Structural interpretation of different stages of deformation in uniaxial stretching of polyethylene

B.M Ginzburg
Institute of Problems of Machine Science of the Russian Academy of Sciences

INTRODUCTION

The structural changes during deformation of amorphous-crystalline polymers have been the subject of numerous investigations (see, for example, Refs. 1-22) and they still arouse interest. The use of powerful sources of synchrotron radiation has made it possible to record small-angle and wide-angle X-ray diffraction patterns at different points on the deformation curve of a specimen subjected to uniaxial stretching, at the same time as recording the deformation curve (Refs. 13, 14), which has greatly enriched our knowledge of structural principles for interpreting deformation curves. However, an especially convenient and productive methodology for studies of this kind has been uniaxial stretching and compression of oriented specimens or specimens with single-crystal texture at some angle to the direction of the axes of the macromolecules with simultaneous recording of small-angle and wide-angle X-ray diffraction patterns (Refs. 4-9, 15-22). With this technique, varied information has been obtained concerning the processes of shear deformation of polymers at the supramolecular level: intragranular, interfibrillar and interlamellar shear, planes of easiest slip in crystallites, the link between the mechanical properties of the elements of the supramolecular structure and the macroscopic mechanical properties of the specimens, and so on.

The information obtained permits a general formulation of questions regarding the nature of the deformation curve in terms of structural changes, what determines particular portions of the deformation curve, and its characteristic features. Some questions have been elucidated, as mentioned above, as a result of studies using sources of synchrotron radiation (Refs. 13, 14), where it has been possible to make a detailed investigation of the processes of twinning of crystallites and their martensitic transformations at relatively low strains.

However, the authors of those works investigated the processes of stretching of unoriented systems and their transition to an oriented state, which leads to superimposition of patterns of X-ray scattering from structural elements that are variously oriented relative to the direction of the external stretching force. However, investigation of reorientation at acute angles, especially of specimens with a single-crystal texture (Refs. 6, 9), provides information about processes of shear deformation of crystallites, interlamellar and interfibrillar slip that is easier to interpret and accordingly unambiguous to a higher degree. In several works (e.g. Refs. 6, 8, 9) particular attention was paid to determination of the critical cleavage stresses (initiating various shear modes in the crystallites) and various components of the tensor of the elastic modulus, i.e. relatively small strains were mainly investigated, as before. Processes of transformation of the initial structure into a new structure, connected with formation of “pre-necking” and “necking” regions, were investigated to a far smaller extent.

This article, based on examination of earlier and new experimental data on shear deformation of low-density polyethylene (LDPE), as one of the commonest representatives of the class of flexible-chain amorphous-crystalline polymers, relates the various stages of reorientation (under the action of quasistatic uniaxial tension), on the one hand, to the corresponding structural changes on the other hand. Emphasis will mainly be placed
on interpretation of large strains of specimens based on concepts of various forms of shear deformation of the structural elements. The concept of critical shear angle will be employed, examining the role of the $T_1/T_2$ ratio (where $T_1$ and $T_2$ denote, respectively, the temperature of primary treatment – crystallisation, annealing, orientation – and secondary treatment of the specimen) and analysing the analogy of deformation curves and van der Waals isotherms for liquid-vapour transitions.

The results obtained can explain the wide spectrum of experimental observations made by various authors when investigating the deformation of oriented and unoriented specimens of amorphous-crystalline polymers in different conditions.

METHODS

Films with thickness of 1.4 mm were pressed at 200°C and pressure of 5 MPa from industrial LDPE granules ($M_n \approx 25 000$). The films were quenched in water at room temperature.

