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The influence of chemical structure on the relaxation properties of heat-resistant aromatic polymers

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Abstracts. Data concerning the experimental method for the estimation of the mechanical workability of heat-resistant polymers, based on relaxation measurements, as well as concerning procedures for the fitting of stress relaxation and creep curves with the aid of new memory functions are surveyed. The influence of the chemical structures of various heat-resistant polymers (aromatic polyethers and polyamides, polyimides, polybenzoxazoles, polyoxadiazoles, etc.) on their relaxation behaviour is analysed in detail. Attention is concentrated on the relaxation transitions manifested in the glassy state. The mechanism of the deformation and relaxation in heat-resistant polymers, investigated with the aid of the positron annihilation method, is described. The relaxation behaviour of heat-resistant aromatic polymers down to the temperature of liquid helium is considered. Attention is drawn to the relaxation behaviour. The bibliography includes 167 references.

I. Introduction

Studies on the synthesis and properties of heat-resistant polymers began about 40 years ago and have continued fairly vigorously to the present day. Naturally, in the first investigations attention was concentrated on the limiting strength and deformation properties. However, it soon became evident that, in terms of the strength and deformation on rupture, it is impossible to infer objectively the mechanical workability of the materials. Indeed, a polymeric material is never used when subjected to near breaking loads; even under extreme conditions, the polymers can always realistically operate provided that they are subjected to loads and deformations significantly below the limiting values. Naturally, whatever the load and deformation, relaxation processes develop, the essential feature of which is that at a constant deformation the stress is not constant, as for ideally elastic materials, but relaxes, i.e. diminishes with time. Accordingly, a creep process develops — an increase in deformation with time. The kinetic data for the relaxation processes depend on temperature, i.e. both are manifested whatever the type of load and not only for a constant deformation and load. These processes in fact determine the true mechanical workability of the polymers. The study of relaxation transitions by the dynamic mechanical analysis is particularly important. Such transitions are associated with the freeing of the molecular mobility of different kinetic units, which play an enormous role in the establishment of the properties of the polymer. The study of the mechanism of these transitions and of the influence on the latter by the chemical structure of the heat-resistant polymer has attracted the attention of investigators.

Evidently the above relaxation processes and transitions are important also for composite materials and blends. Significant attention has been devoted in recent years to the mechanism of the relaxation and deformation processes in heat-resistant polymers subjected to a large deformation. The application of positron diagnostic methods (positron annihilation) directly in the relaxation and deformation process made it possible to obtain new data on the changes in the microporous structure of the material. Many questions are associated with the analysis of the nonlinear mechanical behaviour of heat-resistant polymers when the parameters of the relaxation process depend on time and are not constant. Finally, one of the most interesting phenomena, observed in the study of heat-resistant aromatic polymers, consists in the manifestation by the latter of appreciable deformations at low temperatures, down to the temperature of liquid helium, relaxation processes also developing at these temperatures.

All the above questions are dealt with in the present review.

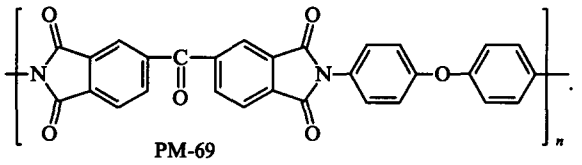
It is noteworthy that the available data on this field were reviewed in 1975 and 1981.[1,2] New heat-resistant aromatic polymers as well as new methods for the investigation of their relaxation properties have now appeared. The results of the study of the relaxation properties of these polymers using new methods constitute the main content of the review.

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II. The influence of the chemical structure of heat-resistant polymers on their mechanical workability estimated from relaxation measurements

There are several approaches to the estimation of the mechanical workability of polymeric materials. According to one of them,[3] a generalised characteristic which makes it possible to take into account the relaxation processes and the viscoelastic behaviour of polymers, is the temperature dependence of the critical stresses, which limits the region of the mechanical workability of the material. A method has been proposed for the estimation of the critical stresses in solid materials[3,4] the essential feature is as follows. A series of relaxation curves for different deformations ε_0 are plotted at a constant temperature. Fig. 1 presents as an example curves of this kind for the polyimide PM-69



PM-69

With increase in the deformation ε_0, the stress relaxation curves shift upwards to the region of higher stresses.[4] However, on further increase in ε_0, the stress relaxation is appreciably accelerated and the relaxation curves begin to shift towards lower stresses (Fig. 1, curve *7*). Under these conditions, an appreciable decrease in stress is observed over the entire temperature range for the polyimide only in the initial period of the relaxation process and the decrease in stress intensifies only as ε_0 approaches a value close to the yield strength.

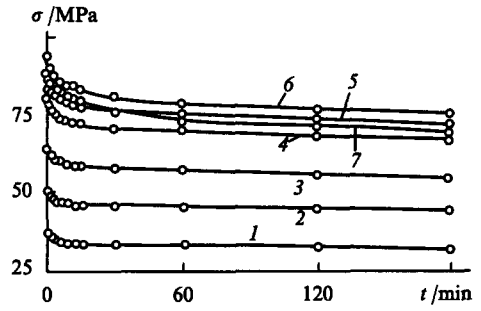


Figure 1. Stress relaxation for polyimide at 220 °C and different initial deformations (%): (*1*) 2; (*2*) 3; (*3*) 4; (*4*) 6; (*5*) 8; (*6*) 10; (*7*) 12.

After this isochronous dependences of the relaxing stress σ on ε_0 are plotted, each of which corresponds to a definite duration of the relaxation process. The isochronous relations as a rule have a maximum, the stress corresponding to the latter being referred to as critical and being designated by σ_c. By carrying out experiments at different temperatures T, one obtains isochronous relations between σ_c and T characterising the possibility of the retention in the material of the maximum stresses σ_c at a specified time t_r.

The isochronous relations for the relaxing stresses in the polyimide PM-69 at different temperatures and for a duration of the stress relaxation of 180 min are presented in Fig. 2. The maximum corresponding to σ_c arises for deformations ε_c ranging from 11.2% at 20 °C to 3.3% at 320 °C. This shows that the polyimide is capable of being used over a wide range of deformations without attaining mechanical softening. The isochronous relations for the polyimide have virtually no linear sections, which indicates the nonlinearity of the mechanical properties of the polyimide.

In order to estimate the mechanical workability of the polymeric material from the $\sigma-\varepsilon_0$ isochronous relations obtained

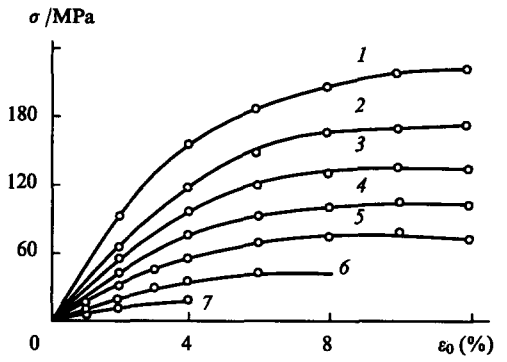
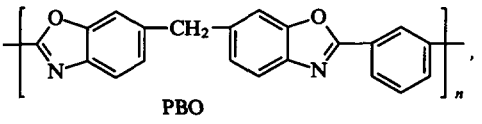


Figure 2. Isochronous variations of the relaxing stress for a process duration of 180 min at different temperatures (°C): (*1*) 20; (*2*) 70; (*3*) 120; (*4*) 170; (*5*) 220; (*6*) 270; (*7*) 320.

at different temperatures, the temperature dependences of the critical stresses are plotted.

The temperature dependences of the critical stresses for the polyimide PM-69 and polybenzoxazole (PBO)



PBO

are presented in Fig. 3. The region bounded by these curves and the coordinate axes defines the conditions under which the polymer may be used without softening and without being disrupted (the region of mechanical workability). Having compared the curves in Fig. 3, we may note that the critical stresses and temperatures for the polyimide are higher over the entire temperature range than for PBO.

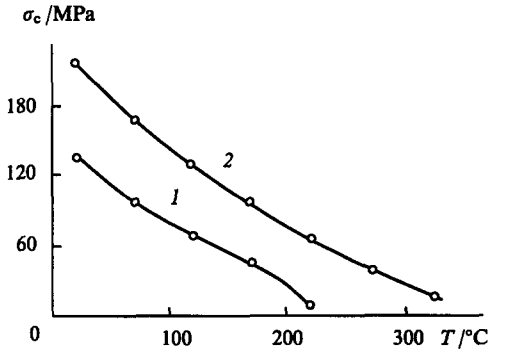


Figure 3. Temperature variations of the critical stresses in PBO (curve *1*) and polyimide (curve *2*) for a relaxation process duration of 180 min.

In the method for the estimation of mechanical workability,[3] the temperature dependences of the critical stresses, obtained for different durations of the relaxation process, are replotted as the dependences of the critical stress on the duration of relaxation t_r. The duration of the retention of the critical stress under stress relaxation conditions is a kinetic characteristic of the mechanical workability of the polymer.

The dependences of $\lg t_r$ on $\lg \sigma_c$ for PBO at different temperatures are presented in Fig. 4. Similar dependences have been obtained for the polyimide[4] and other heat-resistant polymers. In terms of logarithmic coordinates, the $\lg t_r - \lg \sigma_c$ relations for PBO are linear up to 170 °C, whereas at 220 °C a linear section is hardly observed. A linear $\lg t_r - \lg \sigma_c$ relation is as a rule characteristic of other heat-resistant polymers over a very wide temperature range.

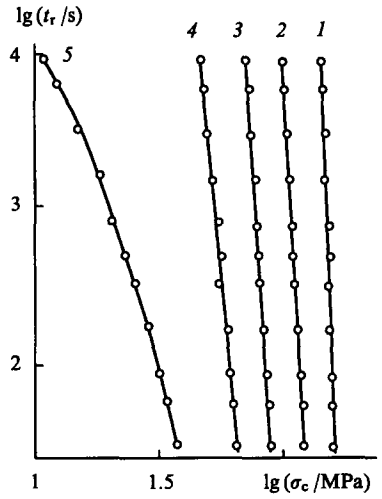


Figure 4. Dependence of the duration of the relaxation process t_r for PBO on the critical stresses at different temperatures (°C): (*1*) 20; (*2*) 70; (*3*) 120; (*4*) 170; (*5*) 220.

The slope of this relation, tan α, is a kinetic characteristic of the rate of the relaxation process along the linear sections of the $\lg t_r - \lg \sigma_c$ relations. The temperature dependences of tan α for PBO and PM-69, obtained from experiments[4] on the stress relaxation under compression conditions, are presented in Fig. 5. Evidently, the temperature dependences of tan α are not identical for all the polymers.

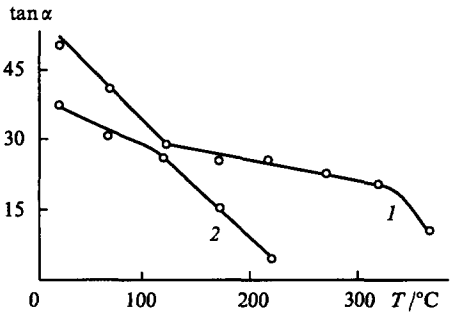


Figure 5. Temperature variation of tan α for the polyimide PM-69 (curve *1*) and PBO (curve *2*).

For PBO in the range of comparatively low temperatures, tan α diminishes somewhat, whilst above 120 °C it increases sharply. In the case of the polyimide, the temperature dependence of tan α is more pronounced below 120 °C, the rate of relaxation diminishing on further increase in temperature. This shows that in the middle of the temperature range of the glassy state at ~120 °C, a transition occurs in both polymers as a result of which the rate of the relaxation processes begins to change. It must be emphasised that the higher the absolute value of tan α the lower the extent to which the relaxation of critical stresses is manifested. For materials used in rigid constructions, the relaxation of critical stresses must be as small as possible. In terms of this feature, the polyimide is somewhat superior to PBO over the entire temperature range. It is noteworthy that the temperature variation of tan α for the polyimide consists not of two sections, as has been observed for other heat-resistant polymers, but of three. Along the first section in the region of comparatively low temperatures, tan α decreases fairly rapidly with increase in temperature; this is followed by a low-slope section, after which tan α diminishes, which indicates a sharp acceleration of the relaxation near the softening temperature. Such a dependence is apparently common to heat-resistant polymers; the middle section, where the relaxation of critical stresses is relatively insensitive to temperature, may be of greatest practical importance.

