

Deformation of interatomic bonds in polymers

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Values of the deformation of macromolecules due to distortion of valency angles and bond lengths have been determined from shifts of the intrinsic infra-red (i.r.) vibration frequencies. It has been shown that in a polymer under stress there exists a small number (a few percent) of overstressed macromolecular segments. The overstressed segments appear to start at a certain value of deformation and upon further stressing the polymer their number increases proportionally to the deformation. Values of deformation of overstressed segments have been determined at a stress corresponding to the strength of macromolecules. Deformation of highly oriented specimens before their rupture was shown to occur via distortion of valency angles and bond lengths. An increase in valency angles makes the predominant contribution to the deformation of chains

INTRODUCTION

Values of deformation prior to the rupture of a polymeric chain must be known in order to construct a molecular mechanism of deformation and fracture of polymers. In the present paper these values are determined for a number of polymers, and a correlation between deformation of bonds in the chain and deformation of a specimen is established.

I.r. spectroscopy has been used for this purpose. It was found¹⁻⁸ that under the action of mechanical forces, the vibration frequencies of the skeleton of a polymeric molecule shift, and this change has been used to determine the effect of mechanical stresses on polymeric chains. The frequency shift is known to result from deformation of interatomic bonds. In this work the frequency shift has been used to determine values of deformation at stresses close to the theoretical strength of polymeric molecules.

EXPERIMENTAL

Highly oriented films of polypropylene (PP), poly(ethylene terephthalate) (PETP), polycapromamide (PCA), polyacrylonitrile (PAN) and polypyromellitimide (PPMI) were used to obtain data on the deformation of segments of polymeric chains at stresses close to the strength of chemical bonds. Investigations showed³ that such stresses appear first in segments of a macromolecule whose length cannot be extended under stress by conformational change but as a result of distortion of valency angles and bond lengths. The absorption bands used in our measurements are given in Table 1. The details of the experimental technique have been described previously².

Determination of values of deformation of polymeric bonds

Figure 1 shows how the band at 976 cm^{-1} for PETP changes under the influence of a stretching stress (σ) of 50 kp/mm^2 .

It is known that the absorption bands in the i.r. region of polymeric molecules consist of the summation of a series of lines due to the same molecular group, but occurring at slightly different frequencies because of small differences in the environment. Due to stress the band maximum shifts towards low frequencies, and simultaneously and intensive

Table 1 Infra-red bands used for measurements

Polymer	i.r. band, α (cm^{-1})	($\text{cm}^{-1}\text{ mm}^2/\text{kp}$)	Modulus of crystallite, E (kp/mm^2)	$\beta \times 10^{-3}$ (cm^{-1})
PP	975	0.026	4800 (10)	0.125
PETP	976	0.084	7600 (10)	0.640
PCA-6	930	0.037	2500 (10)	0.092
PAN	1350	0.08	24 000 (11)	1.920
PPMI	605	0.005	4200 (9)	0.021

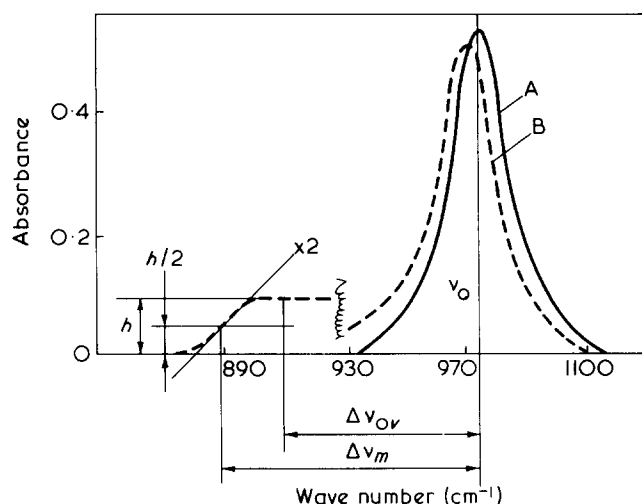


Figure 1 Change in shape of the band at 976 cm^{-1} for PETP under stretching stress: A, $\sigma = 0\text{ kp/mm}^2$; B, $\sigma = 50\text{ kp/mm}^2$; $T = 20^\circ\text{C}$

'wing' about 100 cm^{-1} in width appears in the long-wave range, showing that absorption lines shift under stress by different amounts.