Specimens in the form of a double blade with a working part 18 mm wide and 50 mm long were cut from the films obtained. Then the specimens were submitted to 5-fold stretching at temperature $T_1 = 85^\circ$C and were cooled to room temperature in the fixed state. The films treated in this way had a thickness of 0.7 mm and width of 9 mm. The small width of the samples meant that it was not possible to cut out specimens for reorientation in the form of a double blade. Therefore specimens in the form of strips 3 mm wide and 9 mm long were cut from the initially drawn samples at various angles $\alpha$ to the direction of primary stretching. As a rule, specimens of this shape failed near the grips in the latter stages of deformation. In the X-ray diffraction experiments the specimens were stretched in steps at temperature $T_2 = 20^\circ$C in such a way that the direction of stretching made a specified angle $\alpha$ with the direction of primary stretching. After each step, before recording the X-ray diffraction patterns, the specimens were held under load for 12 hours; this time was sufficient for visible changes in specimen shape and the corresponding X-ray diffraction patterns to cease. After the specimens were fully unloaded they were left in the free state for 36 hours. Specimen strain was determined on a type IZA-2 horizontal comparator from the displacement of marks made beforehand.

The deformation curves were recorded on a laboratory dynamometer on the same specimens, deforming the specimens manually at a rate of a few millimetres per minute.

The wide-angle and small-angle X-ray photographs were obtained from the identical region of the specimen in a KRM-1 camera (Burevestnik NPO, St. Petersburg, Russia). Ni-filtered CuKα radiation was used. $H_v$ diffraction patterns were recorded on a laboratory diffractometer.

RESULTS AND DISCUSSION

The Concept of Critical Shear Angle of the Crystallites

The cornerstone in interpreting processes of reorientation at the supramolecular level is the concept of the critical shear angle of the crystallites $\eta_c$, or the critical value of shear strain (Refs. 5, 7, 16, 17, 22). On attaining this angle the crystallites, by acquiring additional surface energy connected with appearance of additional surface area $\Delta S$ (Figure 1), become thermodynamically unstable and melt, and in their place there is formation of a new supramolecular structure with large periods and with crystallites corresponding to the temperature at which reorientation occurs. The physical meaning of attainment of $\eta_c$ is that the free surface energy of the crystallite becomes equal to the free surface energy of the crystallisation nucleus at the temperature of the experiment (Refs. 7, 17), which is what, in our opinion, leads to fusion of the crystallite during subsequent shear deformation.

![Figure 1. Schematic representation of shear deformation of a crystallite. $\eta$ - angle of shear, $H_0$ and $L_0$ - transverse and longitudinal dimensions, respectively, of the crystallite in the initial state, $W_1$ and $W_2$ - directions of primary and secondary orientation, $\Delta S$ - increase in free surface.](image-url)
the highly-elastic melt (with formation of new crystallites and new fibrils, i.e. a new structure). Thus, transition of the polymer crystallites to a liquid melt can be effected successively by carrying out two processes: deformation, as a result of which a phase transition (or solid-phase amorphisation) occurs, and subsequent heating, as a result of which there is a smooth transition to a liquid state of aggregation.

The value of the critical shear angle $\eta_c$ depends on the nature of the polymer, the size of the initial crystallites (which is determined in its turn by the temperature $T_1$ of primary treatment of the specimen) and the temperature of its secondary treatment $T_2$ (reorientation) (Refs. 5, 7, 16, 17, 22). The value of $\eta_c$ is higher for higher $T_1$ or lower $T_2$. At $T_1 = T_2$ the original and new supramolecular structures cannot be distinguished by diffraction methods, although the fusion-recrystallisation process still takes place, if $T_2$ is above the glass transition temperature. If $T_2$ is below the glass transition temperature, during reorientation we shall observe fusion through solid-phase amorphisation of the specimen.

**Actual Deformation Curves**

For a wide range of values of $\alpha$ angles (45, 65, 75°) the deformation curves (Figure 2) are roughly identical in appearance and have similar values of the yield point $\sigma_y$. For the case when $\alpha = 90°$ there is a stress peak, or upper yield point $\sigma_{yu}$ and then the stress drops to the lower yield point $\sigma_{yl}$. At small $\alpha$ (10, 25°) the deformation curves do not have a plateau parallel to the abscissa – the stress rises continuously with the strain. The initial slope of the curves in Figure 2 increases in the order $\alpha = 45°$, 75°, 25°, 90°; these results are in agreement with the well-known anisotropy of the elastic modulus of oriented PE specimens (Refs. 2, 3, 25). On the whole the curves obtained are in good agreement with data in the literature (Refs. 2, 3). A structural interpretation of the deformation curves for the various types of specimens is given below.