The equation

$$t_r = B\sigma_c^{-\tan\alpha}, \tag{1}$$

where B is a constant for the material, is used to describe the relations between t_r and σ_c.[3]

The nature of the relations between tan α and T changes at the temperature of the relaxation transition in the solid glassy state $T_{ss} \approx 120$ °C (Fig. 5) and may be described by the following equation:

$$\tan\alpha = \begin{cases} a + kT & \text{as } T \leqslant T_{ss} \\ a' + k'T & \text{as } T > T_{ss}, \end{cases} \tag{2}$$

where a, k, a', and k' are constants.

The nature of the temperature dependences of the parameter B for PBO and the polyimide also changes near 120 °C. This is reflected by the different values of the coefficients in the relations describing the temperature dependence of the parameter B.

$$B = \begin{cases} A_0 \exp\dfrac{U}{TR} & \text{as } T \leqslant T_{ss} \\ A_0' \exp\dfrac{U'}{TR} & \text{as } T > T_{ss}, \end{cases} \tag{3}$$

where A_0 and A'_0 are pre-exponential factors and U and U' are the activation energies for the relaxation process.

The coefficients in Eqns (2) and (3) are listed in Table 1. Knowing these parameters, it is possible to predict the mechanical behaviour of the polymers over a wide range of temperatures and stresses.

Table 1. The coefficients in Eqns (2) and (3).

Polymer	a	k	a'	k'	$\lg A_0$	$\lg A_0'$	U	U'
PBO	69	−0.109	112	−0.216	−33.9	−163.4	649	1619
PM-69	118	−0.226	45	−0.04	−100.4	−11.4	1264	565

Note. For all the values of the coefficients presented here, σ_c is expressed in MPa, the time t_r in s, and U in kJ mol^{-1} in calculations by Eqns (2) and (3).

It is noteworthy that the data presented above for PBO and the polyimide have been obtained[4] from measurements of the relaxation processes under the conditions of uniaxial compression. In another study,[5] such measurements were carried out under the conditions of uniaxial elongation. One of the differences in the mechanical behaviour of PBO under the conditions of uniaxial compression and elongation is that in the latter case the maxima in the isochronous relations are absent in the temperature range 22–100 °C. The stresses arising in the polymer with the maximum possible deformation are therefore adopted as the critical stresses σ_c (Fig. 6). The acceleration of the relaxation processes at higher temperatures (210–250 °C) for PBO induced the appearance on the isochronous curves of distinct maxima corresponding to the critical stresses.

We may note that it is possible to discover, from the isochronous relations on the one hand, the specified deformation ε_0 capable of maintaining the maximum possible stresses and, on the other, the duration of the retention of the stress of this magnitude in the polymer.

In order to determine the region of the mechanical workability of PBO under extension conditions, we shall consider the temperature dependence of the critical stresses for constant

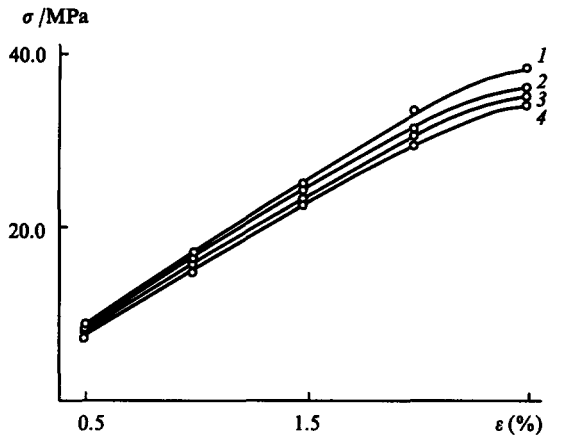


Figure 6. Isochronous dependence of the stress on deformation for PBO at 150 °C and different durations of the relaxation process (min): (*1*) 1.5 (*2*) 30; (*3*) 60; (*4*) 360.

durations of the relaxation process. If a straight line corresponding to the isothermal state is drawn in Fig. 7, it is possible to determine the function $t_r = f(\sigma_c)$. This relation makes it possible to establish the maximum temperature at which the polymer can withstand a stress of a particular magnitude over a specified time t_r.

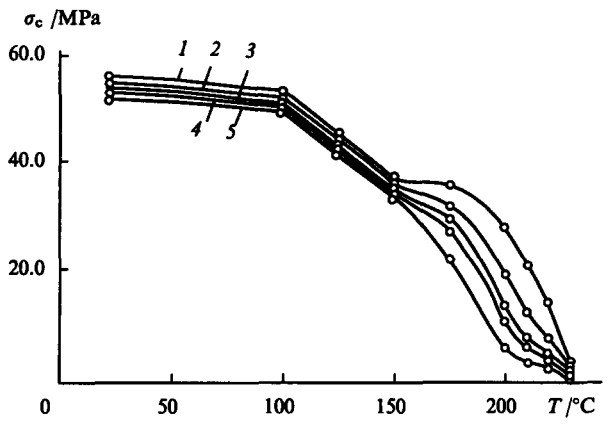


Figure 7. Temperature dependence of the critical stresses for PBO corresponding to different durations of the relaxation process (min): (*1*) 1.5; (*2*) 9; (*3*) 30; (*4*) 60; (*5*) 360.

An analytical relation between σ_c and t_r has been obtained [5] in the form

$$\lg t_r = A\left[1 - \exp\left(-B\sigma_c^{-C}\right)\right], \qquad (4)$$

where the parameters A, B, and C depend on temperature. These parameters are listed in Table 2.

Table 2. The parameters A, B, and C in Eqn (4) for PBO.

T/°C	A	B	C
150	4.39	24.1	9.65
175	4.47	5.91	2.63
200	4.56	4.25	2.08
220	5.03	3.24	1.83
230	4.51	1.77	1.41

Note. For all the coefficients quoted, the time t_r is expressed in s and σ in kg cm^{-2} in calculations by Eqn (4).

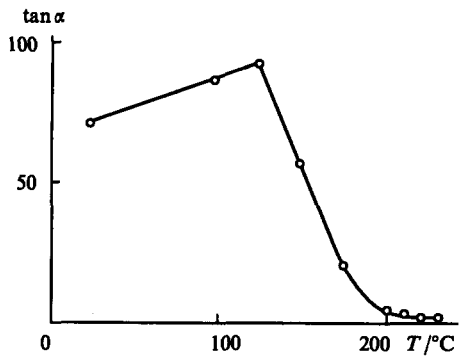
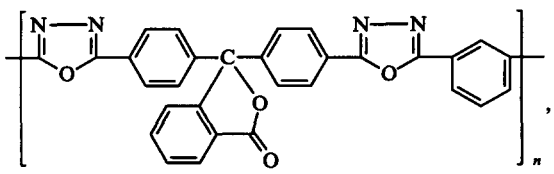


Figure 8. Temperature dependence of tan α for PBO.

The most important parameter, characterising the kinetics of the relaxation process, is the slope of the linear section of the $\lg t_r - \lg \sigma_c$ relation. For polybenzoxazole, the temperature dependence of the slope tan α has a characteristic form (Fig. 8); in the range 20–130 °C, tan α depends only slightly on temperature. Above 130 °C, it diminishes sharply, which indicates the acceleration of the relaxation processes. Such a dependence makes it possible to divide arbitrarily the temperature range of the glassy state into sections, along which the rates of the relaxation processes are different, a sharp acceleration of the relaxation processes being observed in the middle of the temperature range of the glassy state. In this respect, the given polymer behaves similarly to other heat-resistant polymers.

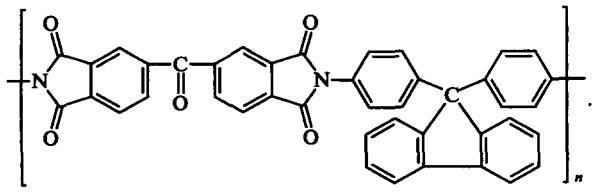
Such substates cannot be observed by the dynamic mechanical analysis, with the aid of which the temperature dependences of the components of the complex modulus of elasticity E^* and of the loss factor tan δ are determined at a particular frequency. The relaxation transitions, observed by the dynamic mechanical method, are manifested at temperatures other than those of the transitions observed from the temperature dependence of the parameters of the static stress relaxation. This is evidently associated with the nonlinearity of the mechanical behaviour, which is manifested for the deformations (several %) specified during tests on polymers under static stress relaxation conditions. We shall deal below with this important question whilst analysing the mechanical behaviour of other heat-resistant polymers.

The relaxation properties of two polymers have been studied in detail:[6] polyoxadiazole (POD)



POD

and the polyimide PI-2



PI-2

The temperature dependences of the critical stresses σ_c for these polymers are presented in Fig. 9. The difference in the viscoelastic behaviour of polyoxadiazole and the polyimide may be noted.

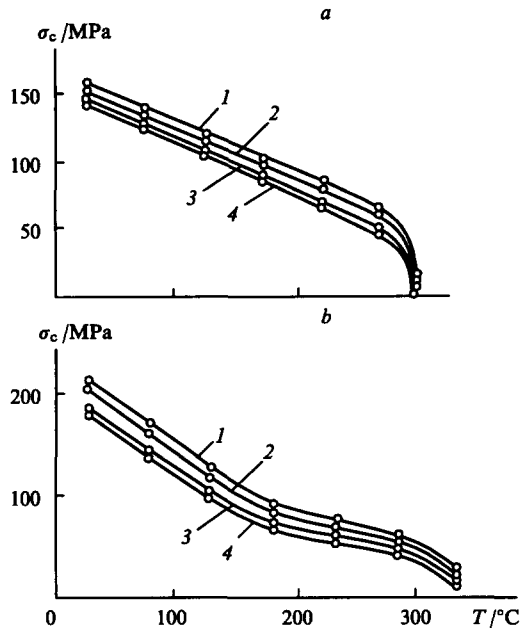


Figure 9. Temperature dependence of σ_c for PBO (*a*) and the polyimide PI-2 (*b*) corresponding to different durations of the relaxation process (min): (*1*) 0.5; (*2*) 1.5; (*3*) 15; (*4*) 60.

At high temperatures, the polyimide PI-2 is superior to POD as regards mechanical stresses which the polymer can withstand without softening for the same temperature and duration of the relaxation process. This is quite natural since PI-2 has a higher glass transition temperature (380 °C compared with 335 °C for POD). However, in the temperature range from 270 to 70 °C, polyoxadiazole is superior as regards critical stresses to PI-2 in the region of comparatively low temperatures.

The temperature dependences of tan α for the above polymers have been analysed by comparison with other polymers.[6] These relations are presented in Fig. 10. The temperature dependences of tan α for polymers of different classes are not the same. The following feature is characteristic of PDO, polyarylate, and a number of other polymers: within a certain range of comparatively low temperatures, tan α remains almost constant or actually increases, while in the centre of the temperature range, corresponding to the glassy state, it begins to decrease sharply. On further increase in temperature, the sharp decrease in tan α slows down and a smooth decrease is observed down to the glass transition temperature. This shows that, long before the glass

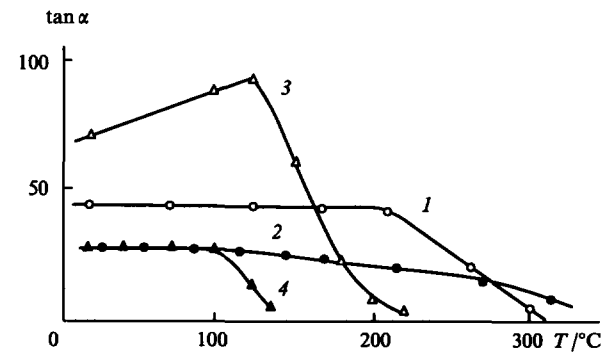


Figure 10. Temperature dependence of tan α for polyoxadiazole (*1*), polyimide (*2*), PBO (*3*), and the polycarbonate based on bisphenol A (*4*).

transition temperature is attained, a relaxation transition takes place as a result of which the relaxation processes in the solid glassy state are rapidly accelerated. In essence we are dealing with a solid–solid transition, the latter differing from the γ- and β-transitions, determined by the dynamic mechanical analysis from the temperature variation of the mechanical loss factor. We shall refer to the transition in the solid glassy state described above as the T_{ss} transition. We shall trace the manifestation of the T_{ss} transition for polymers of different structure (Fig. 10).

