrene, and polycarbonate obtained by phosgenation of 2,2-bis-(4′-oxyphenyl)-propane (molecular weight 75,000) were chosen as the objects of investigation. These polymers have high glass-transition and melting temperatures, lying far above room temperature, which makes it possible to obtain them in the amorphous state by abrupt cooling of the melt to room temperature, at which relaxation processes in them proceed very slowly. In addition, they differ in the degree of flexibility of their molecules and, hence, in their ability to form crystalline structures.

To study the relaxation phenomena occurring in polyethylene terephthalate, isotactic polystyrene, and polycarbonate, the frequency apparatus of Aleksandrov-Gaev was used (⁀1). In the investigations, frequencies of 1400; 140; 14; 1.4; and 0.14 oscillations per 1 min were applied, and a temperature interval from 20 to 230°. The rate of temperature increase in this case was 1° per 1 min; the holding time of the specimen at the measurement temperature was 10 min; the maximum load was 0.7 kg/cm^2. The preparation of tableted specimens for the investigation is described in works ([2,]3,⁀4). X-ray diffraction patterns obtained from specimens of all three polymers prepared for investigation reveal a diffuse halo, indicating their amorphous structure. Amorphous specimens of the polymers were subjected to vibrational compressive deformation by a force varying according to a sinusoidal law with a specified amplitude, over a wide interval of temperatures and frequencies. The results of these investigations are presented in Figs. 1, 2, and 3.

Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

As is seen from Fig. 1, in the temperature interval 60–80° for all frequencies of action of the force (curves 1, 2, 3, and 4), in amorphized polyethylene terephthalate a transition to the highly elastic state begins to occur. Noteworthy is the fact that the change in the glass-transition temperature T_c as a function of the frequency of action is comparatively smaller than the change in the maximum values of deformation upon transition to the highly elastic state $\varepsilon_{\max}$, which was not observed for rubbers and ordinary amorphous polymers ([1,5]). If T_c is taken to be the temperature at which the bend of the thermomechanical curve begins, then the interval in which its change occurs does not exceed 10°. At the same time, the deformation magnitudes $\varepsilon_{\max}$ depend strongly on frequency, increasing uniformly as it decreases.

With a further increase in temperature, the deformability of polyethylene terephthalate decreases sharply, which, as X-ray studies have shown, is associated with crystallization of the polymer. On the radiographs obtained from specimens deformed at various frequencies up to 110°, distinct diffraction rings are observed. For all frequencies of the applied force, crystallization of the polymer led practically to a loss of deformability up to the melting temperature of the crystals, at which

Fig. 1. Dependence of deformation (arb. units) on temperature for amorphized polyethylene terephthalate at different frequencies of the applied force.
1 –140; 2 –14; 3 –1.4; 4 –0.14 oscillations per minute

Fig. 2. Dependence of deformation (arb. units) on temperature for amorphized isotactic polystyrene at different frequencies of the applied force.
1 –140; 2 –14; 3 –1.4; 4 –0.14 oscillations per minute

the transition of polyethylene terephthalate to a viscous-flow state begins.

Another crystallizing polymer—isotactic polystyrene—after its amorphization shows, for different frequencies of the applied force, a completely analogous dependence of deformation on temperature (curves 1, 2, 3, and 4 in Fig. 2). It also has a comparatively small interval in which T_c changes as a function of the frequency of action. Upon transition to the highly elastic state, however, a considerable dependence of the values of deformation $\varepsilon_{\max}$ on frequency is already observed, although they are smaller than in polyethylene terephthalate. Likewise, a further increase in temperature leads to crystallization of the polymer (on radiographs of specimens deformed at different frequencies up to 140°—distinct diffraction rings) and to a practical loss of deformability for all frequencies up to the melting temperature of the crystals, where flow of the polymer begins.

The most interesting dependence of deformation on temperature is observed for

Fig. 3

Figure 2: Fig. 3

the poorly crystallizing polycarbonate (Fig. 3). In this case, changing the frequency of the applied force influences not only the magnitude of the deformation $\varepsilon_{\max}$, but also the character of the thermomechanical curve. From curve 1 in Fig. 3 it is seen that, at high frequencies of action, the high-molecular amorphous polycarbonate does not exhibit highly elastic properties up to the temperature of its transition to the viscous-flow state. This result is well explained by relaxation phenomena in the polymer. It corresponds to the case in which the relaxation time of the polymer is much greater than the time of action of the force and, as a consequence, chain molecules or secondary structural formations do not have time to exhibit the necessary mobility. Thermomechanical curves 2 and 3 in Fig. 3 show that a decrease in the frequency of action already makes it possible to realize all three regions corresponding to the three physical

states of an amorphous polymer. With a further decrease in frequency (curves 4 and 5 in Fig. 3), polycarbonate already exhibits properties typical of an amorphized polymer crystallizing during its testing. X-ray structural examination of specimens deformed at different frequencies up to temperatures near the transition to the viscous-flow state showed that in all cases, except for the specimen deformed at the slowest frequency, the polymer has an amorphous structure.

