The effect of plastic deformation under high pressure on the thermal effects in polyacrylamide

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Summary

Differential scanning calorimetry (DSC) and thermogravimetry were used to investigate polyacrylamide obtained under different conditions and subjected to plastic deformation under a pressure of 0.5–2.0 GPa. On the thermograms there were two endothermic peaks, one of which was associated with the rupture of hydrogen bonds, and the second with thermal imidisation. Plastic deformation led to a reduction in the enthalpies of both peaks. The enthalpies of endothermic processes depended on the presence in the specimens of trapped electrons.

In the process of plastic deformation under high pressure, carried out on a high-pressure apparatus of the Bridgman anvil type, the crystalline phase of amorphous–crystalline polyethylene and polypropylene breaks down to an ultradisperse state, when the size of the regions of coherent scattering amount to several nanometres [1, 2]. Along with rearrangement of the crystalline phase, considerable changes were also found in the amorphous phase of the polyolefins. Thus, the results obtained in Zhorin et al. [3] indicated that in the amorphous phase of PE, during treatment under pressure, ultrafine ordered regions were formed. The relaxation processes in such ultradisperse systems begin long before melting and, according to differential scanning calorimetry (DSC) data obtained in Zhorin et al. [4], appear on the thermograms in the form of broad endothermic peaks.

To date, most results obtained concerning the effect of plastic deformation under pressure on the structure of polymers and on the relaxation processes in them during heating have related to flexible-chain polymers. In Rogovina et al. [5] it was established that, during plastic deformation under high pressure, in cellulose, transformation of the structural form occurs – this is perhaps the only example of a study of the effect of plastic strains under high pressure on the structure of a rigid-chain polymer.

At the same time, it is of great interest to study the processes of structural rearrangement in rigid-chain polymers containing in their structure polar functional groups capable of forming intra- and intermolecular hydrogen bonds.

One of the polymers that contain functional groups capable of forming hydrogen bonds is polyacrylamide. This polymer can be produced in a radical liquid-phase process, by thermal initiation in a melt, and by plastic deformation of the solid monomer under high pressure in the range from 0.5 to 2.0 GPa. In all cases, the process of polymerisation proceeds by the double bond with the formation of a linear polymer.

In Zhorin [6] it was established that the flow stress of polyacrylamide obtained in solid phase is more than 30% higher than that of a polymer produced by radical liquid-phase polymerisation. In Zhorin et al. [7] it was established that the enthalpy of dissolution of the solid-phase polymer depends strongly not only on the pressure under which the polymer was produced but also on the degree of conversion of the monomer during polymerisation. Thus, the properties of the polymer, determined by intermolecular interaction, depend considerably on the way in which the polymer is produced.
It was of interest to investigate by DSC the thermal processes in polyacrylamide produced under different conditions, and also the effect on these processes of plastic deformation under high pressure.

EXPERIMENTAL

To produce the polymers, use was made of chemically pure acrylamide with \( T_m = 84^\circ C \). Polyacrylamide was produced by three methods: radical polymerisation in an acetone solution, using benzoyl peroxide as the initiator (radical polymer); thermal polymerisation of the monomer melt at 135°C (thermal polymer); plastic deformation of the monomer under a pressure of 1 GPa, varying the anvil turn angles (degrees of strain) to produce a polymer at different stages of monomer conversion (solid-phase polymer). In all cases, after synthesis, non-reacted monomer was washed out of the reaction mixture with ethyl alcohol. Radical and thermal polymers were subjected to plastic deformation under a pressure of 1 GPa at room temperature on anvils of hardened steel KhVG with a diameter of the working surfaces of the anvil of 20 mm. For the investigation, an edge zone of specimens of 3 mm width was selected. Investigation of thermal processes in the polymers was conducted on a DSC Q100 calorimeter (TA Instruments) at a heating rate of 20 deg/min; the weight of the specimens was 5–7 mg. The thermogravimetric investigation was conducted on a Q500 instrument (TA Instruments) with a rate of rise in temperature of 10 deg min\(^{-1}\); the weight of the specimens was 5–10 mg. IR spectra were recorded on a Nicolet 5700 spectrometer (TA Instruments) in a reflection regime.

RESULTS AND DISCUSSION

On heating thermograms of all the initial polymers there were two endothermic peaks, the temperature position of which hardly differed for the different polymers (Figure 1). During the cooling of specimens heated to 350°C, it was not possible to record any thermal processes, just as during reheating immediately after cooling. Thus, endothermic processes in the investigated specimens could be found only during the first heating.