A weak temperature dependence of tan α over a wide temperature range is characteristic of polyoxadiazole and the polyimide PI-2. Thus tan α for polyoxadiazole hardly depends on temperature up to 220 °C and only then begins to decrease appreciably, particularly at 300 °C, i.e. near the glass transition temperature. This trend is even more marked for the polyimide; a sharp decrease in tan α is observed only at 320 °C, tan α retaining a virtually constant value over a wide temperature range. In terms of this feature, the above polymers have a significant advantage compared with PBO and polyarylate, because their relaxation properties hardly depend on temperature up to the glass transition temperature.

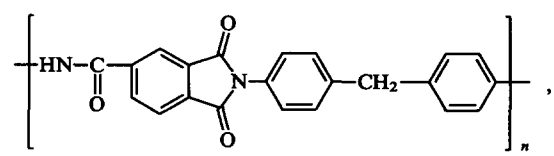
It was noted above that the absolute value of tan α characterises the rate of relaxation of the critical stresses, i.e. the workability of the polymer under extreme conditions. The higher the value of tan α, the less the extent to which the critical stresses relax. In this respect, PBO is significantly superior to POD and PI-2 in the temperature range 20–120 °C, but the disadvantage is lost as the temperature rises.

Thus heat-resistant aromatic polymers can be divided into two classes taking into account their relaxation properties. The first class includes polymers in which the stress relaxation within a certain range of comparatively low temperatures is manifested to only a slight extent even under extreme conditions (on exposure to critical stresses). However, in the middle of the temperature range of the glassy state observed, the relaxation stress increases sharply, which may lead to the loss of mechanical workability long before the attainment of the glass transition temperature. The second class includes polymers in which the stress relaxation is much more marked (this is indicated by the low values of tan α), but the parameters of the relaxation processes are stable up to the glass transition temperature even under extreme conditions. Such polymers are POD and PI-2.

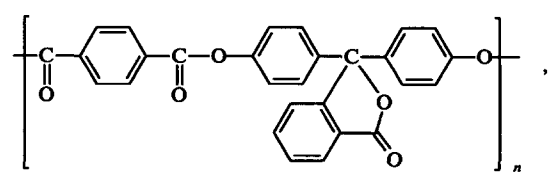
Consequently, if the conditions of use of the polymeric material requires it to retain the stresses established in it, then polymers of the first class must be chosen as such materials. However, these may be usable over a comparatively narrow temperature range. On the other hand, if the polymeric materials must exhibit distinct viscoelastic properties, polymers of the second class must be chosen.

The mechanical behaviour of the following polymers has been investigated:[7]

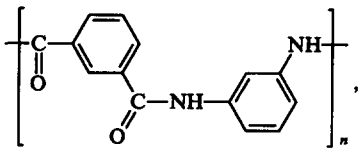
the polyamidoimide



the polyarylate



the aromatic polyamide (Phenylon S-4)



and POD.

In the investigation mentioned above, film specimens were studied under the conditions of uniaxial elongation. For all the heat-resistant systems investigated, a series of relaxation curves were obtained at a constant deformation ε_0 over a wide range of variation of the latter in the region of linear and nonlinear viscoelasticity (up to disruptive deformation at different temperatures over a wide range of temperatures of the glassy state of the polymers).

The critical stresses σ_c and their temperature variations were determined from these curves. Such a variation for the polyarylate is presented in Fig. 11, while the temperature variations of tan α

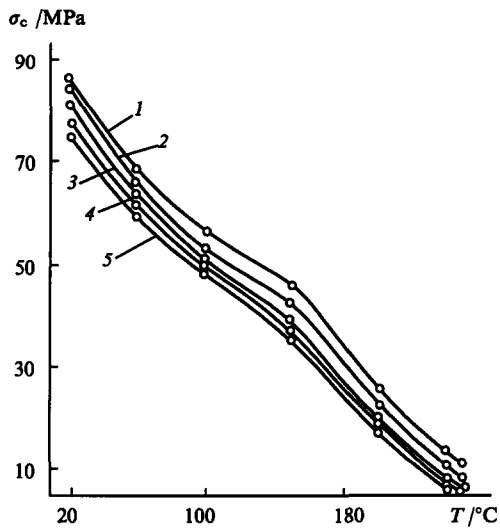


Figure 11. Temperature dependence of the critical stresses in polyarylate for different durations of the relaxation process (min): (*1*) 1; (*2*) 3; (*3*) 10; (*4*) 30; (*5*) 60.

for all four polymers are shown in Fig. 12. When account is taken of the temperature variations of tan α, it is possible to divide the temperature range of the glassy state for the systems investigated into sections where the rates of the relaxation processes are

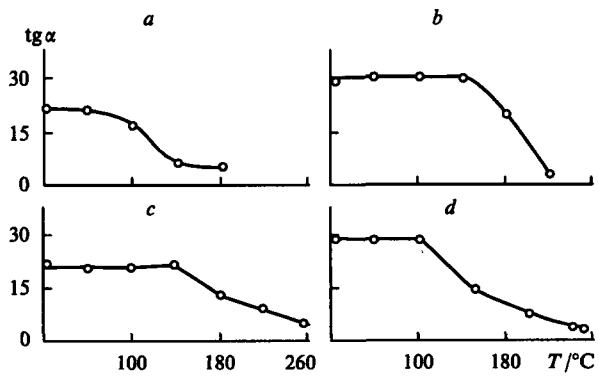


Figure 12. Temperature dependence of tan α for polyamidoimide (*a*), POD (*b*), Phenylon S-4 (*c*), and polyarylate (*d*).

different. For all the systems, a sharp acceleration of the relaxation processes is then observed in the middle of the temperature range of the glassy state.

An appreciable expansion of the temperature range in which the parameters of the relaxation behaviour are found to be independent of temperature is characteristic of polyoxadiazole and phenylon S-4 films: compared with polyarylate and polyamidoimide films, the temperature range in which tan α is constant increases up to 140 °C.

As mentioned above, the critical stress σ_c depends on the time t_r and relaxes in exactly the same way as the usual stresses σ. With increase in process time, the relaxation σ_c slows down and as $t_r \to \infty$ the relaxation becomes negligible. The corresponding values of σ_c will be referred to (conventionally) as equilibrium critical stresses and will be designated by $\sigma_{c\infty}$.

The temperature dependence of $\sigma_{c\infty}$ confines the region of stresses and temperatures in which there are no rapid relaxation processes, i.e. limits the region of the mechanical workability of the polymers under the conditions of stress relaxation. Fig. 13 presents the temperature variations of $\sigma_{c\infty}$ for four polymers. The influence of the structure of the polymers on their relaxation behaviour may be analysed on the basis of these relations. The first factor to which attention must be drawn is the marked difference between the critical stresses for all the systems in the range of low temperatures. Naturally, the higher the glass transition temperature of the polymer the higher are the temperatures at which finite equilibrium stresses are retained. However, an increase in the heat resistance of the polymer (in particular in the glass transition temperature) promotes a significant increase in the mechanical stresses capable of being retained in the polymeric material under the conditions of stress relaxation and at low temperatures (Fig. 13). At 22 °C the critical equilibrium stress is 53 MPa for the polyamidoimide, 70 MPa for POD, 75 MPa for the polyarylate, and 103 MPa for phenylon S-4.

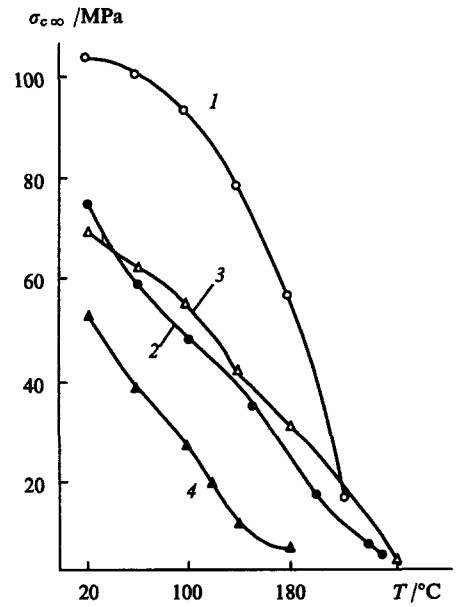


Figure 13. Temperature dependence of the equilibrium critical stresses in Phenylon S-4 (*1*), polyarylate (*2*), POD (*3*) and polyamidoimide (*4*).

Thus, if the polymeric material is required to retain its workability at high mechanical stresses, then preference must be given to heat-resistant aromatic polymers even in the region of low temperatures.

Extrapolation of the temperature variations of the equilibrium critical stresses to their zero value makes it possible to determine the glass transition temperature of an amorphous

polymer, which is smallest among all the glass transition temperatures determined at finite rates of application of mechanical and thermal influences. This temperature apparently constrains the actual temperature range in which the solid polymer may be used as a constructional material without breaking under the influence of stresses (up to critical stresses).

The crystallisation of polymers is known to increase significantly their strength and resistance to mechanical disruption. For example, phenylon, a crystalline aromatic polyamide, withstands much greater stresses in the temperature range 22–220 °C, without breaking or softening, compared with other heat-resistant systems, although their glass transition temperatures are higher than that of phenylon (Fig. 13). A sharp decrease in the equilibrium critical stresses has been observed for phenylon, although at comparatively low temperatures its mechanical workability is significantly greater. Thus, provided that it is possible, the crystallisation of heat-resistant systems is an effective means of expanding the region of workability towards higher stresses.

It was noted above that the plotting of the temperature variations of the critical stresses is one of the procedures for generalising the results of relaxation measurements. Another method for such generalisation involves the application of the principle of the temperature–time analogy (TTA). According to this principle, one plots master lg E_r–lg (t/a_T) relaxation curves, where a_T is the shift factor. Curves are plotted by displacing the lg E_r–lg t relaxation curves at different temperatures along the lg t axis. Fig. 14 presents the initial relaxation curves and the master curve for PBO,[5] as well as the temperature variation of the shift factor. The latter is a complex function which does not obey the Williams–Landell–Perry equation over the entire temperature range of the glassy state. Each substate has its own lg $a_T = f(T-T_0)$ relation.

The occurrence of transitions from one substate to another must be taken into account for objective estimation of the mechanical workability of the polymer under the conditions of stress relaxation. If the polymer is used as a constructional material at temperatures close to the glass transition temperature, it can be subjected to very small loads for a short time. However, when polymeric materials are used under the conditions of variable temperatures, where a transition from one substate to another, involving a sharp acceleration of relaxation processes, is observed, the mechanical workability may be lost at a temperature much lower than the glass transition temperature. Thus the region of stable mechanical workability of PBO is in the temperature range 22–125 °C, which corresponds to a substate in which the rate of relaxation processes is relatively insensitive to temperature.

Fig. 15 presents the initial relaxation curves and the master relaxation curve for PI-2.[6] The generalised curve for PI-2 is smooth and only a slight decrease in E_r with increase in lg t is observed.

The temperature variations of the shift factor lg a_T are well described by the power function

$$\lg a_T = C(T-T_0)^n, \tag{5}$$

where C is a constant for the material, T_0 the reduction temperature, and n the power exponent.

The possibility of describing the dependence of lg a_T on $T-T_0$ by a power function has been demonstrated also for other heat-resistant polymers.[8] The quantities C and n depend on the deformation ε. This indicates the nonlinearity of the mechanical behaviour of the polymers. The dependences of C and n on ε are as follows:

$$C = C_0 e^{\gamma\varepsilon}, \tag{6}$$

$$n = a\varepsilon + b, \tag{7}$$

where C_0, γ, a, and b are constants for the material.