**Figure 2.** Deformation curves in uniaxial stretching of oriented specimens of LDPE at different angles to the direction of primary stretching; $T_1=85°C$, $T_2=20°C$. 1 - $\alpha=25°$; 2 - 45°; 3 - 75°; 4 - 90°.

**Figure 3.** Diagram of a deformation curve with reorientation of specimens of LDPE; $T_1=85°C$, $T_2=20°C$, angle of reorientation $\alpha=75°$. Photomicrographs corresponding to different portions of the deformation curve are shown. The numbers by the radiographs denote the magnitude of deformation and the large period. For other explanations, see text.

$\alpha = 45-75°$

Figure 3 shows, in most general form, a diagram of the deformation curve in stress-strain coordinates for LDPE specimens during secondary stretching (reorientation) in the following conditions: difference in temperatures $T_1$ and $T_2$ (85 and 20°C respectively) large enough for the initial structure and the new structure, arising as a result of breakdown of the initial structure, to be clearly distinguishable in the X-ray diffraction patterns; angle of reorientation $\alpha$ between the directions of the primary stretching $W_1$ and of secondary stretching $W_2$ large enough for the main stages of the structural changes during reorientation to show up. The X-ray diffraction patterns in Figure 3 correspond to $\alpha = 75°$.

After primary drawing, the specimens possessed c-texture of the crystallites; the width of the azimuthal intensity distribution of the equatorial reflections 110 and 200 was 10-12°. Intense meridional reflections, corresponding to large periods 170-180 Å, were observed in the small-angle X-ray diffraction patterns. The following regions and corresponding stages of structural changes in the specimens can be identified provisionally on the deformation curve.
On portion OA there is elastic deformation of the specimen, accompanied by reversible shear deformation of the crystallites, which is manifested as displacement of the small-angle reflections along the direction of the layer lines. The intragranular shear deformation is accompanied by rotation of the c-axis towards the direction of the secondary stretching (cf. Figure 3a and 3b). Simultaneously, the amorphous regions of the penetrating chains are turned in the opposite direction (Figure 4). Therefore their tendency to turn in the direction of reorientation and the tendency of the fibrils to preserve integrity lead to interlamellar shear W1. (Ref. 17).

On portion AB there is development of a kink band, or "pre-necking" zone and plastic strain of the specimen as a whole; where there are fibrils, the crystallites reach the critical shear strain ηC, they melt, and are replaced by a new structure, corresponding to the reorientation temperature T2; fusion is not caused by adiabatic heating of the specimen, nor by negative pressures on the crystallites, as has often been assumed in the literature (Ref. 2), but by decrease of the melting point of the crystallites of the initial structure in the preceding stages of reorientation, but they are deformed to a lesser extent and their critical angle of shear is also much smaller, since they are of smaller dimensions (Ref. 7). Note the following results, which are important in our opinion. Firstly, contrary to a common misconception, the axes of the macromolecules in the crystallites of the "neck-shaped" part of the specimen are not aligned immediately along the direction of reorientation: for an actual test specimen there is merely a jump of the angle of orientation by 10-20°, but the angle of deviation from the direction of stretching is more than ~20° (see Figure 3d). Secondly, during unloading of the specimen (transition from point C to point C') the shear strain of the crystallites not only decreases, but in addition the crystallites are subject to shear deformation in the opposite direction. A similar effect is observed on unloading a specimen that has reached the pre-rupture state (see below).

The stress σy corresponds to the maximum stress at which reversibility of the new structure is preserved when it is stretched from a position corresponding to point C'; during further stretching on portion CD, irreversible processes of fusion and recrystallisation of the crystallites of the new structure take place, and judging from the rotation of the X-ray diffraction patterns this can be interpreted erroneously as a corresponding rotation of the entire structure without transformation of the crystallites. Nevertheless, the processes of fusion and recrystallisation take place, but the crystallites of the new structure and the crystallites arising when they melt are indistinguishable by diffraction methods, since they both form at exactly the same temperature.