The vibration frequency of a polymer molecule is a function of (a) force constants dependent on the interaction of forces between the atoms in the molecule and between the molecules; (b) anharmonicity of vibrations; and (c) conformation of the polymer molecule. By 'conformation' we mean the dependence of frequency on the distance between the ends of regularly constructed sections. In the course of the deformation of a polymer under stress, force constants, molecular conformation and the vibrations anharmonicity change. The influence of some of these factors on the frequency shift has previously been discussed^{4,7,8}.

Gubanov and Kosobukin⁴ have shown theoretically that the stretching of a polymer molecule produces a change in the valence angles and bonds, and a decrease in the force constants. There are a number of skeletal frequencies for which an unambiguous dependence exists between the frequency shift and the force. In general this dependence cannot be expressed analytically, but when the frequency shift $\Delta\nu$ is less than $0.1\nu_0$ (ν_0 being the vibration frequency of a free molecule) it can be assumed that the frequency shift is directly proportional to the force $\Delta\nu = \alpha\Sigma$.

Gubanov and Kosobukin also showed that the shape of the i.r. absorption lines of an isolated molecule changes with the force⁴. They have shown that the line is always symmetrical and has a dispersion shape. Its half-width increases under stress. They also investigated the influence of the force on the molecular absorption coefficient K , and have found that K hardly changes under force (not more than 30%).

These authors also examined how the change of frequency resulting from changes in the vibration anharmonicity and intermolecular forces that occur when a molecule suffers deformation, and have shown that these effects are small when compared with shifts caused by chain deformation⁴.

Woll *et al.*^{6,7} and Evans *et al.*⁸ studied the influence of intermolecular forces and the conformation of polymer molecules on frequency shift, were of the opinion that a change in these quantities may considerably affect the frequency change of the band maximum in a stressed body.

As the frequency shift is conditioned by many factors, it is necessary to check whether the experimentally measured shift is unambiguously connected with deformation, and for this purpose the shifts in the centre of gravity of i.r. absorption bands (*not the band maximum*) under stress were compared. The results are shown in *Figure 2* for PETP and PP. The polymer structures were modified by thermal treatment, viz, cooling in liquid nitrogen, exposure at room temperature and at a temperature close to the melting point of the polymer. The specimens were also subjected to varying degrees of stretching $\lambda = L/L_0$, where L and L_0 are the initial and final lengths of the specimen, respectively.

The spectra of the specimens were recorded at temperatures in the range 150° to 100°C . It was assumed that a variation in the initial structure and temperature would change both the conformational structure and the intermolecular forces. Measurements of the conformation-sensitive bands ($502, 845, 900, 975, 1040 \text{ cm}^{-1}$) for PETP showed that the *trans*-isomer concentration changed from 20 to 80%.

As can be seen from *Figure 2*, the shift does not depend either on the temperature of the experiment or on the conditions of specimen preparation. An unambiguous dependence exists between shift $\Delta\nu$ and stress Σ :

$$\Delta\nu = \alpha\Sigma \quad (1)$$

where α is a proportionality factor. These results suggest that the changes of the conformational structure and molecular interaction have no appreciable effect on α . Therefore it can be supposed that the deformation of polymer molecules is the main reason for the interatomic vibration frequency shift.

Using Hooke's law, equation (1) becomes:

$$\Delta\nu = \beta \cdot \epsilon \quad (2)$$

where $\beta = \alpha \cdot E$ and E is the elasticity modulus of a chain found from X-ray diffraction data⁹⁻¹¹; ϵ is the deformation of a chain segment. Values of β for the polymers studied are given in *Table 1* and ϵ may be calculated from equation (2). For the numerical evaluation of ϵ , the absorption band was divided into two parts. For this purpose, the band maximum was extended to low frequencies symmetrically to the high frequency band as shown in *Figure 1*. Then if the frequency $\Delta\nu_m$ corresponds to the maximum of the symmetrical part, and $\Delta\nu_{0\nu}$ to the centre of gravity of a long frequency part, the differences for the band studied are $\Delta\nu_m = \nu_0 - \nu_m$ and $\Delta\nu_{0\nu} = \nu_0 - \nu_{0\nu}$. Comparing $\epsilon_{0\nu} = \Delta\nu_{0\nu}/\beta$ and ϵ_m we find that

$$\frac{\epsilon_{0\nu}}{\epsilon_m} = \frac{\Delta\nu_{0\nu}}{\Delta\nu_m} \simeq 10 \div 100$$

depending on the value of specimen deformation.