Table 1 gives the enthalpies of the endothermic peaks for the different initial polymers. It turned out that the enthalpies for the radical polymer and for the solid-phase polymer practically coincide, while the enthalpies for the thermal polymer were lower than in the first two. The formation of the supermolecular structure of the polymer largely depends on the molecular mobility of the medium in which the process proceeds. The supermolecular structure of the radical polymer was formed in solution, that of the thermal polymer in melt, and that of the solid-phase polymer in monomer crystal. Data on the matching of the enthalpies of endothermic processes in the radical and solid-phase polymers make it possible to assume that the molecular mobilities in solution and in deformed crystal are similar.

Table 1. The enthalpy of endothermic peaks with maxima at 120°C (\( \Delta H_{120}, \text{J/g} \)) and 300°C (\( \Delta H_{300}, \text{J/g} \)) for the initial polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( \Delta H_{120} )</th>
<th>( \Delta H_{300} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radical</td>
<td>220</td>
<td>380</td>
</tr>
<tr>
<td>Thermal</td>
<td>130</td>
<td>320</td>
</tr>
<tr>
<td>Solid-phase</td>
<td>180</td>
<td>370</td>
</tr>
</tbody>
</table>

The endothermic peaks on the thermograms are associated with processes of intermolecular bond rupture. This can occur both with phase transitions (melting, evaporation) and with relaxation processes. To clarify the nature of the endothermic processes occurring in polyacrylamide specimens, the thermogram of the radical polymer was recorded during heating at a rate of 5 deg min\(^{-1}\). From the data given in Table 2 it can be seen that, with increase in the heating rate, the temperature of the maxima of the peaks increased, while the enthalpies of the peaks decreased. Such behaviour indicates that the endothermic peaks on the thermograms are associated with the occurrence in the polymer of relaxation processes. If phase transitions occurred in the specimens, the characteristics of the peaks in calorimetric measurements would not depend on the heating rate.

Table 2. Temperatures of the maxima of endothermic peaks (\( T, ^\circ C \)) and enthalpies (\( \Delta H, \text{J/g} \)) for the radical polymer with different heating rates

<table>
<thead>
<tr>
<th>5 deg/min</th>
<th>20 deg/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T, ^\circ C )</td>
<td>( \Delta H, \text{J/g} )</td>
</tr>
<tr>
<td>95</td>
<td>340</td>
</tr>
<tr>
<td>274</td>
<td>440</td>
</tr>
</tbody>
</table>

Figure 1. Thermogram of the initial radical polyacrylamide
To clarify the question of the mutual influence of low-temperature and high-temperature processes, a specimen of the radical polymer was heated to 170°C, cooled, and then reheated to 350°C. In this case, on the thermogram there was only an unaltered high-temperature peak.

The specimen of radical polymer was heated to 170°C, in order to burn off the low-temperature exothermic peak, and stored under room conditions for 1 month. On the thermogram of this specimen there was an endothermic peak with a maximum at 115°C and an enthalpy of 220 J/g (Δ\(\text{H}_{115}\)), and also an endothermic peak with a maximum at 303°C and an enthalpy of 380 J/g (Δ\(\text{H}_{300}\)). Thus, the low-temperature endothermic peak was restored, and the high-temperature peak hardly changed. This result indicates that the endothermic processes in the polymer proceed independently of one another.

It is known that, during the heating of polyacrylamide above 100°C, its imidisation occurs, which is accompanied with the release of ammonia. If the imidisation process occurred completely in polymers, the reduction in weight in the specimens would amount to 12%. It was of interest to investigate the temperature dependences of changes in weight in polymer specimens prepared by different methods.

It turned out that the reduction in weight of specimens during heating for all the investigated polymers occurred in two temperature ranges. From room temperature to 200°C, a monotonic reduction in weight by 11.3% occurred; with further increase in temperature, the rate of reduction in weight increased, and at 350°C the weight losses reached 30–32% (Figure 2).

A reduction in weight in the specimens, like the endothermic peak, could only be observed during the first heating—the radical polymer was heated to 170°C, cooled to room temperature, and then reheated; in this case, on the thermograms there was no endothermic peak in the temperature range 30–200°C, and the reduction in weight did not exceed 1%.