On portion DE there is elastic stretching of the new structure that has been drawn out to the maximum. On portion DE the crystallites are twisted somewhat as a result of the shear deformation that took place, and the axes of the macromolecules in them are aligned along direction W2 (Figure 3e). During specimen unloading, in portion DE there is first a decrease in shear strain of the crystallites of the new structure (Figure 3e', e''), and then there is displacement of the crystallites in the opposite direction, with formation of a four-point small-angle X-ray diffraction pattern (Figure 3e'''). Simultaneously,
the c-axes of the crystallites are deflected anticlockwise from direction W₂.

The displacement of the crystallites in the opposite direction can be explained on the basis that prior to unloading, crystallites formed from the amorphised material that arose as a result of fusion of the initial structure; these new crystallites are not deformed during their formation, and are incorporated into the general structure of the specimen. During subsequent unloading of the specimen, however, the remnants of the initial structure (apparently, at the molecular level) partly regain their orientation, and subject the new crystallites to shear deformation in the opposite direction.

During further stretching of the specimen, so-called fibrillisation is often observed: splitting of the specimen into a multitude of thread-like macroscopic formations (Refs. 26, 27) on account of rupture of the interfibrillar bonds. The start of fibrillisation is accompanied by the appearance of a picture of strong diffuse scattering on the small-angle X-ray diffraction patterns, extending across the direction of stretching (see, for example, Chapter 2, p. 55, in the symposium (Ref. 10)).

\[ \alpha = 90^\circ \]

Let us examine deformation corresponding to angles \( \alpha = 90^\circ \) or close to that (\( \geq 80^\circ \)) (Figure 5). Even in the range of elastic strain, an increase in width of the azimuthal distribution intensity of the equatorial reflections can be seen in the larger-angle X-ray diffraction patterns (Figure 5a, b). This increase is connected with splitting of the system of crystallites into two subsystems, which are in a state of unstable equilibrium with their c-axes oriented in opposite directions relative to the direction of stretching (Figure 5c); it can also be seen from Figure 5c that the small-angle reflections from strongly deformed crystallites merge together. This is even more distinct on transition to irreversible deformation, when reflections arise from the new structure (Figure 5d, e). From a state of unstable equilibrium, the system undergoes the transition to necking, but there is then a drastic redistribution of the number of crystallites in favour of one of the subsystems (Figure 5e), and thereafter the structural changes (Figure 5e-g) have practically the same character as when \( \alpha = 75^\circ \).

The stress peak that forms on the deformation curve is due to the very same unstable equilibrium, connected with stretching of the crystal layers across the direction of the chains (Figure 6). After the peak, the stress drops roughly to the same level as for other large angles of reorientation. Similar results were obtained by Keller and Rider for HDPE (Ref. 2, p. 281). Their data show that the yield point has a fairly shallow minimum near angle of reorientation \( \alpha = 60^\circ \), but increases considerably at \( \alpha \) angles close to \( 90^\circ \) and to a much greater extent at small \( \alpha \).

Small \( \alpha \) values. The curves observed at small \( \alpha \) angles are characterised by degeneration of the necking stage, and a more or less uniform decrease in specimen cross-sectional dimensions is observed. On the small-angle X-ray diffraction patterns, after elastic deformation and reversible
of the “pre-necking” portion AB on the deformation curve right until specimen rupture occurs at strain $\varepsilon \approx 300\%$. A similar picture is observed at $\alpha = 10^\circ$, the only difference being that reflections from the new structure are barely visible. Nevertheless, the new structure undoubtedly exists, since the strain before rupture reaches 100-120%, and the magnitude of the large periods drops to values ($\sim 110$ Å) that are characteristic of the new structure. The shear strain of the crystallites [see the small-angle X-ray diffraction patterns in Figure 7d-f] in both cases, $\alpha = 10$ and 25°, reaches 50-60° and exceeds the angle of reorientation. This means that shear deformation takes place not only by rotation of the macromolecules in the crystallites, but also by sliding of the macromolecules relative to one another without rotation. This type of deformation also occurs at large $\alpha$, but it predominates at small $\alpha$.