Segments with deformation $\epsilon_{0\nu}$ were previously referred to a overstressed². The concentration of such segments is

$$\eta = \frac{S_{0\nu}K}{SK_{0\nu}}$$

where $S_{0\nu}$ and S are the areas of the wing and the band, respectively, and $K_{0\nu}$ and K are absorption coefficients in the wing and the maximum of a stressed polymer.

As shown by Gubanov *et al.*⁴, the absorption coefficient under force hardly changes, i.e. $K_{0\nu} \simeq K$, and thus $\eta = S_{0\nu}/S$.

Deformation of interatomic bonds in stressed polymers

Figure 3 shows the dependence of the number of overstressed segments, η , and of the mean deformation of the overstressed segment, $\bar{\epsilon}_{0\nu}$, on the deformation of a specimen up to rupture. Overstressed segments are practically absent up to a certain limiting value of deformation, ϵ_0 . At higher deformations a certain number of overstressed segments appear, their concentration increasing proportionally to the deformation. The mean deformation of an overstressed segment, $\bar{\epsilon}_{0\nu}$, increases with the deformation of a specimen by 10–20% prior to rupture. The effect is reversible; and when the deformation of the specimen decreases due to a decrease in a load, the number of overstressed segments, as well as stresses on them, diminish by corresponding values.

Table 2 shows values of $\bar{\epsilon}_{0\nu}$ for stresses close to breaking. As we can see from the Table, the values obtained attain several tens of per cents. The question therefore arises: may we use Hooke's law for chains with such large deformations? To answer this question we determined $\bar{\epsilon}_{0\nu}$ without using Hooke's law and equations (1) and (2).

The molecular mechanism of deformation of polymers has previously been studied¹²⁻¹⁴ and was found that at small deformations the main contribution to an increase in the length is made by changes in chain lengths due to conformational transitions.