In the temperature range of the existence of a low-temperature endothermic peak, two processes can occur that lead to a reduction in weight of the specimens: these processes are the escape of adsorbed water and the release of ammonia during imidisation, which can occur in the polymer at temperatures above 100°C. In order to separate the contribution of each of these processes, a specimen of radical polymer heated to 170°C was stored for 1 month under room conditions. It turned out that, during the heating of this specimen in the range 30–200°C range, the reduction in weight amounted to 10%. Thus, during prolonged storage under room conditions, relaxation processes occur in polymer specimens, leading to restoration of the low-temperature endothermic peak and to the recovery of their ability to lose weight. The obtained results make it possible to conclude that the endothermic peak on the thermograms of polyacrylamide and the reduction in weight during heating in the range 30–200°C are associated mainly with the escape of adsorbed water and not with the formation of ammonia during imidisation of the polymer.

In the radical polymer, the maximum of the low-temperature endothermic peak lies at 110°C; at this temperature, the enthalpy amounts to roughly half the full value for this peak. At the same time, the reduction in weight in the range 30–110°C amounted to 9.5%, and in the range 110–200°C to 1.8%. Thus, the enthalpy corresponding to a 1% reduction in weight in the range 30–110°C is 5.3 times lower than the analogous parameter for the range 110–200°C. This result indicates the wide set of energetic states characterising the interaction of adsorbed water molecules and polymer chains.

Specimens of radical polyacrylamide, after heating to 170°C, had a beige or light brown colour and possessed good water solubility. After heating to 250–350°C, specimens were foamed, had a dark brown colour, and were not water soluble. The change in colour of the specimens during heating to 170°C indicates the occurrence in the specimens of chemical transformations; however, chemical processes proceed in the polymer most intensively at temperatures above 170°C.

On the thermogram of the radical polymer heated to 600°C, in the temperature range 350–500°C there were two overlapping exothermic peaks with maxima at 395 and 470°C; the total enthalpy of these peaks amounted to 110 J/g. In this temperature range, the reduction in weight of the specimen amounted to 50%. Thus, the overall reduction in weight in radical polyacrylamide at 600°C amounts to only 78.

Figure 2. The temperature dependences of weight losses for radical polyacrylamide: 1 – initial; 2 – deformed at α = 150°; 3 – deformed at α = 600°; treatment pressure 1 GPa.
comparison, an LDPE specimen was heated to 600°C. It turned out that at 420°C the weight of the specimen decreased by 13%, and in the range 420–510°C the reduction in weight was even 87%. In this temperature range, an endothermic peak with an enthalpy of 210 J/g was present on the thermogram. Thus, intensive breakdown of the polymer can be accompanied with both exothermic and endothermic processes.

The deformation of the polymers investigated under a pressure of 1 GPa did not change the general form of the thermograms – two endothermic peaks were present, the position of which on the temperature scale varied in a 3–5 deg range. However, the enthalpies of the endothermic peaks depended considerably on the magnitude of strain (the anvil turn angle) (Figure 3). In the radical polymer, as the anvil turn angle increased, \( \Delta H_{120} \) decreased by a factor of 2.2, and \( \Delta H_{300} \) by a factor of 2.1; in the solid-phase polymer, \( \Delta H_{120} \) decreased by a factor of 2.4, and \( \Delta H_{300} \) by a factor of 1.8; in the thermal polymer, \( \Delta H_{120} \) increased by a factor of 1.8, and \( \Delta H_{300} \) decreased by a factor of 1.2.

Along with the reduction in the enthalpies of both endothermic peaks in all the deformed polymers, a reduction in the amount of escaping water in the range 30–200°C from 11.0–11.5% to 7% was recorded. The investigated polymers were heated to 170°C, in order to remove the low-temperature endothermic peak and adsorbed water, and were stored for 1 month under room conditions. On the thermograms of these specimens there were endothermic peaks \( \Delta H_{120} \) and \( \Delta H_{300} \), and the reduction in weight during heating amounted to 10.5%. Thus, relaxation also occurs in the deformed polymers under room conditions, leading to restoration of the low-temperature endothermic peak on the thermograms and the amount of adsorbed water.

The reduction in the enthalpies of endothermic processes in the polymers may be connected with the reduction in the number of amide groups, some of which would be able to react during deformation under pressure. However, comparison of IR spectra of the initial radical polymer and the polymer deformed under a pressure of 1 GPa, and also polymers obtained with different degrees of strain (anvil turn angles of 50 and 60°), showed complete matching of their structure. This makes it possible to speak of imidisation not occurring in the polymers and amide groups being retained during deformation under a pressure of 1 GPa.