The shear strain of the crystallites can in principle even exceed the critical angle of shear, because under the action of the tensile load along the direction of the axes of the macromolecules there can be a considerable increase in melting point of the crystallites (Ref. 28).

### Deformation Ranges of Various Stages in Structural Changes

Table 1 shows the deformation limits of various stages of structural changes for different $\alpha$ values. When similar structural changes are achieved in the initial stages of deformation, maximum elongations are required at $\alpha = 45^\circ$. Completion of the processes of reorientation at $\alpha = 45-90^\circ$ occurs roughly at identical specimen elongations ($\sim 600\%$). At $\alpha = 10$ and 25°, specimen rupture occurs prior to complete transition from initial to new structure (at $\sim 100\%$ and $\sim 300\%$, respectively).

### Transition from the Unoriented to the Oriented State

The initial unoriented state of the films of PE that we used is characterised by spherulitic structure [Figure 8a] – there

<table>
<thead>
<tr>
<th>Angle of reorientation $\alpha$, degrees</th>
<th>Elongation of the test section of the specimen $\varepsilon$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reversible strain</td>
</tr>
<tr>
<td>10</td>
<td>60</td>
</tr>
<tr>
<td>25</td>
<td>80</td>
</tr>
<tr>
<td>45</td>
<td>170</td>
</tr>
<tr>
<td>65</td>
<td>120</td>
</tr>
<tr>
<td>75</td>
<td>100</td>
</tr>
</tbody>
</table>

*It was not possible to determine the extent of the last stages of deformation owing to failure of the specimens in the grips.*
is a characteristic 4-lobed pattern on the Hv-diffraction patterns of linearly polarised light. Reflections of the annular or circular type were observed on the X-ray diffraction patterns. The diameter of the spherulites was 16 µm for crystallisation temperature $T_c = 105°C$. In the first stages of deformation in the elastic range, the larger-angle X-ray diffraction patterns show that a crystallite texture forms in the system, with deviation of the c-axes from the direction of stretching; small-angle X-ray diffraction patterns and Hv-diffraction patterns show that the spherulite is drawn out in the direction of stretching, and assumes an elliptical shape (Ref. 29). It is known that the rays of the spherulite in its equatorial regions are rotated towards the direction of stretching. Since the macromolecules in PE spherulites are mainly oriented perpendicularly to the rays, during subsequent stretching the angles between the external force and the direction of the macromolecules in the crystallites are mainly close to 70-90°. Correspondingly, the deformation curves are in this case also extremely similar to the curves at large $\alpha$.

On portion AB we already observe not only elastic, but also plastic strain, caused by partial breakdown of the initial structure (dip on the meridian of the elliptical reflection on the small-angle X-ray diffraction patterns) and formation of a new fibrillar structure (appearance of the reflection shown by the dashed line in the same X-ray diffraction patterns) (Figure 8c, c'). Splitting of the lobes, caused by co-existence of the initial and new structure, can also be seen in the Hv-diffraction patterns during specimen unloading (Figure 8c') (Ref. 29). The initial structure (obtained at the crystallisation temperature of 105°C) proved to be extremely stable and does not break down before the end, even in the pre-rupture state of the specimen (Figure 8d, d').

As the crystallisation temperature is lowered, the stability of the structure decreases, and there is a sharper transition to necking. Figure 9a shows photographs of specimens that crystallised at different temperatures, and were then deformed at room temperature up to the necking stage. With approximately equal temperatures of crystallisation and deformation (as also in the case of reorientation at $T_1 = T_2$) necking is hardly observed, and the specimen width decreases more or less uniformly when tracked along its longitudinal axis (Figure 9b).

![Figure 8](image8.png)

**Figure 8.** Diagram of a deformation curve with uniaxial stretching of unoriented specimens of LDPE; temperature of crystallisation $T_c = 85°C$, deformation temperature $T_2=20°C$. Photomicrographs and small-angle Hv-diffraction patterns of linearly polarised light are shown, corresponding to various portions of the deformation curve. The numbers near the radiographs denote the magnitude of deformation. The diffraction patterns in Figure 8c', d' were obtained with complete unloading of the specimens whose diffraction patterns are shown in Figure 8c, d respectively. Explanations in text.