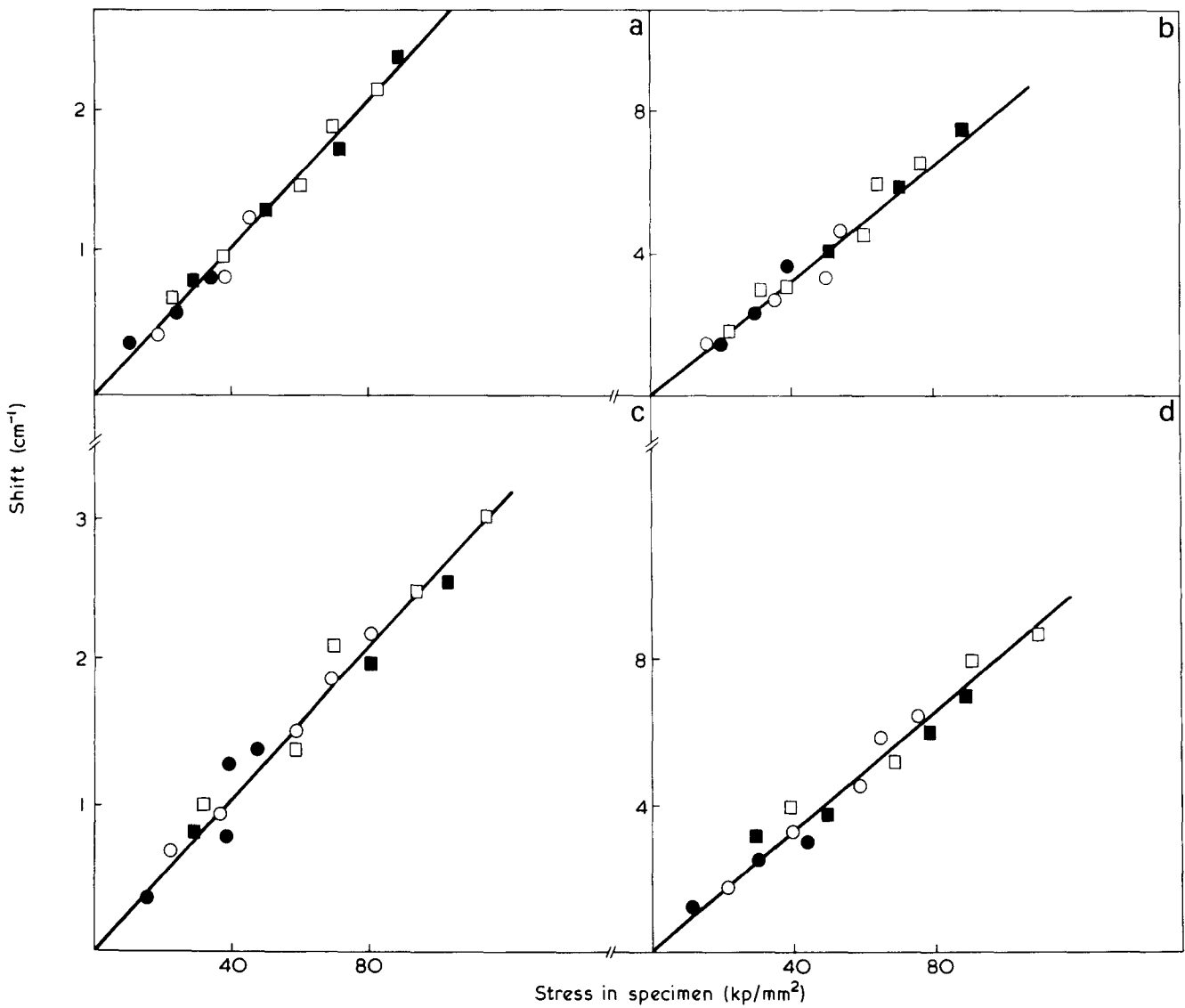


Figure 2 Dependence of shift of the centre of gravity of the band at 975 cm^{-1} for PP(a,c) and the band at 976 cm^{-1} for PETP (b,d) from the stress σ for the specimens with the different initial structure (a,b): □, An oriented specimen, $\lambda = 8$; ■, an oriented specimen, $\lambda = 12$; ○, a hardened specimen; ●, a tempered specimen) and at the temperatures of recording the spectrum for the specimen with a constant degree of orientation, $\lambda = 8$ (c,d) □, -120°C ; ■, -65°C ; ○, $+20^\circ\text{C}$; ●, $+100^\circ\text{C}$

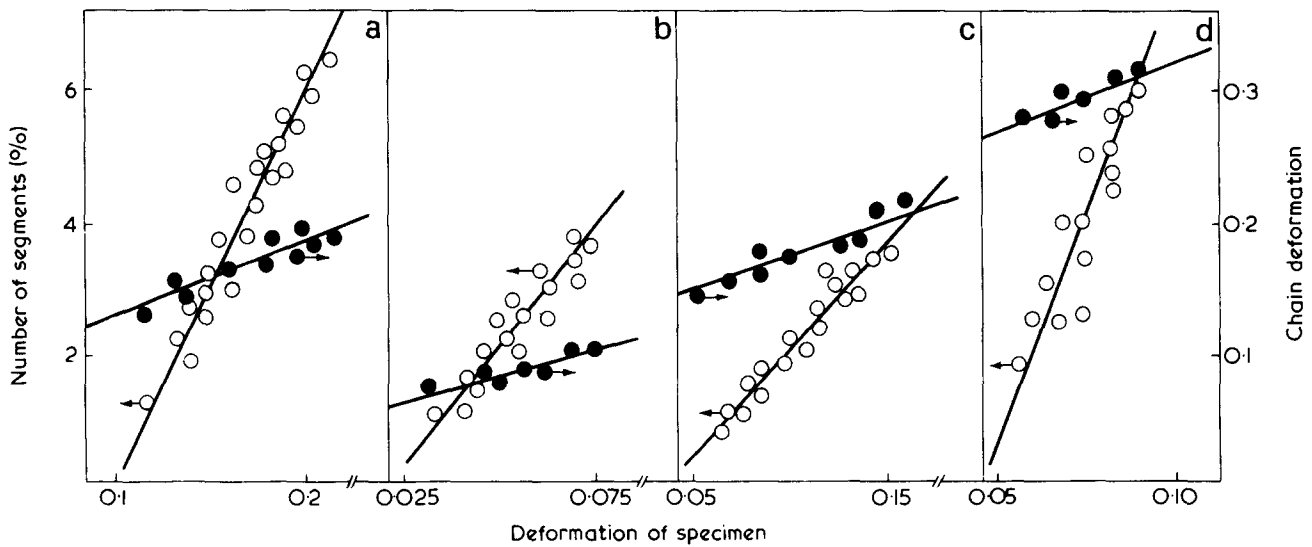


Figure 3 Dependence of number of overstressed segments, n , and chain deformation, $\bar{\epsilon}_{0V}$, on relative elongation of a specimen ϵ_{sp} : (a) PP; (b) PETP; (c) PCA; (d) PPMI