The viscoelastic behaviour of a series of heat-resistant polymers under isothermal stress relaxation conditions was characterised above. The study of the behaviour of heat-resistant

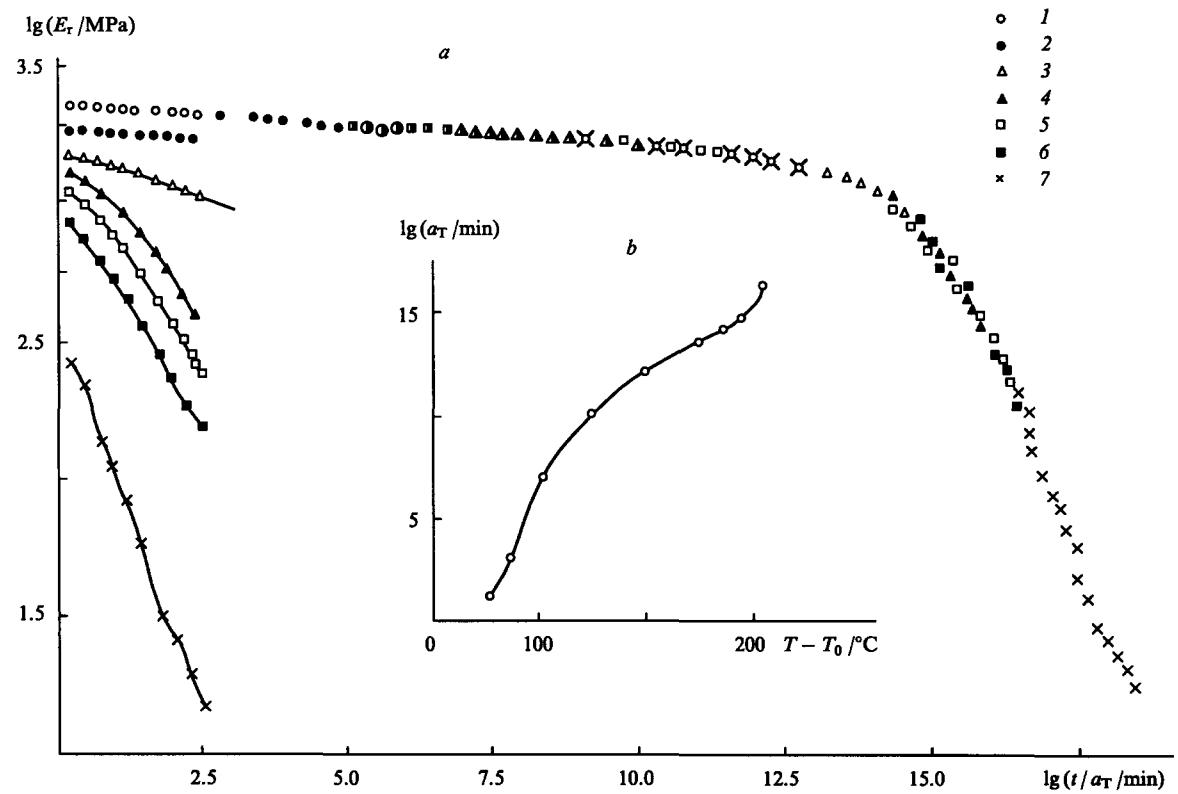


Figure 14. Master curve lg E_r — lg (t/a_T) for PBO (*a*) at ε_0 = 1.5% [test temperature (°C): (*1*) 22; (*2*) 125; (*3*) 175; (*4*) 200; (*5*) 210; (*6*) 220; (*7*) 230; adjusted to a temperature of 22 °C] and temperature dependence of the shift factor a_T (*b*).

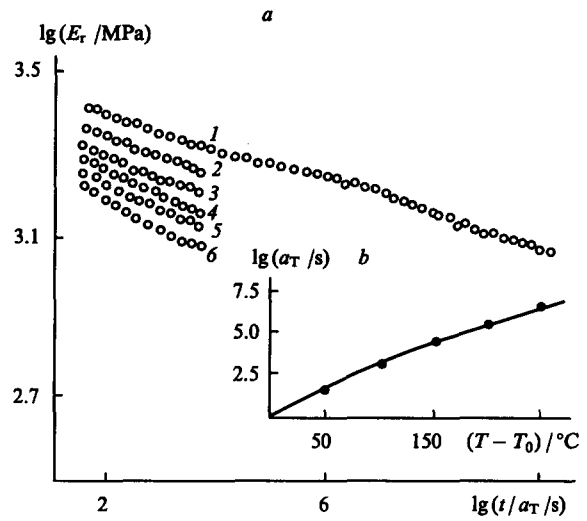


Figure 15. Initial and master relaxation curves (*a*) and temperature dependence of the shift factor (*b*) for the polyimide PI-2 at $\varepsilon_0 = 2.8\%$ and different temperatures (°C): (*1*) 20; (*2*) 70; (*3*) 120; (*4*) 170; (*5*) 220; (*6*) 270. Adjusted to a temperature of 20 °C.

polymers under creep conditions is also of fundamental interest, because in many cases such polymers are used under precisely such conditions. However, one should note that few investigations of this kind have been made.[9-12]

The characteristics of the viscoelastic behaviour of heat-resistant bulky polymers under isothermal creep conditions have been investigated in relation to PBO.[11] The experiments on creep over the entire range of temperatures and stresses possible for the given polymer made it possible to characterise fully the region of its mechanical workability and to compare it with the similar region under stress relaxation conditions.

Fig. 16 presents, as an example, creep curves obtained at a constant temperature and for different stresses. Evidently the consecutive increase in stress at a constant experimental temperature leads to a steady displacement of the creep curves into the region of greater deformations. The nonmonotonic (accelerated) increase in deformations and in the rate of creep with increase in stress has been observed in the region of high temperatures and stresses.

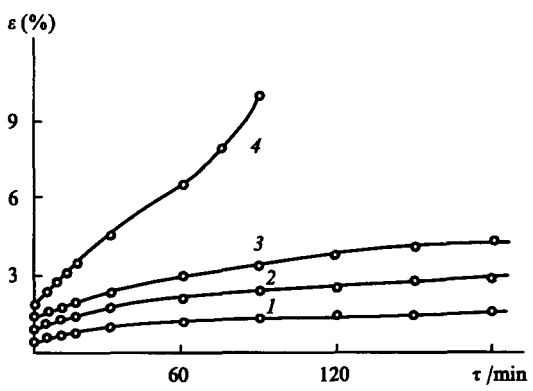


Figure 16. Creep curve at 210 °C for different stresses (MPA): (*1*) 10; (*2*) 15; (*3*) 20; (*4*) 25.

In order to generalise the experimental data on creep, two procedures are used. The first involves the plotting of isothermal dependences of the creep deformation on stress; the critical stresses σ_c, above which the acceleration of the creep process

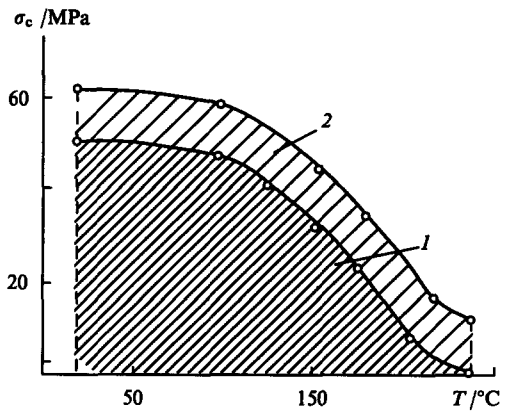
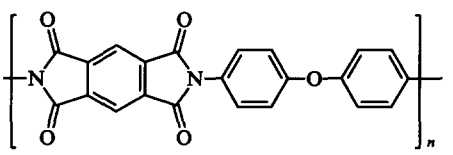


Figure 17. Regions of mechanical workability for PBO under isothermal stress relaxation (region *1*) and creep (region *2*) conditions.

begins, are determined from the bend in these relations. The $\sigma_c - T$ temperature relation yields a characteristic of the mechanical workability of a heat-resistant material under creep conditions. The regions of workability of PBO under creep and stress relaxation conditions may be compared in Fig. 17. Evidently, the curves confining the region of the workability of PBO are similar, which indicates that the processes underlying the viscoelastic behaviour are common to such cases.

The relaxation properties of a polyimide film based on pyromellitic dianhydride and bis(4-aminophenyl) ether have been investigated in just as much detail under creep conditions.[12]



Apart from the procedure described above, another method has also been used to generalise data on creep, which involves the plotting of master $I = \varepsilon/\sigma$ compliance curves using the principle of the temperature–time analogy. For this purpose, the $\lg I - \lg t$ relations at different temperatures but for constant stresses are shifted along the lg t axis by an amount lg a_T until they coincide with the master curve.

The master compliance curves for the polyimide film for different levels of stress are presented in Fig. 18. Evidently, the master compliance curves diverge appreciably, which indicates a nonlinear mechanism of their behaviour. A similar analysis has

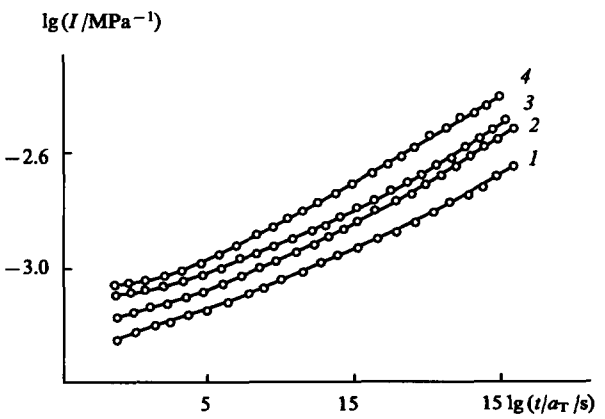
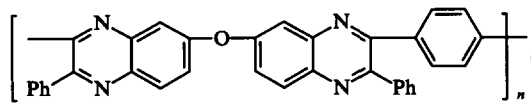


Figure 18. Master compliance curves for a polyimide film corresponding to different stresses (MPa): (*1*) 50; (*2*) 70; (*3*) 90; (*4*) 110.[12]

been carried out for PBO.[11] The relaxation properties of polyphenylquinoxoline (PPQ)

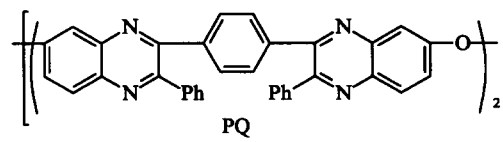


PPQ

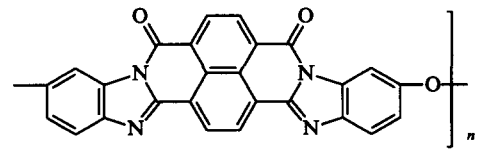
and PI-2 (the chemical structure of the polyimide is shown above) have been investigated as a function of the prehistory of their preparation from solutions.[13] Pure solvents and their mixtures with a small amount of precipitants were used as solvent media. The addition of precipitants (~2%–5% relative to the solvent) leads to the formation of films with an enhanced strength and a significantly greater deformability. When films are prepared from solution, it is possible to regulate the rate of stress relaxation and creep (Fig. 19). Master compliance curves have been constructed by the horizontal shift along the lg t axis of compliance curves obtained at a single temperature but for different stresses (Fig. 19*a*) and for a single stress but at different temperatures (Fig. 19*b*). In all cases, the compliance of the films obtained from a mixture of the solvent and a precipitant is greater than that of the films obtained from the solvent alone.

Having analysed the relation between three parameters — the intrinsic viscosity $[\eta]$, the Huggins constant K_H, and the second virial coefficient A_2 — Matevosyan et al.[13] concluded that, judging from the values of A_2 and K_H, the thermodynamic quality of the solvents is impaired after the addition of a small amount of the precipitant. This is quite reasonable. However, judging from the values of $[\eta]$, this property improves. Apparently, the addition of small amounts of the precipitant gives rise to a specific interaction between the polar groups of the polymer and the solvent molecules, which leads to a considerable anisometry of the molecules and to an increase in swelling. As a consequence of this, $[\eta]$ increases, while the mechanical properties of the film obtained from complex solvent media are appreciably superior to those of films obtained from the pure solvent. When large amounts of the precipitant are added, $[\eta]$ diminishes and the properties of the films are markedly impaired. This in fact accounts for the anomalous increase in $[\eta]$.

Thus, by changing the composition of the solvent medium in the preparation of heat-resistant aromatic polymer films from solutions involving the addition to the latter of a small amount of a precipitant, it is possible to regulate within wide limits the relaxation as well as the strength and deformation properties of the films. This is also indicated by the data obtained in a study[14] of the strength and relaxation properties of films based on the copolymer of phenylquinoxaline (PQ) and naphthoylenebenzimidazole (NBI) having a regular structure.