![Figure 9](image9.png)

**Figure 9.** Effect of crystallisation temperature $T_c$ on necking in unoriented specimens of LDPE in uniaxial stretching at $T_2=20°C$. (a) general appearance of the specimens; (b) relative reduction of specimen width with tracking from the undeformed part to the neck. 1 - $T_c=105°C$; 2 - $T_c=80°C$; 3 - $30°C$.

**Effect of the Ratio of the Temperatures $T_1$ and $T_2$ on the Form of the Deformation Curves**

Experiments have been carried out (Refs. 6, 29) to investigate the effect of the temperature $T_2$ on the form of the deformation curves during reorientation of LDPE at right angles. A diagram of these curves is shown in Figure 10a. With increase in the deformation temperature $T_2$, the slope of portion OA decreases, the stress decrease...
BC is smaller, and necking is less and less distinct, i.e. the change in transverse dimensions of the specimen is less abrupt. Reduction of the stress decrease BC was also observed for various types of PE in (Ref. 14), and for polyvinylidene fluoride in Siesler’s work (see Chapter 4, p. 161 of the symposium, Ref. 10).

When the temperature \( T_2 \) rises to temperature \( T_1 \), portion CE and the decrease BC generally disappear. This can be explained on the basis that the initial structure undergoes transition, through fusion, to a self-similar structure, which should appear on the X-ray diffraction patterns simply as rotation of the scattering pattern. It can be assumed to a first approximation that this does occur, and rotation of the X-ray diffraction pattern and disappearance of necking were observed at \( T_1 = T_2 = 85^\circ C \) and at \( T_1 = T_2 = 20^\circ C \), the only proviso being that the equality \( T_1 = T_2 \) is observed (Ref. 7).

The Various Portions of the Deformation Curve

Thus, in the most general case the results of investigation of the processes of deformation of amorphous-crystalline polymers permit the following portions of the deformation curve to be identified (Figure 11).

(1) A portion OA, where elastic deformation is observed, moreover the stress is directly proportional to the strain (i.e. Hooke’s law is observed); the stress corresponding to the end of the section at point A is called the limit of proportionality.

(2) A portion AB, where the strain is reversible as before, but Hooke’s law is not obeyed, i.e. deformation is viscoelastic; for polymers the region of viscoelastic deformation can be very large, extending practically from \( \varepsilon = 0 \) to several tens percent; the region of viscoelastic deformation is characterised by hysteresis effects and large mechanical losses; note that using deformation methods (at high exposures, for times much longer than the relaxation times of the mechanical stresses) stages (1) and (2) are indistinguishable; viscoelastic deformation also has the effect that the slope of portion AB, and – for polymers – often of portion OB as well, depends on the strain rate d\( \varepsilon / dt \) – the larger the strain rate, the greater is the slope, i.e. the greater is Young’s modulus E, which has been called the relaxation modulus.

(3) The portion BC (or BC’), or more precisely its starting point B, characterises the start of plastic, irreversible deformation, connected with partial fusion of the crystallites of the initial structure and appearance of a new structure – amorphous, if the deformation temperature is below the glass transition temperature, or amorphous-crystalline, if the deformation temperature is above the glass transition temperature; in the latter case there is formation of new crystallites and an oriented structure with new large periods, corresponding to the deformation temperature; on portion BC (or BC’) the proportion of new structure increases at the expense of a decrease in the proportion of the initial structure; on attainment of a certain critical proportion of new structure (approximately 75% for LDPE) it is combined into a new phase in the macrovolume, which is manifested as necking; moreover, necking need not necessarily be accompanied by a decrease in stress on the deformation curve CC”, or by formation of a so-called “sharp” yield point; a “sharp” yield point

![Figure 10. Diagram of a series of deformation curves of LDPE as a result of reorientation at different temperatures (a) and van der Waals isotherms (b). Explanations in text.](image)