Table 2 Deformation of overstressed polymeric chains

Polymer	$\bar{\epsilon}_{0v} = \frac{\sum \epsilon_f}{E_c}$ (%)	ϵ_f at 20°C (%)	$\bar{\epsilon}_{0v} \equiv \Delta\epsilon_{sp}$ (%)	$\frac{L_0}{L_a}$	ϵ_{f0} at 10K (%)	ϵ_{theor} (%)
PP	19	25	23		33	26
PETP	10	18	15		25	23
PCA-6	21	45	21		60	36
PAN	3	3	—		8	9
PPMI	31	47	—		60	33

Figure 4 illustrates the change in the concentration of overstressed segments and *gauche*-isomers for PETP under the influence of the deformation (the concentration of *gauche*-isomers was estimated from the band intensity at 500 cm^{-1}). As the deformation grows, the number of *gauche*-isomers diminishes due to the transition to the more elongated *trans*-isomers. Such a transition according to the authors of the works cited, is the main process in the molecular mechanism of deformation. In the case of a highly oriented PETP, the concentration of *gauche*-isomers rapidly decreases with deformation only until a certain value of ϵ_0 is attained, then the number of isomers changes in a much less pronounced way. At the same value of the deformation of a specimen an appreciable number of overstressed segments appear and these increase proportionally to the deformation ϵ_{sp} (Figure 3). One may consider that at $\epsilon_{sp} = \epsilon_0$ possibilities of elongation of a specimen due to conformation transitions are exhausted and further elongation is possible only at the expense of the distortion of valency angles and bond lengths of the polymeric chains. If such assumptions are valid, one must expect a considerable increase in the elasticity modulus at ϵ_0 . It was found earlier¹⁵ that the modulus of a specimen increased several times. The product of the elasticity modulus of an overstressed polymeric chain by the number of such chains proved to be equal to the modulus of a specimen. This leads to the conclusion that the deformation of a specimen on reaching a certain limiting value is caused by distortion of valency angles and bond lengths of macromolecules. An increase in deformation at the expense of distortion of valency angles and bond lengths, Δv_{sp} , can be found from the $\eta - \epsilon_{sp}$ dependence; $\Delta\epsilon_{sp} = v_f - \epsilon_0$, where ϵ_f is the deformation just before rupture and ϵ_0 is the deformation value extrapolated to the axis of the abscissa (overstressed segments appear at $\epsilon_{sp} > \epsilon_0$). Our experiments with specimens whose strength and orientation varied within wide limits indicated that ϵ_0 and ϵ_f depend upon the conditions of preparation of specimens, whereas the slope of the $\eta - \epsilon_{sp}$ dependence remained constant within the limits of experimental error.

According to the Hess model¹⁶, highly oriented polymers as used in the present work consist of microfibrils oriented in the direction of stretching with a diameter of about 100 Å. Amorphous and crystalline regions alternate along the fibrils. X-ray diffraction studies carried out by Zhurkov and his coworkers¹⁷ indicate that deformation of specimens occurs mainly at the expense of the length of amorphous regions. It was shown³ that overstressed segments of polymeric molecules are predominantly concentrated in amorphous regions of a polymer. These facts allow one to neglect the crystal deformation and calculate the deformation of a polymeric chain as

$$\bar{\epsilon}_{0v} \approx \Delta\epsilon_{sp} \left(\frac{L_0}{L_a} \right) \quad (3)$$

where L_0 and L_a are the lengths of the long period and amorphous region, respectively.

The value of L_0/L_a in our case was 2.1 for PP. It changed with temperature of stretching from 1.6 to 2.3 for PETP and from 2 to 1.7 for PCA. The value of $\bar{\epsilon}_{0v}$ in Table 2 was found to be independent of the L_0/L_a ratio and had the same value for specimens obtained at various temperatures of stretching. The Table shows values of ϵ_{0v} calculated using equations (1) and (3). It is noteworthy that calculation of the chain deformation using equation (3) is independent of the validity of Hooke's law and spectroscopic error in the determination of $\bar{\epsilon}_{0v}$.