In the case of the slowest frequency, the X-ray diffraction pattern shows the appearance of a faint diffraction ring, indicating the formation of a structure of a higher order than that of the original specimen. It should be especially noted that the flow temperature T_{t} of polycarbonate depends significantly on the frequency of the applied force. The strong decrease in T_{t} is apparently the result of the superposition of several phenomena. Along with relaxation processes, as viscosity measurements have shown, under these conditions destruction of the polycarbonate also occurs, leading to a decrease in its molecular weight.

Fig. 3. Dependence of deformation (arb. units) on temperature for amorphized polycarbonate at different frequencies of action of the force: **1** –1400; **2** –140; **3** –14; **4** –1.4; **5** –0.14 oscillations per minute

Thus, as the investigations performed show, under the specified experimental conditions amorphized polyethylene terephthalate and isotactic polystyrene exhibit the properties of both amorphous and crystalline polymers. As amorphous polymers they display a broad relaxation spectrum during the transition from the glassy to the high-elastic state. The properties of crystalline polymers appear in them at higher temperatures, when crystallization processes have already taken place. From this point on, practically no frequency dependence is observed for these polymers. It should be noted that under the action of large loads, for a number of crystalline polymers it was possible to detect such a dependence more distinctly (6). The poorly crystallizing polycarbonate behaves

quite differently. Since the duration of the experiment is comparatively short, and the rate of temperature increase is too high for crystallization processes to take place, this polymer, when deformed at high frequencies, displays properties characteristic of amorphous polymers. Only when deformed at low frequencies, as a result of acceleration of structural transformations under the influence of mechanical action, does it exhibit the properties of an amorphized crystallizing polymer (4).

From Figs. 1, 2, and 3 it is clearly seen that all the polymers studied, upon transition to the high-elastic state, have a broad relaxation spectrum. If one plots the dependence of the maximum deformation values during the transition to the high-elastic state, $\varepsilon_{\max}$, on the logarithm of the frequency of action of the force, $\lg \omega$, then for each of the polymers a linear dependence of these quantities on the logarithm of the frequency is observed (Fig. 4). By extrapolating the straight lines to the abscissa axis, one can determine the frequency at deformation with which the polymer will not exhibit high-elastic properties, up to the melting temperature of the crystals. For polycarbonate it is 1400 oscillations per minute; for isotactic polystyrene, approximately 3000–4000; for polyethylene terephthalate, 4500–5500. On the basis of an estimate of the flexibility of the chains from the magnitude of the temperature interval between T_c and T_t (the difference $T_t - T_c$) and the value of T_c (7), the polymers studied can be arranged in order of increasing

their rigidity, in the following order: polyethylene terephthalate, isotactic polystyrene, polycarbonate. Then, as is clearly seen from Fig. 4, the following conclusion may be drawn: the higher the flexibility of the polymer chains, the greater the values of the deformation $\varepsilon_{\max}$.

Thus, in the present work, using polyethylene terephthalate, isotactic polystyrene, and polycarbonate as examples, the relaxation properties of amorphized crystallizing polymers have been studied. During the transition to the highly elastic state, these polymers exhibit a broad relaxation spectrum and, in contrast to rubbers and ordinary amorphous polymers, a significant dependence of the values of $\varepsilon_{\max}$ on frequency. For polycarbonate, moreover, a dependence of the character of the thermomechanical curves on frequency is also observed. By means of thermomechanical and X-ray structural methods of investigation, it has been shown that polymers with sufficiently flexible chains, in the course of thermomechanical tests, simultaneously exhibit the properties of amorphous and crystalline polymers, whereas a polymer with more rigid chains, depending on the frequency of the action, reveals the properties either of an amorphous or of an amorphized crystallizing polymer.

Fig. 4. Dependence of the maximum deformation (conventional units) on the logarithm of the frequency for:
1 –polyethylene terephthalate;
2 –isotactic polystyrene;
3 –polycarbonate

On the basis of the study of the relaxation properties of the polymers used, a linear dependence of the values of $\varepsilon_{\max}$ on the logarithm of the frequency has been established. By extrapolation, approximate frequencies were found at deformations at which polyethylene terephthalate and isotactic polystyrene should not exhibit highly elastic properties. It is also shown that, with increasing flexibility of the polymer chains, the values of the deformations $\varepsilon_{\max}$ increase.

Moscow State University
named after M. V. Lomonosov

Received
17 VII 1964

CITED LITERATURE

1. Yu. S. Lazurkin, ZhTF, 9, 1261 (1939).
2. A. A. Frolova, P. V. Kozlov, DAN, 149, 1390 (1963).
3. A. A. Frolova, P. V. Kozlov, V. A. Kargin, DAN, 153, 394 (1963).
4. P. V. Kozlov, A. A. Frolova, L. F. Silchenkova, DAN, 145, 125 (1962).
5. A. P. Aleksandrov, Yu. S. Lazurkin, ZhTF, 9, 1249 (1939).
6. V. A. Kargin, T. I. Sogolova, N. P. Pavlichenko, Vysokomolek. soed., 4, 738 (1962).
7. A. A. Tager, *Physicochemistry of Polymers*, 1963, pp. 191, 194.

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