![Figure 11. A most general schematic representation of the deformation curve of amorphous-crystalline polymers. Explanations in text.](image)
can only form in cases when there is stretching of an initial unoriented structure, or there is stretching (reorientation) of an initial oriented structure at a certain angle $\alpha$ close to $90^\circ$ ($\alpha = 90^\circ \pm \Delta \phi$, where $\Delta \phi$ is the angle of disorientation of the crystallites) relative to the direction of the chains in the crystallites; for crystallites in which the direction of the chains is perpendicular to the direction of the external tensile force there is development of unstable equilibrium (bifurcation), resulting in the "sharp" yield point, since the cleavage stress required for shear deformation of the crystallites across the chains is always greater than the cleavage stress during shear deformation of the crystallites in any other direction relative to the direction of the chains at an angle $45^\circ < \alpha < 90^\circ$.

The magnitude of the “sharp yield point” $C'C$ must be less in the case of stretching of unoriented systems than in the case of reorientation of oriented systems at an angle of $90^\circ$; in reorientation the magnitude of the “sharp” yield point should decrease with increase in deviation of angle $\alpha$ from $90^\circ$ (all the way to $\alpha = 45^\circ$), as well as with increase in the angle of disorientation of the crystallites $\Delta \phi$ (i.e. with decrease in initial draw ratio), with increase in deformation temperature and with decrease in the temperature of primary treatment, giving rise to a decrease in the proportion of crystallites in the system and impairment of their ordering.

(4) Portion CD is characterised by propagation of necking along the specimen and transition of the initial structure to a new structure on the scale of the whole specimen (in contrast to microphase separation on portion BC).

(5) Portion DE characterises the additional orientation of the new structure.

(6) Portion EF characterises elastic deformation of the new oriented structure.

(7) Portion FG characterises the formation of interfibrillar cracks, leading to macroscopic fibrillisation of the specimen and its failure.

**Analogy of Deformation Curves and van der Waals Isotherms for Low-molecular Compounds**

The changes in the structure of highly oriented specimens of LDPE during their reorientation and analysis of data available in the literature concerning the mechanical behaviour of specimens of crystalline polymers led us to conclude that there is some analogy between the deformation curves in coordinates of stress $\sigma$ – strain $\lambda$ (or draw ratio) and the van der Waals isotherms for low-molecular substances (Ref. 28), if we ignore the fact that transition from the initial structure to the new structure proceeds via fusion, and assume that this transition takes place directly.

Let us compare the deformation curves and the isotherms (Figure 10a and 10b); analogous portions of the curves are designated with identical letters. On portion OA of the deformation curves there is elastic shear deformation of the crystallites of the initial structure; on the isotherms there is compression of vapour. At point A on the deformation curve, plastic deformation arises when the crystallites reach the critical angle of shear, corresponding to the critical specific free surface energy; on the isotherms the density of the vapour reaches the saturated vapour density.

On portion AE of the deformation curves (at $\alpha = \text{const.}$) there is transition of the initial structure to the new structure (there is a jump-like change in the angle of shear of the crystallites); at node AE on the isotherms (at $P = \text{const.}$) there is a jump-like transition from vapour to liquid, i.e. a jump-like change in density. The abscissa of any point on segment AE of the deformation curve characterises the relative volumetric content of initial and new structure in the specimen as a whole, and the values of the free surface energy of the crystallites of the initial and new structure are equal on this portion of the deformation curve; at node AE the abscissa characterises the relative volumetric content of liquid and vapour; the chemical potentials of the liquid and vapour are equal in this segment.

At point E the transition is concluded in both cases; on further deformation of the polymer there is stretching of the new structure, and with decrease in $V$ on the isotherm there is compression of the liquid. Table 2 summarises the analogous parameters characterising the isotherms and the deformation curves.

| Table 2. Analogous parameters for van der Waals isotherms and deformation curves |
|:-----------------|:-----------------|
| **Isotherms** | **Deformation curves** |
| Pressure | Stress |
| Saturated vapour pressure | Recrystallisation stress |
| Volume | Draw ratio |
| Density | Angle of shear of the crystallites |
| Density of the saturated vapour | Critical angle of shear of the crystallites |
| Chemical potential | Free surface energy of the crystallites |
| Critical temperature | Temperature of primary treatment |
| Temperature of the isotherm | Deformation temperature |

*International Polymer Science and Technology, Vol. 32, No. 1, 2005*
The proposed analogy, like any other, is not complete, but its examination may prove rewarding for further development of research into the link between structure and mechanical properties of polymers. Let us first examine some additional results, which fall within the scope of the analogy.