As we can see from Table 2, the $\bar{\epsilon}_{0v}$ values calculated from equations (2) and (3) coincide with each other. Thus we conclude that Hooke's law holds with sufficient precision for overstressed polymeric chains.

It should be noted that the elasticity modulus of the polymer chain is a function of the chain deformation and temperature because of the anharmonicity of the potential function. The assumption made is therefore not exactly correct. The value of $\bar{\epsilon}_{0v}$ calculated from equations (2) and (3) have an i.r. inaccuracy (20–30%) and that is why one can consider the elasticity modulus as a constant. The calculation, carried out by Kosobukin¹⁸ has shown, that the elasticity modulus can change at strain of not more than 20%.

As was noted, the concentration of overstressed segments is directly proportional to the deformation of a specimen and an increase in the number of overstressed segments may be caused by either the growth of the total number of stressed chains or an increase in the lengths of deformed

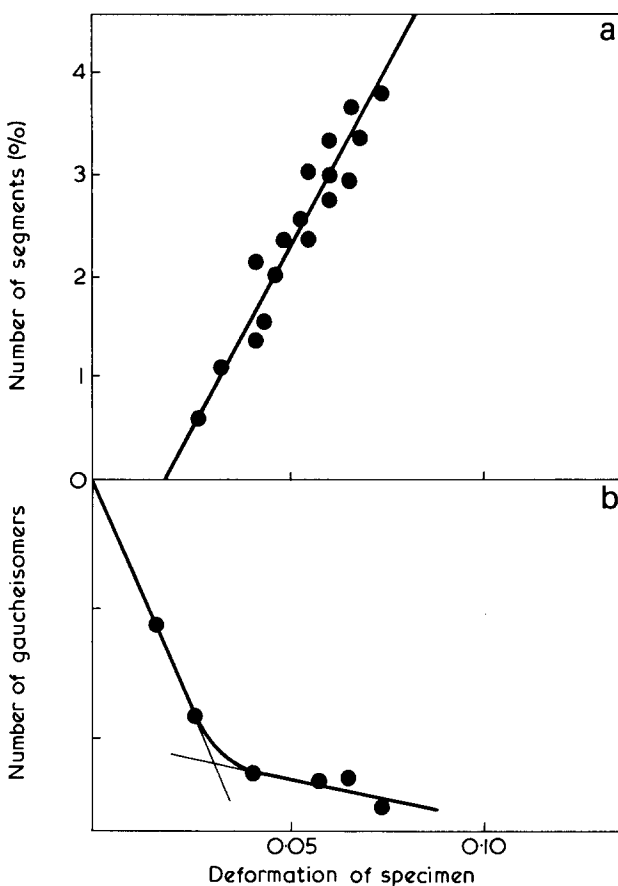


Figure 4 Change in concentration of overstressed segments $\bar{\epsilon}_{0v}$ (a) and number of *gauche* isomers (arbitrary units determined from band intensity at 500 cm^{-1}) (b) on relative elongation of a specimen ϵ_{sp} for PETP

Table 3 Parameters of supermolecular structure

Polymer	Temperature of stretching (°C)	L_a/L_0 (X-ray)	L_a/L_0 (i.r.)
PP	150	0.48	0.58
PETP	240	0.42	0.30
	230	0.48	0.33
	220	0.50	0.42
	205	0.63	0.49
	180	0.63	0.49
PCA-6	200	0.50	0.4
	150	0.43	0.36
	100	0.33	0.3
	20	0.36	0.3
PPMI	—	—	0.10

chains. Neglecting crystal deformation, the deformation of a specimen can be represented as:

$$\Delta\epsilon_{sp} = \bar{\epsilon}_{0v} \left(\frac{L_x}{L_0} \right) \quad (4)$$

where L_x is the length of an overstressed chain (which may be less than the length of the amorphous region). On the other hand, the number of overstressed segments can be expressed via the number of stressed polymeric chains N_c :

$$n = N_c \cdot \left(\frac{L_x}{L_0} \right) \quad (5)$$

From equations (4) and (5) we obtain:

$$n = \frac{N_c}{\bar{\epsilon}_{0v}} \Delta\epsilon_{sp} \quad (6)$$

Upon deformation of a specimen the deformation of an overstressed segment changes slightly and may be assumed to be constant. This indicates that the main contribution to an increase in the number of overstressed segments is caused by the growth of the lengths of overstressed chains, but not by the increase in the number of chains under stress. It follows from Figure 3 and equation (4) that at $\epsilon_{sp} < \epsilon_0$ the length of an overstressed chain, L_x , practically equals zero. At $\epsilon_{sp} > \epsilon_0$ the length of an overstressed chain increases proportionally to the deformation of a specimen and attains approximately the length of the amorphous layer L_a prior to failure. This follows from the data of Table 3 where values of L_a/L_0 are determined from equation (4) and from X-ray diffraction analysis data.

Thus, starting from a certain limiting value of deformation ϵ_0 , the lengths of overstressed segments of a chain increase rapidly and attain the length of the amorphous region just before failure.

We believe that ϵ_0 is determined by intermolecular interactions in amorphous regions. At small stresses, intermolecular forces in the polymer transfer stress from one molecule to another and in this way prevent the appearance of greatly overstressed segments in the specimen. At a certain stress these forces become incapable of inhibiting non-uniform distribution of stresses over segments and, as a result overstressed segments with limited lengths appear in the specimen. A further increase in deformation of the specimen gives rise to progressive rupture of intermolecular bonds which in its turn increases the lengths of overstressed chains.

Deformation of the polymeric chain prior to rupture

The values of ϵ_f of the most stressed segments of the macromolecule is of interest in elucidating the mechanism of polymer fracture.

The maximum deformation of polymer segments is

$$\epsilon_m = \frac{\Delta\nu_m}{\beta}$$

where $\Delta\nu_m$ is the maximum shift of the vibration frequency for a polymer segment. For accurate determination of $\Delta\nu_m$ it is necessary to decompose the band into the component lines. Calculations show¹, however, that the $\Delta\nu_m$ value cannot be determined accurately since absorption diminishes weakly with the frequency and the absorption measurement precision in the wing is low. Therefore for an approximate evaluation of $\Delta\nu_m$ the following procedure in which there is no need to decompose the band into component lines was used. A tangent was drawn at the edge of the wing of the long waveband L (Figure 1) through the point $h/2$ and the distance between the band maximum in the non-stressed state and the point of intersection of the frequency axis is taken to be $\Delta\nu_m$. Evidently, the value $\Delta\nu_m$ so found is dependent on the half-width of the line, Γ_0 , and to take account of this dependence, the line half-width was subtracted from $\Delta\nu_m = \Delta\nu_m^1 - 0.8 \Gamma_0$.

The line half-width is unknown since even for an unloaded specimen, the band consists of lines located at different frequencies. For the determination of Γ_0 unloaded specimens were exposed at a high temperature, for a prolonged period (which according to current concepts improves their structure) and the absorption spectra and the half-widths of absorption bands were determined. The line half-width Γ_0 is assumed to be equal to the band half-width for such a specimen. The actual half-width is, of course, less than the assumed value.

Figure 5 shows the dependence of the maximum deformation of a segment, ϵ_m , on the specimen deformation, ϵ_{sp} ,

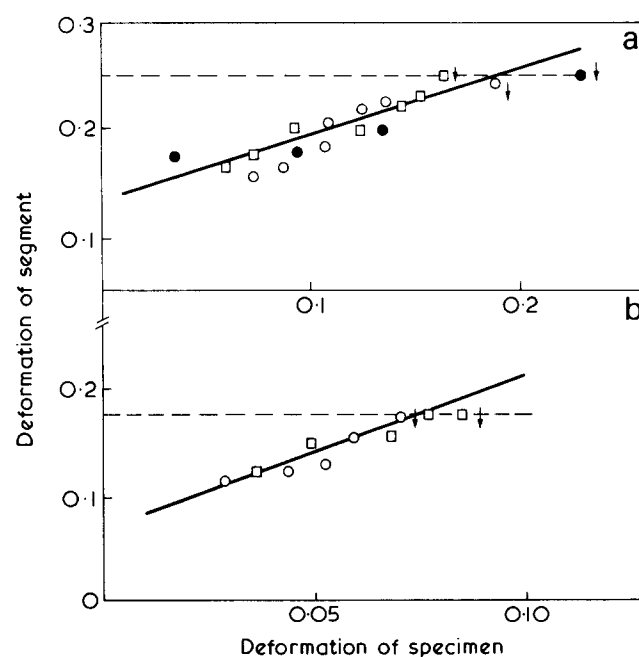


Figure 5 Dependence of ϵ_m from the deformation of specimen ϵ_{sp} for the specimens with the several degrees of orientation; a, PP, b, PETP, ●, $\lambda = 4.5$; ○, $\lambda = 8$; □, $\lambda = 12$. The sign ↓ shows breaking stress values.