One of the reasons for the reduction in \( \Delta H_{120} \) in polyacrylamide may be the change in the supermolecular structure of the polymer during deformation. In Zhorin et al. [8] it was established that, on the thermograms of cellulose, there is an endothermic peak with a maximum at 120°C, which was attributed to the process of hydrogen bond rupture during heating. The behaviour of the low-temperature endothermic peak in polyacrylamide replicates entirely the behaviour of the endothermic peak in cellulose. However, the enthalpy of the peak in cellulose increased by a factor of 3 as a result of plastic deformation. Polyacrylamide and cellulose are rigid-chain polymers with \( T_g \) above 200°C. Therefore, the structural changes occurring in these polymers during plastic deformation cannot differ significantly. It is possible that change in the enthalpies of the endothermic peaks with a maximum at 120°C in different directions as a result of deformation may be due to the difference in the mechanisms of hydrogen bond formation with the participation of OH groups in cellulose and of NH_2 groups in polyacrylamide.

During plastic deformation, structural defects are formed in the polymers, which are electron traps. The appearance of electrons in the specimens is connected both with electron emission during degradation of the polymers and with electron injection into the polymers from the anvil metal; thus, a system of electrical charges is formed in the polymers. As the specimens should retain electrical neutrality, the appearance of electrons in the polymers should be compensated for by the polarisation of functional groups or fragments of macrochains. This may lead to a change in the nature and energy of intermolecular interaction.

The cell in which deformation of the specimens under pressure was carried out comprises a capacitor; between the two conducting plates ( anvils) there is a dielectric layer (the treated polymer). The processes
The enthalpy of polymerisation decreased by 30%. Thus, irradiation of deformed specimens of methacrylamide during deformation of pre-excited states. After UV irradiation, the effect was attributed to the formation in the monomers of high enthalpies of thermal polymerisation in acrylamide and methacrylamide subjected to deformation under high pressure were higher than in the initial monomers. This effect was attributed to the formation in the monomers during deformation of pre-excited states. After UV irradiation of deformed specimens of methacrylamide, the enthalpy of polymerisation decreased by 30%. Thus, UV irradiation led to deactivation of the pre-excited states in the deformed monomer.

In deformed specimens of polyacrylamide there are stable radicals formed during degradation of the polymer during treatment under pressure [11], and also trapped electrons. The number of stable radicals and trapped electrons in the specimens increases with increase in the degree of strain (anvil turn angle). Similarly to these characteristics, there is also a change in the enthalpy of the high-temperature endothermic peak.

On rupture of the chemical bonds, the energy of the initial substance is lower than the energy of the products formed. Pre-excited states in the deformed polymer will lead to a reduction in the energy differences of the initial and final states, which will lead to a reduction in the thermal effect of this stage of the chemical process. Thus, the balance between the endothermic effect of bond rupture and the exothermic effect of imide ring and ammonia formation will be broken, and the overall thermal effect in the deformed specimens will not be zero as in the initial polymer, but exothermic. In the experiment, this is manifested by a reduction in the enthalpy of the endothermic process of escape of ammonia. The greater the influence of the pre-excitation states on the process of chemical bond rupture, the lower will be the resulting enthalpy of the process. Thus, the reduction in $\Delta H_{300}$ with increase in the degree of strain that was observed in the experiment may be attributed to the formation in the polymer of pre-excited states, which affect the chemical process at the stage of chemical bond rupture.

The deformed polyacrylamide was subjected to UV irradiation, and also deformation of the polymer was carried out on insulated anvils. It turned out that, in the first case, $\Delta H_{300}$ increased by 15%, and in the second case the increase amounted to 20%. Thus, it can be said that, in both cases, deactivation of the pre-excited states occurred.

In Zhorin et al. [10], deformation of acrylamide was carried out in a magnetic field; such treatment led to an increase in the enthalpy of thermal polymerisation in the deformed specimens. Specimens of deformed polyacrylamide were subjected to ‘magnetic treatment’, which consisted in polymer powder being strewn onto a sheet of paper, and then a samarium–cobalt magnet being passed repeatedly beneath the sheet. In such a specimen, $\Delta H_{300}$ decreased by 18–20%, i.e. the magnetic field activated the occurrence of a chemical process. There is insufficient energy of the magnetic field to change the supermolecular structure of the polymer, but sufficient energy to influence the behaviour of stable radicals and trapped electrons.

In specimens of solid-phase polyacrylamide, the magnitude of $\Delta H_{300}$ depended on pressure, decreasing as the pressure of treatment increased. Thus, the magnitude of $\Delta H_{300}$ after deformation under a pressure of 1.0 GPa was 25% lower, and under a pressure of 2.0 GPa 33% lower, than in a specimen deformed under a pressure of 0.5 GPa. Thus, the effect of preactivation is intensified with increase in deformation pressure.

REFERENCES