PQ



NBI

These systems are characterised by a regular alternation of various heterocyclic fragments, which is in fact responsible for their improved solubility in organic solvents compared with copolymers having an irregular structure and obtained by the interaction of various bis(*o*-phenylenediamines) with 1,4-bis-(phenylglyoxalyl)benzene and the dianhydride of naphthalene-1,4,5,8-tetracarboxylic acid.[15]

The high viscous characteristics of the copolymers based on PQ-containing bis(*o*-phenylenediamines) made it possible to obtain films from them. These films have been prepared[14] from two solvent media: *m*-cresol and a 3:1 tetrachloroethane (TCE)–phenol mixture.

The initial and final relaxing stresses † for films obtained from the TCE phenol mixture are lower at all temperatures than for films obtained from *m*-cresol (Fig. 20). A significant difference is observed at ~150 °C, where the relaxation processes occur most vigorously. On the one hand, this confirms the existence of a pronounced relaxation transition in the range of temperatures far from the glass transition temperature. On the other hand, this indicates a significant influence of the prehistory of the specimens prepared from the same polymer on their relaxation behaviour.

A similar result has been observed in the analysis of creep data. The specimen prepared from the tetrachloroethane–phenol

† The initial and final relaxing stresses are respectively the stress at the moment of the completion of the 'instantaneous' imposition of the deformation and the stress developing over a finite period of observation.

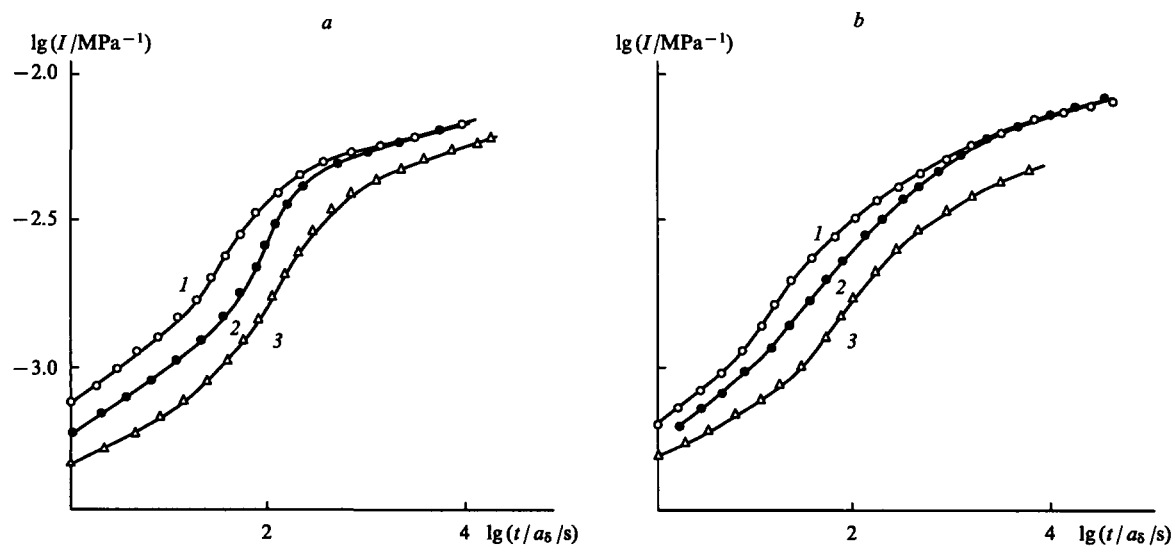


Figure 19. Master compliance curves for polyphenylquinoxaline corresponding to different stresses (*a*) and temperatures (*b*). The films were obtained from chloroform with added 5% of ethanol (*1*), 2% of toluene (*2*), and pure chloroform (*3*).

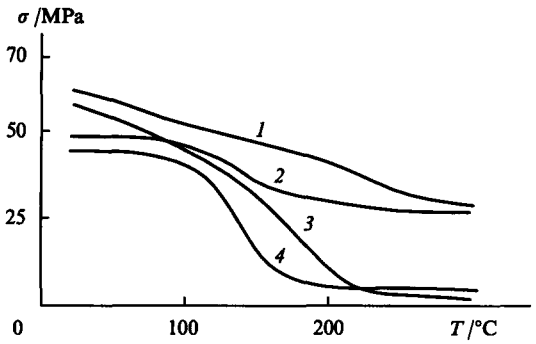


Figure 20. Temperature dependences of the initial (curves *1* and *2*) and final (curves *3* and *4*) relaxing stresses for copolymer films obtained from *m*-cresol (curves *1* and *3*) and from the TCE : phenol = 1 : 3 mixture (curves *2* and *4*). Initial deformation 3%.

mixture has a significantly greater creep deformation at various stresses than the specimen obtained from *m*-cresol. In order to account for these data, the quality of the solvent medium was examined in relation to the polymer. The quality of the solvent may be estimated with the aid of a new solubility criterion introduced by the present author and his coworkers.[16,17] It has the form

$$\mu \leqslant 1.374\Phi\left(\Phi - \sqrt{\Phi^2 - 1 + a}\right) = \beta, \qquad (8)$$

where $\mu = \delta_p^2/\delta_s^2$ (δ_p and δ_s are the solubility parameters of the polymer and the solvent),

$$\Phi = \frac{4(V_p V_s)^{1/3}}{(V_p^{1/3} + V_s^{1/3})^2}, \qquad (9)$$

(V_p and V_s are the molar volumes of the repeat unit of the polymer and the solvent respectively), and $a = \gamma_{ps}/\gamma_s$ (γ_{ps} is the interfacial tension at the polymer–solvent boundary and γ_s is the surface tension of the solvent).

The results obtained[14] are presented in Table 3, from which it is seen that in the case of PPQ the quantity μ is much smaller than β for both solvents. Consequently PPQ should dissolve readily in both solvents (which has in fact been observed experimentally), while the presence of PQ units in the copolymer should lead to the appearance or a significant improvement of the solubility when PQ rings are combined with other heterocycles.

Table 3. Solubility criteria for different polymer : solvent pairs.

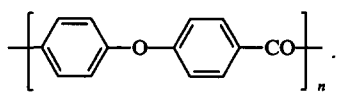
Solvent	μ	β
PPQ polymer unit		
m-Cresol	0.851	1.100
TCE : phenol	0.897	1.082
PNBI polymer unit		
m-Cresol	0.980	1.080
TCE : phenol	1.080	1.070

On the other hand, μ for polynaphthoylenebenzimidazole (PNBI) either differs very little from β being smaller, or is greater than the latter; this means that the polymer dissolves very sparingly or is insoluble, which has also been observed experimentally. In the case of a heterounit polymer containing PQ and NBI units, solubility should be observed for different ratios of the PQ and NBI units.

As regards the influence of the quality of the solvent medium, it can be seen from Table 3 that the inequality of the criteria (8) is enhanced on passing from the TCE–phenol mixture to *m*-cresol. Consequently, on passing from *m*-cresol to the TCE–phenol mixture, the quality of the solvent is somewhat impaired. According to the results of Matevosyan et al.[13], this should lead to an increase in deformability both under the conditions of continuous uniaxial extension and under creep conditions. In the measurement of the stress relaxation for films obtained from solvents of a poorer thermodynamic quality, the relaxation processes should be more far-reaching, and, other conditions being equal, the decrease in the relaxing stresses should be more pronounced, which has been confirmed experimentally.[14]

The results of relaxation measurements carried out under isothermal conditions were examined above. Such experiments require a very long time. However, the method for the determination of the regions of mechanical workability described by the present author[3] may prove useful in characterising the mechanical behaviour of polymers over a wide range of temperature and stresses.

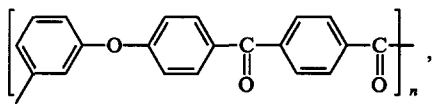
The essential feature of the method consists in the measurement of the stresses which arise in the specimen during its thermal expansion whilst retaining a constant deformation imposed initially under the conditions of uniaxial compression. With increase in temperature, the stresses in the specimen increase as a consequence of thermal expansion, and then, as a result of its softening under load, they begin to diminish and become zero on complete softening of the specimen. The temperature dependences of the stress for polyketone **A** are presented in Fig. 21.[18]



A

The geometrical locus of the maxima on these curves together with the coordinate axes confine the region of stresses and temperatures in which the solid polymeric material is not disrupted and does not soften under the specified conditions of the tests.

Apart from polyketone **A**, polyketones **B** and **C** having the following structure have also been investigated:[18]



B

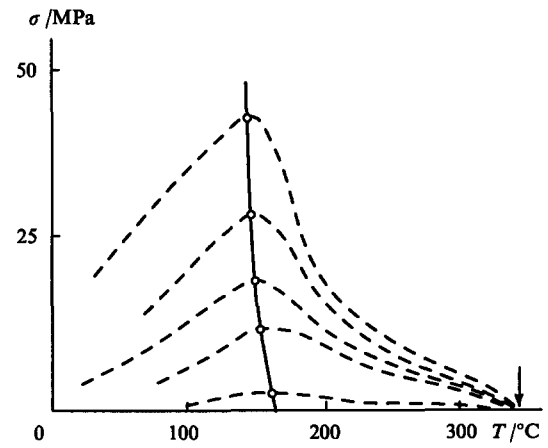
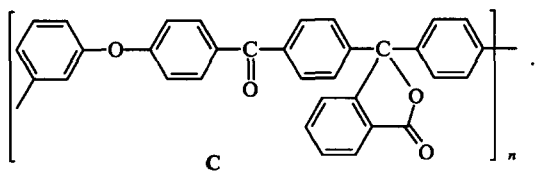


Figure 21. Region of the workability of polyketone **A**, the arrow indicates the softening temperature, which is close to the melting point.



C

We shall compare the heat resistances of all three polyketone specimens. For this purpose, we shall combine on one figure the curves confining the regions of the workability of these polymers (Fig. 22). It is seen from the figure that specimens **A** and **B** have virtually identical heat resistances and are significantly inferior to specimen **C** in this respect. All this is valid for the region of comparatively large mechanical stresses. As regards the region of small stresses at high temperatures, preference must be given to the partly crystalline specimens **A** and **B**. This is confirmed by the data presented in Fig. 21. For polyketone **A**, the mechanical stresses appreciably diminish after passing through a maximum, but, with increase in temperature, this decrease slows down and the curves form a 'loop'. The stresses relax very slowly and become zero at a high temperature, close to the melting point. Such relaxation behaviour is characteristic of semi-crystalline polymers.

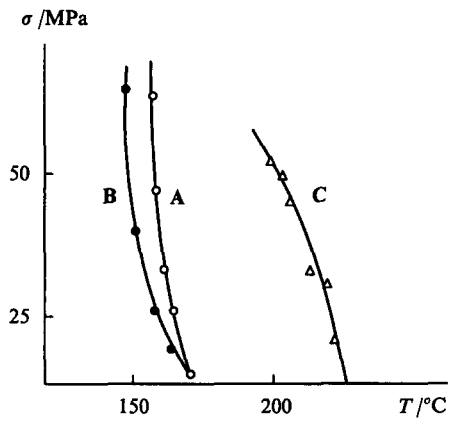
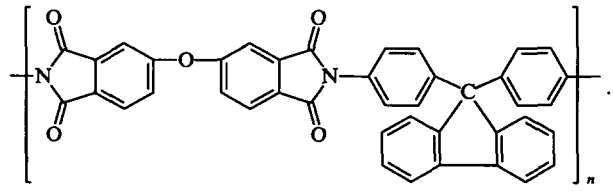


Figure 22. Curves confining the region of the mechanical workability of polyketones **A**, **B**, and **C**.

Thus the crystallisation of aromatic polyketones does not lead to an increase in heat resistance in the region of large mechanical stresses, where the softening of the specimen is associated with the properties of the amorphous component. However, crystallisation increases significantly the temperature at which the specimen softens fully (in the region of low mechanical stresses or in their complete absence).

The influence of the degree of conversion into a monolithic form on the relaxation properties of an aromatic polyimide having the following chemical structure has been studied:[19]



The need for such investigations arises because the processing of aromatic heat-resistant polymers by traditional methods (for example by hot pressing) does not always lead to the formation of monolithic specimens, although it is known that even in the nonmonolithic form heat-resistant polymers are capable of withstanding large mechanical loads at elevated temperatures. The following question arises in this connection: to what extent do the mechanical properties of truly monolithic specimens differ from those of nonmonolithic specimens comprising materials pressed at high temperatures and pressures and consisting of individual grains of the initial powder?