for PP and PETP specimens having different orientations. With the increase of the specimen deformation ϵ_m increases and, irrespective of the specimen orientation, all the specimens break down for the same value of ϵ_m denoted as ϵ_f . The existence of ϵ_f independent of the specimen orientation is in agreement with the presence of the limiting value of stress in the chains, Σ_f , described previously, at which polymer molecules rupture³. Using Σ_f we obtain $\epsilon_f = \Sigma_f/E =$ constant.

Vettegren *et al.*³ have found that Σ_f , which determines the probability of thermal fluctuation decomposition of the polymer molecule is dependent on temperature:

$$\Sigma_f = \Sigma_{f0} - \frac{RT}{\Delta T} \cdot \ln \frac{\bar{L}}{\bar{L}_0} \quad (7)$$

where Σ_{f0} is the strength of a polymeric molecular at 0K; R , is the universal gas constant; ΔV is the activation volume of rupture of apolymeric chain, \bar{L}_0 is a constant equal to 10^{-12} – 10^{-14} sec.

According to the theory of the effect of pressure on chemical reactions¹⁹ the probability, W , of rupture of polymer molecules, is given by:

$$W = W_{0\text{exp}} \frac{U_0 + P\Delta V}{RT} \quad (8)$$

where U_0 is the activation energy of decomposition at zero pressure, ΔV is the activation volume, W_0 is a constant equal to 10^{12} – 10^{14} sec⁻¹.

In our case the body is subjected to tension and substituting for P and introducing the expected time of molecule rupture $\bar{L} = 1/W$ we obtain:

$$\bar{L} = \bar{L}_0 \exp \frac{U_0 - \Delta V\epsilon}{RT} \quad (9)$$

Rewriting this equation with respect to Σ :

$$\Sigma = \frac{U_0}{\Delta V} - \frac{RT}{\Delta V} \ln (\bar{L}/\bar{L}_0) \quad (10)$$

Equations (7) and (9) are very similar. Vettegren *et al.*³, comparing the experimental value $\Sigma_{f0} = U_0/\Delta V$ with the theoretical strength of polymer molecules ($\Sigma_{\text{theor}} = U/\Delta V$) and the experimental ΔV with the theoretical value of the activation value, found that the theoretical and experimental values are close to one another. Hence it may be supposed that the Σ_f value found from experiment corresponds to the rupture stress for polymer molecules.

Using Hooke's law, pre-rupture deformation is given by:

$$\epsilon_f = \epsilon_{f0} - \frac{RT}{E\Delta V} \ln \bar{L}/\bar{L}_0 \quad (11)$$

The values of ϵ_f and ϵ_{f0} for the polymers studied are given in Table 2. It is necessary to keep in mind that the elasticity modulus is a function of temperature; that is why the value of ϵ_{f0} obtained from equation (11) is greater than the real value.

It is of interest to clarify the elements of polymeric

structure whose deformation mechanism makes the maximum contribution to the deformation of the chain. It is well known that the elasticity modulus of valency angle deformation is smaller by an order of magnitude than the modulus of bond stretching. It is natural to assume that valency angles will change first upon the deformation of a specimen. Assuming therefore that a hypothetical polymeric chain is represented by a straight line, we may estimate the increase in deformation due to a transition from the normal configuration to the hypothetical one. Using the published values of chain lengths and data on the conformation of polymeric chains^{20,21} the calculation of the increase in the chain length ϵ_{theor} due to the maximum increase in valency angles are given in Table 2. A comparison of ϵ_{f0} with ϵ_{theor} shows that the increase in valency angles makes the predominant contribution to the observed chain deformation.

It may be noted that the theoretical value of rupture deformation is not dependent on \bar{L} , T and therefore in comparing the experimental data with theory, we have to compare ϵ_{f0} and ϵ_{theor} rather than ϵ_f and ϵ_{theor} .

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