Portions AB and DG in Figure 10 correspond to metastable states that are really attainable in the case of low-molecular compounds. In the case of polymers, portion AB corresponds to coexistence of two types of structures, corresponding to regions of the specimen that are more turbid than the regions where one structure exists. As the temperature rises, the horizontal portion AE of the van der Waals isotherms decreases, disappearing completely at a critical point. Apparently, the same should happen on the deformation curves, but so far no particular attention has been paid to the change in extent of the plateau-like portions.

It has been established experimentally that the decrease BC disappears for LDPE at temperatures that are 10-20°C lower than \( T_1 \) (Ref. 30).

This is natural, since in all cases of existence of a critical state of two-phase systems the properties of the phases become very similar as the critical point is approached, and it is always difficult to locate the critical point (Ref. 31).

Since the temperature \( T_1 \) is the analogue of the critical temperature when investigating deformation curves and since we are able to alter the temperature \( T_1 \) beforehand, the curve joining the critical points in coordinates \( \sigma \sim \lambda \) is a critical curve (Ref. 32).

The proposed analogy provides an explanation of a number of results previously published in the literature. Thus, with orientation of PE, necking can occur over a fairly wide range of elongations (Ref. 33). This can be explained on the basis that the transition from the metastable state to a stable state is due to various causes of a random character (defects in the specimen, increased stresses near the grips, etc.). The turbidity of the specimen in the region between its initial part and the necking (Ref. 30) can be explained by the presence of heterophase fluctuations, with dimensions of the order of the wavelengths of visible light. In an investigation of multiple reorientation of specimens at right angles it was established that necking does not occur even during secondary reorientation (Refs. 34, 35). In light of the analogy being discussed, this is connected with the fact that during secondary reorientation we already have the equality \( T_1 = T_2 \), i.e. stretching is being carried out at the critical temperature.

We shall now point out some specific features of the deformation curves of polymers that do not fit in with the proposed analogy. The main discrepancy is that the nature of the deformation curves depends on the angle of reorientation. This is evidently due to the dependence of the deformation behaviour of the crystallites on the angle between the direction of the macromolecules in the cristaite and the direction of application of the force (Refs. 2, 5, 7, 22). Then the case of simple orientation, i.e. specimen transition from the unoriented to the oriented state, should be regarded as the combined transformation of various immiscible vapours into a single liquid. This can be represented graphically as a series of straight segments of the type OA, in Figure 10, emerging from one point with different slope and going across to a node AE on one level of stresses or pressures. The curves in Figure 2 for large \( \alpha \) confirm these considerations.

Examine the kinetics of phase transformations of the vapour–liquid type, Frenkel noted (Ref. 36) that if the law of distribution of heterophase fluctuations with respect to dimensions does not take into account the interaction between the elements of the new formation during phase transition, this should lead to formation of a disperse system of elements of the new phase in a medium consisting of the remnants of the initial phase; for example, in the vapour–liquid transition there would be formation of "droplets of macroscopic dimensions, which would not coalesce into a continuous liquid phase" (e.g. mist). The formation of new structure (occupying up to 75% of the total volume) in a medium of the initial structure, which is observed during reorientation, can be likened to the predicted phenomenon.

The proposed analogy makes it possible to view the dependence of the character of the deformation curves on the temperature, strain rate etc. from different perspectives; it suggests a number of new forms of processing these curves, for example construction of "phase diagrams" in coordinates \( \sigma, \lambda \); for analysis of these "phase diagrams" we can try using equations similar to the Clausius-Clapeyron equations, and calculate the thermal effects of the transitions, and so on (Ref. 37).

REFERENCES

13. B.M. Ginzburg et al.: Vysokomolek. soed., Role of temperature and direction ... Sent to press.

NOTE: REF. 28: DZHEIL, F. – IS THIS P.H. GEIL?