Analysis of the relaxation behaviour of the polyimide[19] showed that the master relaxation curves for specimens with different degrees of conversion into a monolithic form are disposed fairly close to one another. Consequently nonmonolithic specimens of this heat-resistant specimen have good mechanical characteristics close to those for the truly monolithic material.

The mechanical behaviour of heat-resistant aromatic polymers at low temperatures is of special interest. In the early studies,[20-24] it was already noted that the stability of the heat-resistant polymers is fairly high at low temperatures. A high deformability even at −270 °C is characteristic of these polymers.[22] Heat-resistant polymers are therefore of significant interest as cold-resistant materials for use in structures associated with cryogenic techniques. However, the characteristic features of the relaxation mechanical behaviour of such polymers at low temperatures have been investigated only recently (one should note that Perepechko and Voloshilov[23,24] carried out a dynamic mechanical analysis of the polymers).

The stress relaxation and creep processes have been studied in detail for PBO and POD.[25] In the study of the stress relaxation and creep in PBO and POD, it was established that the relaxation processes in such polymers are pronounced in the region of low temperatures. Analysis of experimental data on the stress relaxation showed that, over the entire temperature range employed (from 20 to −145 °C), a shift of the relaxation curves into the region of higher stresses is observed during the growth of deformation. Under these conditions, the increase in deformation is accompanied by an appreciable acceleration of the relaxation in the initial period. Fig. 23 presents as an example the relaxation curves for PBO at −75 °C and for different initial deformations. A decrease in temperature to −145 °C leads to a significant retardation of the relaxation processes.

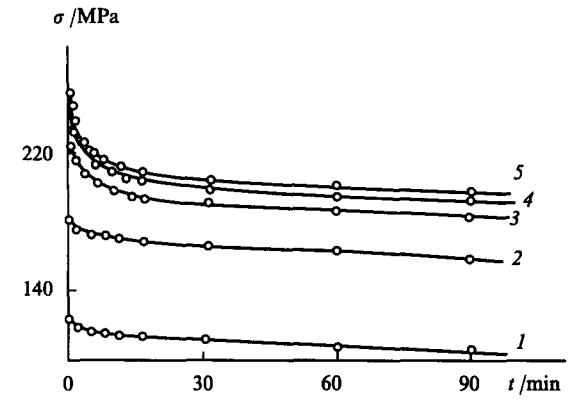


Figure 23. Stress relaxation curves for PBO at −75 °C and different initial deformations (%): (*1*) 4; (*2*) 6; (*3*) 8; (*4*) 9; (*5*) 10.

A similar pattern in the variation of the relaxation processes is observed in the study of the behaviour of the above polymers under creep conditions. As an example, Fig. 24 presents creep curves for POD at −120 °C and for different initial stresses. Evidently, an increase in the applied stress at a constant experimental temperature leads to a steady displacement of the creep curves towards greater deformations. Under these conditions, more marked relaxation processes are observed following an increase in stress. With decrease in temperature, the creep weakens appreciably, although at −50 and −75 °C it is manifested quite strikingly.

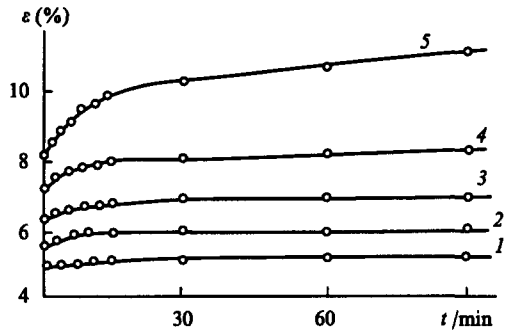


Figure 24. Creep curves for POD at −120 °C and different initial stresses (MPa): (*1*) 120; (*2*) 180; (*3*) 220; (*4*) 260; (*5*) 290.

It was noted above that, when the temperature is varied in the region of the glassy state, a change in the rate of relaxation processes and the appearance of relaxation transitions are characteristic of heat-resistant polymers. Such transitions have been discovered for heat-resistant polymers in the study of their relaxation properties in the region of raised temperatures. We shall now consider the relaxation transitions at low temperatures.

The temperature dependence of the parameter tan α for PBO is presented in Fig. 25. Evidently, this relation consists of two sections. In the range from 293 to 203 K, the quantity tan α changes only slightly. With decrease in temperature in the range from 203 to 128 K, it begins to increase sharply. The greater the value of tan α, the smaller the extent to which the relaxation of stress is manifested. A decrease in temperature leads to a significant alteration of the segmental and group mobilities of macromolecules, which is ultimately reflected in the rate of relaxation.

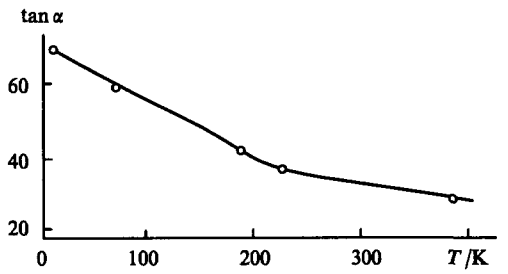


Figure 25. Temperature dependence of tan α for PBO; deformation 8%.

Thus the temperature dependence of tan α for PBO makes it possible to observe a relaxation transition at 203 K in the low-temperature region and to identify subregions with different rates of the relaxation processes.

In the range of positive temperatures, a distinct T_{ss} transition is observed for PBO within the glassy state, so that one may conclude that the appearance of several T_{ss} transitions is characteristic of heat-resistant polymers. It must be emphasised yet again that one is dealing with transitions discovered under the conditions of static relaxation measurements, where the degree of deformation is greater by many orders of magnitude than under the conditions of dynamic mechanical analysis, i.e. when the nonlinearity of the mechanical behaviour plays a significant role.

The experiments described above, involving the study of the mechanical behaviour of heat-resistant polymers, were carried out in the range of temperatures from room temperature to the temperature of liquid nitrogen. Subsequently, the temperature range was extended[26] down to the temperature of liquid helium. PBO and PI-2 were studied.

The stress-strain curves for PBO and the polyimide PI-2 at different temperatures are presented in Fig. 26. The results showed that the above heat-resistant polymers do not undergo brittle rupture down to 77.3 K. The stress-strain curves have fluidity plateaus, which indicates mechanical softening. The strength properties increase linearly by a factor of ~2–2.5 on cooling from 300 to 77.3 K.

A quasi-brittle rupture accompanied by a sharp sound, takes place at 4.2 K. In this case, the specimens are deformed up to ε = 8%–10% for PBO and ε = 6% for the polyimide PI-2.

Above 77.3 K, the polymeric specimens did not lose their integrity on deformation up to 25%. At 77.3 K (in liquid nitrogen), the specimens are deformed further up to ε ≈ 20% beyond the fluidity plateau and then disintegrate, the rupture being accompanied by a sharp sound.

In order to obtain a more objective deformation and rupture picture for heat-resistant polymers at low temperatures, tests have been carried out at different rates of deformation.[26] The rate of deformation has little effect on the strength properties of PBO and the polyimide at low temperatures (the changes amount to 10%–20%). The results indicate an anomalous influence of the rate of compression on the strength characteristics of PBO. Thus, on raising the rate of compression from 0.1 to 1 mm min^{-1}, the strength does not increase, as is usually observed, but actually decreases. This is characteristic of all test temperatures. Such an effect can be accounted for only by the different nature of the structural transformations occurring as the rate of compression is changed.

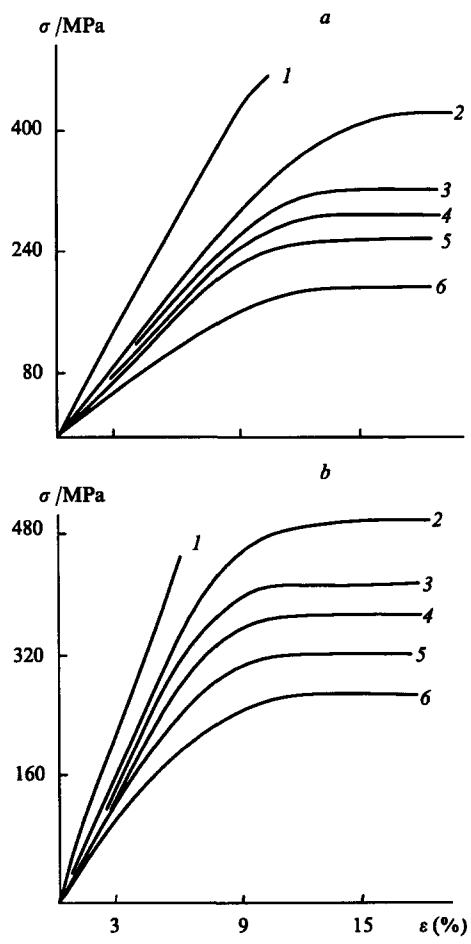
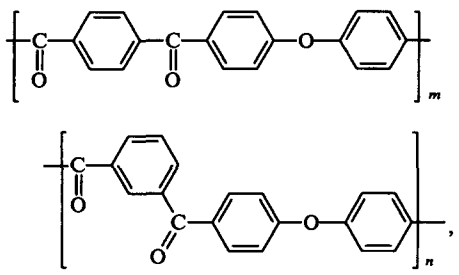


Figure 26. Uniaxial compression curves for PBO (*a*) and the polyimide PI-2 (*b*) at different temperatures (K): (*1*) 4.2; (*2*) 77.3; (*3*) 103; (*4*) 150; (*5*) 200; (*6*) 300.

Table 4. The yield stresses for a series of polymers during thermocycling.

Polymer	Temperature range of thermocycling /K	σ_y (MPa) for different numbers of thermocycles												
		0	10	50	100	200	300	400	500	600	700	800	900	1000
MK-M-3	(77–398)±5	88	85	85	85	86	88	87	87	–	–	–	–	–
PBO	(77–473)±5	199	204	200	200	201	200	192	188	–	–	–	–	–
PI-2	(77–473)±5	270	272	271	272	274	273	267	268	263	280	270	268	269
F-4	(77–473)±5	17	15.5	15	16.5	15.4	12.9			–	–	–	–	–
PKIT	(77–423)±5	191	210	174	189	181	181	192	199	–	–	–	–	–

Another procedure used in the tests for cold resistance consists in the thermocycling of the polymer materials and the study of the influence of such thermocycling on their mechanical properties. This procedure has been used[27] for a number of polymers: the polycarbonate MK-M-3,[28] the fluoroplastic F-4,‡ the polyimide PI-2, PBO, and the polyketone PKIT having the following chemical structure:



$m:n = 0.7:0.3$.

The resistance of the test polymers to the effects of repeated thermocycles was determined by analysing the state of the PI-2, PBO, and F-4 specimens after heating to 473 ± 5 K, the PK-M-3 specimen after heating to 398 ± 5 K, and the PKIT specimen after heating to 423 K and subsequent rapid cooling with liquid nitrogen.

After a definite number of thermocycles, some of the specimens were used to obtain stress-strain curves at room temperature. The average values of the yield stress σ_y determined from them as a function of the number of thermocycles are presented in Table 4. After 500 thermocycles, the mechanical properties of PK-M-3 hardly changed.

For PBO, the influence of thermocycling up to 300 cycles is also insignificant. On further use, a slight impairment of its properties begins and after the attainment of 500 cycles σ_y diminishes by 5%.

The mechanical properties of the polyimide PI-2 did not charge on thermocycling and the polyketone PKIT also showed a high resistance to thermocycling.

In contrast to heat-resistant aromatic polymers, the fluoroplastic (fluoroplast) F-4 exhibited an extremely low resistance to thermocycling. Its yield stress diminishes after only 10 cycles. After 100 cycles, the cracking and disintegration of the specimens begin. It may be that this is associated with the transformation of the crystal structure of the fluoroplastic as a result of cyclic temperature changes.

III. Stress relaxation and creep curves

In the early studies of the stress relaxation and creep processes for heat-resistant aromatic polymers, the Kohlrausch equation

$$\sigma(t) = \sigma_0 \exp\left(-\frac{t}{\tau_r}\right)^k + \sigma_\infty , \tag{10}$$

was widely used. Here $\sigma(t)$ is the current (relaxing) stress, σ_0 the initial stress which develops at the moment of the completion of the 'instantaneous' creation of the deformation, τ_r the relaxation time, and σ_∞ the 'equilibrium' stress.

The memory function, leading to this equation, has the form[29]

$$f(t-\tau) = \frac{E_1}{\tau_r} k \left(\frac{t-\tau}{\tau_r}\right)^{k-1} \exp\left[\left(-\frac{t-\tau}{\tau_r}\right)^k\right], \tag{11}$$

where E_1 is the modulus of elasticity, t the finite duration of relaxation time, τ the current relaxation time, and k a constant for the material.

A similar memory function for the description of the creep process has been used by Bronskii:[30]

$$\varphi(t-\tau) = I_1 \frac{m}{\theta}\left(\frac{t-\tau}{\theta}\right)^{m-1} \exp\left[\left(-\frac{t-\tau}{\theta}\right)^m\right], \tag{12}$$

where I_1 and m are constants for the material and θ is the retardation time. When this memory function is substituted in the Boltzmann equation, we obtain the following relation for the description of creep under the conditions $\sigma = \sigma_0 = \text{const}$:

$$\varepsilon(t) = \sigma_0 I_\infty \left\{1 - \exp\left[\left(\frac{t}{\theta}\right)^m\right]\right\}. \tag{13}$$

Here $I_\infty = I + I_1$ is the equilibrium compliance, I the 'instantaneous' compliance, and σ_0 the constant stress for which creep is measured.

Eqn (13) describes satisfactorily the creep of polymeric materials. The creep hardly changes after the specimen has been exposed for some time to a constant stress. However, in many instances the so called steady creep section is observed on the creep curves, but the deformation increases with time approximately in accordance with a linear law. To a first approximation, this can be taken into account by formulating the creep memory function in the form

$$\varphi(t-\tau) = I_1 \frac{m}{\theta}\left(\frac{t-\tau}{\theta}\right)^{m-1} \exp\left[\left(-\frac{t-\tau}{\theta}\right)^m\right] + \frac{1}{\eta}, \tag{14}$$

where η is the viscosity of the system.

Having substituted Eqn (14) in the Boltzmann equation, we obtain

$$\varepsilon(t) = \sigma_0 I_\infty \left\{1 - \exp\left[-\left(\frac{t}{\theta}\right)^m\right]\right\} + \frac{\sigma_0}{\eta} t, \tag{15}$$

where $\sigma_0 I_\infty = \varepsilon_0$ is the equilibrium deformation.

The most complex question in fitting the Kohlrausch equation to the stress relaxation and creep curves concerns the reliability of the estimation of the parameters of this equation. A detailed description of the procedure for the determination of the parameters of Eqn (15) may be found in the communication of Askadskii et al.[31]

Creep curves for a series of linear and network solid polymer systems based on heat-resistant polymers have been calculated. The parameters of Eqn (15) for such systems are listed in Table 5.

‡ Equivalent to Teflon (Translator).

Table 5. Parameters of Eqn (15) for a series of linear and network solid polymer systems.

No.	System	ε_0 (%)	θ /min	m	$10^{-14}\eta$ /P	ξ [a]
1	Polyarylate F-2	15.42	1.89	0.37	8.94	0.85
2	Polyphenyl-quinoxaline	13.03	16.81	0.59	6.89	0.62
3	Composition based on 100 parts of F-2 and 50 parts of the epoxy polymer UP-612	8.59	0.097	0.096	6.14	0.16
4	Polyarylate F-2 preheated at 200 °C for 20 h	6.34	3.89	0.093	1.97	0.046
5	Composition based on 100 parts of F-2 and 10 parts of the epoxy polymer UP-612	4.98	0.0084	0.0036	3.77	0.063

[a] The sum of squares of the differences between the calculated and experimental quantities.

The calculated points, obtained with the aid of Eqn (15) and the data in Table 5, fit satisfactorily on the experimental creep curves for different polymers (Fig. 27). The sum of squares of the differences between the calculated and experimental values is in the range from 0.046 to 0.85 (Table 5).

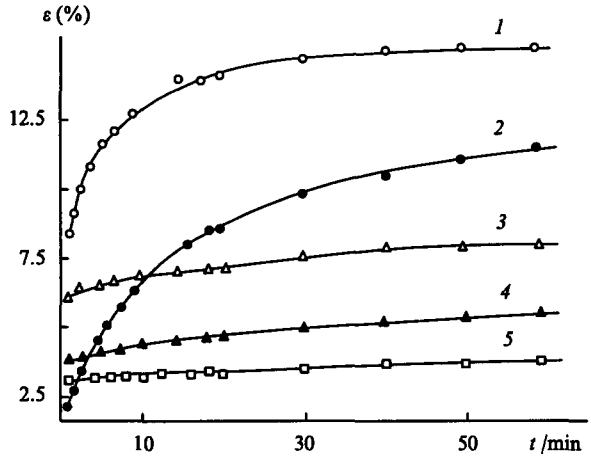


Figure 27. Creep curves for linear and network systems determined for stresses of 400 MPa (curves *1* and *4*) 200 MPa (curve *2*), 1200 MPa (curve *3*), and 600 MPa (curve *5*) at 150 °C (curves *1* and *4*), 240 °C (curve *2*), 20 °C (curve *3*), and 90 °C (curve *5*).

In further studies of the relaxation properties of heat-resistant polymers, the stress relaxation and creep curves were fitted using new memory functions, proposed by the present author.[32] These memory functions are based on the consideration of the change in the entropy of the specimen during stress relaxation. The first memory function was obtained by analysing the kinetics of the interaction of the relaxators and the transition of the 'product' of this interaction to a nonrelaxing material. The term 'relaxator' is applied to various kinetic units, including individual groups of atoms (links, segments), which interact with one another within the limits of their kinetic volumes; undergoing a change in structure during the processes, they are converted into nonrelaxing materials. Here we are dealing not with a chemical interaction but with an interaction of a physical kind. For example, the formation of microblocks — regions with the densest packing playing the role of physical network nodes — may be assigned to such interactions. During stress relaxation, the microblocks may break down and appear at other sites, which leads ultimately to a decrease in the relaxing stresses. One can consider also other instances of interactions of this kind. For example, the interaction of microdefects within the limits of individual microcavities may lead to their fusion in the course of stress relaxation and to the removal of the stress concentration. Thus, the kinetic units may be of different nature. This leads to the appearance of subsystems which may interact weakly with one another. However, one can apparently identify isotypical units which determine the course of the relaxation process.

If the relaxators considered are isotypical, the memory function assumes the form [32]

$$T_1(\tau) = -\frac{S_0}{k_B m_1}\{[(\alpha-\alpha_0)\ln(\alpha-\alpha_0)+ \\ +(1-\alpha+\alpha_0)\ln(1-\alpha+\alpha_0)]^{-1}-0.5\}, \quad (16)$$

where S_0 is the initial entropy of the system (specimen), k_B the Boltzmann constant, $m_1 = m_1^* \int_0^\infty T_1^*(\tau)d\tau$ [here m_1^* is the total number of microheterogeneities in the specimen and $T_1^*(\tau)$ is the time-dependent factor of the memory function, enclosed in braces, in Eqn (19) (see below)], α is the fraction of relaxators relative to the total number of kinetic units in the system, and α_0 the fraction of relaxators which have reacted by the time when the creation of a constant deformation has been completed (the quantity α_0 was assumed [32] to be constant for all the materials and equal to 10^{-10}).

The quantity α depends on time and hence the entropy production takes place during the relaxation process i.e. the entropy increases as a consequence of the mixing of the relaxators and nonrelaxators.

Two types of memory functions have been considered.[32] As noted above, the first is based on the allowance for the kinetics of the interaction of the relaxators, which is described by an irreversible nth order reaction. In this case, the time variation of α assumes the form

$$\alpha(\tau) = \frac{1}{(1+k^*\tau/\beta)^\beta}, \quad (17)$$

where $k^* = kc_0^{n-1}$, k is the rate constant for the interaction of the relaxators, c_0 their initial concentration, n the reaction order, and $\beta = (n-1)^{-1}$.

The memory function (16) has a physical significance only when $\alpha(\tau) \geqslant 0.5$. Here one may note that, if we have a system comprising heterotypical kinetic units where each type introduces a perceptible contribution to the relaxation process, then we have not one but several interaction constants. In this case, the function (16) becomes complicated and this leads formally to the appearance of a spectrum of relaxation times. However, experiments and calculations have shown (see above) that a satisfactory description of the stress relaxation is attained in the presence of only one interaction rate constant.

The second memory function, based on the consideration of the diffusion in the material of the specimen of the nonrelaxators formed, has the form

$$T_2(\tau) = -\frac{S_0}{k_B m_2}\left[\frac{1}{a\tau^\gamma\ln(a\tau^\gamma)+(1-a\tau^\gamma)\ln(1-a\tau^\gamma)}+\frac{1}{\ln 2}\right], \quad (18)$$

where $m_2 = m_2^* \int_0^\infty T_2^*(\tau)d\tau$ [here m_2^* is the total number of diffusing microheterogeneities in the specimen and $T_2^*(\tau)$ is the time-dependent factor of the function $T_2(\tau)$ enclosed in square brackets in the equation] and $a\tau^\gamma$ is the fraction of sites occupied at time τ by kinetic units during their random wandering in the lattice [33] (here a is the velocity of an elementary migration step, while γ characterises the influence of constraints).

We shall consider in greater detail the memory functions based on the analysis of the kinetics of the interaction of relaxators and their conversion into a nonrelaxing material.

If this process is considered as an irreversible nth order reaction, then substitution of Eqn (17) in Eqn (16) leads to the following expression:

$$T_1(\tau) = -\frac{S_0}{k_B m_1}\left\{\left[\left[\frac{1}{(1+k^*\tau/\beta)^\beta} - \alpha_0\right]\ln\left[\frac{1}{(1+k^*\tau/\beta)^\beta} - \alpha_0\right] + \right.\right. \quad (19)$$
$$\left.\left. + \left[1 - \frac{1}{(1+k^*\tau/\beta)^\beta} + \alpha_0\right]\ln\left[1 - \frac{1}{(1+k^*\tau/\beta)^\beta} + \alpha_0\right]\right]^{-1} - 0.5\right\}.$$

In a simplified version, when $k^*\tau \ll 1$, the function (19) simplifies to [32]

$$T_1(\tau) = -\frac{S_0}{k_B m_1}\{(k^*\tau + \alpha_0)[\ln(k^*\tau + \alpha_0) - 1]\}^{-1}. \quad (20)$$

In order to employ these memory functions in fitting the strain relaxation or creep curves, it is essential to find their integrals for different durations of the relaxation process. Such a procedure has been carried out [34] with the aid of a computer for different pairs of the parameters k^* and β and for different process times ranging from 0.5 to 10^5 arbitrary units. The tabulated integrals of the time-dependent factor of the memory function (19) have been published.[34]

The interaction of the relaxators has been considered [32, 34] as a unilateral irreversible nth order reaction, i.e. it was assumed that the interacting relaxators are converted into a nonrelaxing material and that this process is irreversible. This factor in fact required the introduction of the condition $\alpha(\tau) \geqslant 0.5$. In another study,[35] the interaction of the relaxators was considered as a reversible bilateral nth order reaction, the kinetic equation for which assumes the form

$$-\frac{d\alpha}{d\tau} = k\alpha^n - k(1-\alpha)^n. \quad (21)$$

Eqn (21) has been formulated subject to the condition that the rate constants for the direct and reverse reactions are the same and equal to k. As a result of this, at the time when the system reaches equilibrium the fractions of the relaxators and nonrelaxators become identical and equal to 0.5.

In order to find the dependence of the degree of conversion α on the time t, the Runge–Kutta numerical method for the automatic selection of the integration step was used.[35] The integrals of the time-dependent factor of the function $T_3(\tau)$ were found by computer. This integral has the form $\int_0^t T_3^*(\tau)d\tau$, where

$$T_3^*(\tau) = \{[(\alpha - \alpha_0)\ln(\alpha - \alpha_0) + \quad (22)$$
$$+(1 - \alpha + \alpha_0)\ln(1 - \alpha + \alpha_0)]^{-1} - 0.5\}.$$

The values of $T_3^*(\tau)$ for different parameters k and β have been published.[35]

In order to be able to use the functions $T_1(\tau)$, $T_2(\tau)$, and $T_3(\tau)$ to fit the stress relaxation curves, it is essential to substitute them in the Boltzmann equation

$$\sigma(t) = \sigma_0\left[1 - \int_0^t T_i(\tau)d\tau\right], \quad (23)$$

where σ_0 is the initial stress.

On substituting the functions $T_1(\tau)$, $T_2(\tau)$, and $T_3(\tau)$ in the above equation and going over to the relaxing modulus, we obtain

$$E_r = E_0\left[1 + \frac{S_0}{k_B m_1}\int_0^t T_1^*(\tau)d\tau\right], \quad (24)$$

$$E_r = E_0\left[1 + \frac{S_0}{k_B m_2}\int_0^t T_2^*(\tau)d\tau\right], \quad (25)$$

$$E_r = E_0\left[1 + \frac{S_0}{k_B m_3}\int_0^t T_3^*(\tau)d\tau\right]. \quad (26)$$

The time-dependent factors of the functions $T_1^*(\tau)$, $T_2^*(\tau)$, and $T_3^*(\tau)$ are described by Eqns (18) and (19) (the expressions in braces) and Eqn (22) jointly with Eqn (21) respectively.

If Eqns (24)–(26) reproduce satisfactorily the experimental relaxing modulus curves, then the E_r — $\int_0^t T_1^*(\tau)d\tau$, E_r — $\int_0^t T_2^*(\tau)d\tau$, and E_r — $\int_0^t T_3^*(\tau)d\tau$ plots should be linear and their slopes should be respectively E_0S_0/k_Bm_1, E_0S_0/k_Bm_2, and E_0S_0/k_Bm_3; the intercepts on the ordinate axis should be equal to E_0.

In order to implement the above procedure, it is necessary to have the tabulated integrals $\int_0^t T_1^*(\tau)d\tau$, $\int_0^t T_2^*(\tau)d\tau$, and $\int_0^t T_3^*(\tau)d\tau$. Such data are available.[34, 35] A computer program, with the aid of which the curves may be fitted has also described in the above communications. Its essential feature is that the values of the above integrals in the form of three sets for different pairs of parameters k^* and β and also α and γ are first introduced into the computer memory. Next each experimental $E_r(t)$ relation is fitted by the linear equation (24), (25), or (26) and the pairs of parameters k^* and β and also α and γ, for which the sum of squares of the deviations of the experimental values of $E_r(t)$ from the calculated ones is a minimum and the correlation coefficient r is a maximum, are chosen automatically.

The stress relaxation curve fitting procedures described above are suitable only in the region of linear mechanical behaviour, where the parameters of the relaxation process are independent of the deformation level. We shall consider briefly the methods for the fitting of relaxation curves also in the nonlinear region of the mechanical behaviour, which is more characteristic of polymers.

At the present time, the commonest method for the fitting of stress relaxation curves in the nonlinear region of mechanical behaviour is one based on Il'yushin's principal cubic theory.[36] According to this theory, the relaxation modulus is fitted initially in the linear region of viscoelasticity and then fitting involves the introduction of yet another parameter and the employment of the same memory function but with different parameters – the parameters of the relaxation curves in the nonlinear region. Another procedure involves the employment of equations containing a fractional power exponent of the time, the exponent being assumed to depend on the degree of deformation [37] kept constant during the relaxation process. A satisfactory agreement between the experimental and calculated curves is achieved in both cases, but the physical significance of the new parameters introduced is not elucidated.

An approach to the description of the stress relaxation curves in the nonlinear region with the aid of physically well-founded parameters, entering into the memory functions presented above, has been proposed.[38] The essential feature of this fitting procedure is as follows: we formulate an expression for the temperature dependence of the rate constant

$$k^* = k_0^*\exp\left(-\frac{\Delta U}{RT}\right),$$

where k_0^* is the pre-exponential factor and ΔU the activation energy for the interaction of the relaxators.

During the deformation of polymers, their free volume is known to increase (in this case, the free volume is understood as the 'empty volume', which represents the difference between the true volume of the polymeric body and the van der Waals volume of the atoms which they occupy in the polymeric body.[39] On pronounced deformation of solid (glassy and crystalline) poly-

mers and on transition to the yield stress, the free volume increases to a fairly large value, which facilitates significantly the jumps of kinetic units from one position to another. This actually leads to enforced elasticity, i.e. to enforced softening of the material. It has been postulated [38] that the activation energy for the interaction of relaxators decreases with increase in the mechanical stress σ and the rate constant for the interaction of the relaxators was formulated as follows:

$$k^* = k_0^* \exp\left(-\frac{\Delta U_0 - \delta E_r \varepsilon_0}{RT}\right), \quad (27)$$

where E_r is the relaxation modulus, ΔU_0 the initial activation energy for the interaction of the relaxators, $\sigma_r = E_r \varepsilon_0$ the relaxing stress, and δ the fluctuation volume in which the elementary step in the interaction of the relaxators takes place. Then

$$\alpha(\tau) = \left[1 + \frac{\tau k_1^* \exp(\delta E_r \varepsilon_0 / RT)}{\beta}\right]^{-\beta}, \quad (28)$$

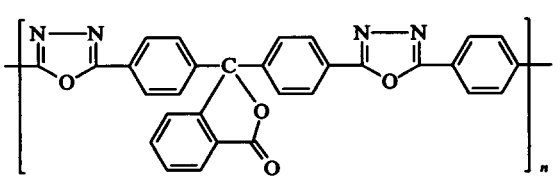
where $k_1^* = k_0^* \exp(-\Delta U/RT)$.

The fitting procedure consists in the determination of the value of δ for which the function $\varphi(\delta)$, representing the sum of squares of the deviations of the experimental values from the calculated ones, is a minimum:

$$\varphi(\delta) = \sum_{i=1}^{n} (E_{i2} - E_{i1})^2,$$

where n is the number of experimental points and E_{i2} and E_{i1} are the values of the relaxation modulus calculated by Eqn (24) and determined experimentally respectively. The calculations are performed on a computer. The algorithm for the calculations consists in the following steps: the relaxation moduli for the experimental relaxation curves are introduced successively into the computer in order of increasing deformations ε_0. Each curve introduced, except the first, is compared with the curve which is the average of the relaxation moduli derived from the curves introduced previously. If each modulus for the same relaxation time is smaller for the curve introduced than for the average curve and the arithmetical mean of the relative deviations exceeds 10%, it is assumed that such a curve refers to the nonlinear region of mechanical behaviour. The parameters of the memory function corresponding to the linear region are then calculated for the average curve and the curve referring to the nonlinear region is fitted on their basis.

The relaxation curves for polyoxadiazole have been fitted [38] at different temperatures and for different deformations. The results of the calculations are presented in Table 6. In addition to the data in Table 6, we may note that the rate constant k^* for the interaction of the relaxators at both temperatures is 0.1 min^{-1}; the values of β, $(S_0/k_B m_1) \times 10^4$, and r_1/r_2 [the ratio of the correlation coefficients for the memory functions $T_1(\tau)$ and $T_2(\tau)$ in the nonlinear region of mechanical behaviour] at 21 and 170 °C are respectively 7.2 and 5.2, 0.3 and 0.2, and 0.9991/0.9952 and 0.9981/0.9639. In curve fitting by the method of Askadskii and Valetskii,[38] the correlation coefficients at the temperatures indicated are 0.9999 and 0.9997 respectively. Polyoxadiazole having the following structure was investigated:



In terms of absolute magnitude, the correlation coefficients in curve fitting by the above method [38] are appreciably greater and much more stable than in fitting by the method of Il'yushin.[36]

Table 6. The results of the fitting of the parameters of the memory functions for POD in the linear and nonlinear regions of mechanical behaviour.

ε(%)	δ/kJ mol^{-1} MPa^{-1}	r[a]
Temperature 21 °C		
5	0.937	0.9782
5.56	0.840	0.6274
6.12	0.755	0.9915
6.67	0.724	0.9864
Temperature 170 °C		
5.68	0.477	0.9991

[a] The correlation coefficient obtained in fitting by the method of Il'yushin.[36]

Furthermore, it was noted that the memory function $T_1(\tau)$ fits the relaxation curves for solid polymers in the linear region more satisfactorily than the function $T_2(\tau)$.

We shall consider the results of the study of the relaxation properties of a series of heat-resistant polymers using the memory functions described above. The stress relaxation has been studied in detail [40] for two polymers – polyoxadiazole and polyimide.

Fig. 28 presents the time variations of the relaxation modulus for POD and polyimide at 20 °C. The data corresponding to the

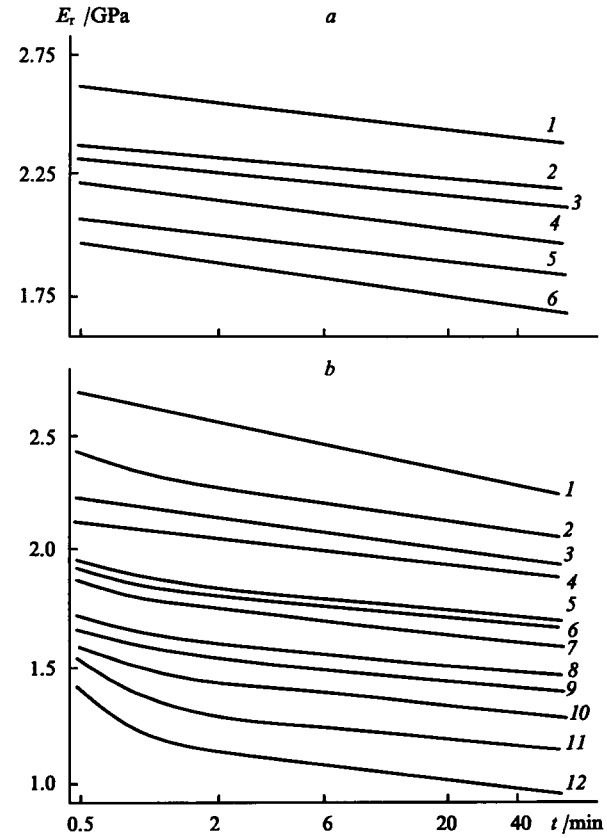


Figure 28. Time variation of the relaxation modulus E_r at 20 °C for polyoxadiazole (*a*) and polyimide (*b*) in the linear (curve *1*) and nonlinear (curves *2–12*) regions.
a: (*1*) single averaged relation; ε(%): (*2*) 5.56; (*3*) 6.67; (*4*) 7.23; (*5*) 7.78; (*6*) 8.33;
b: (*1*) single averaged relation; ε(%): (*2*) 4.46; (*3*) 5.02; (*4*) 5.56; (*5*) 6.82; (*6*) 8.33; (*7*) 8.99; (*8*) 10.23; (*9*) 11.57; (*10*) 12.36; (*11*) 13.95; (*12*) 15.34.

linear region of mechanical behaviour were averaged and a single relaxation relation was obtained. A deviation from the average relation towards a decrease in E_r is observed at $\varepsilon_0 = 5.56\%$ for polyoxadiazole (Fig. 28*a*). In the range of ε_0 from 1.7% to 5.0%, linear mechanical behaviour is observed. In terms of this feature, polyoxadiazole is superior to other known polymers, for which the region of nonlinear behaviour begins at significantly smaller deformations.

For polyimide, the deviations from linear mechanical behaviour are observed already at $\varepsilon_0 = 4\%$ (Fig. 28*b*), while the region of linear mechanical behaviour covers the range of ε_0 from 1.7% to 3.4%, i.e. significantly shorter than the analogous range for polyoxadiazole.

At higher temperatures, the range of deformations in the region of linear behaviour becomes narrower but not uniformly. Fig. 29 presents the temperature variation of the limiting deformation ε_{lim}, for which a linear viscoelastic behaviour is still observed. For polyoxadiazole, ε_{lim} is significantly greater than for polyimide. A common feature of these polymers is a small decrease in ε_{lim} with increase in temperature and also the existence of a region in which ε_{lim} is independent of temperature after which, as the glass transition temperature is approached, ε_{lim} decreases.

The results of the fitting of stress relaxation curves in the linear region of viscoelastic behaviour are presented in Tables 7 and 8.

For the above polymers, the memory function $T_1(\tau)$ 'works' best, its employment leading to a correlation coefficient close to unity, i.e. the experimental and calculated values of E_r are the same. Curve fitting with the aid of the memory function $T_2(\tau)$ leads to a significantly smaller correlation coefficient. Since the memory function $T_1(\tau)$ describes the kinetics of the relaxation of relaxators and their conversion into a nonrelaxing material while the memory function $T_2(\tau)$ describes the kinetics of the diffusion of these kinetic elements in the material, in the given instance the

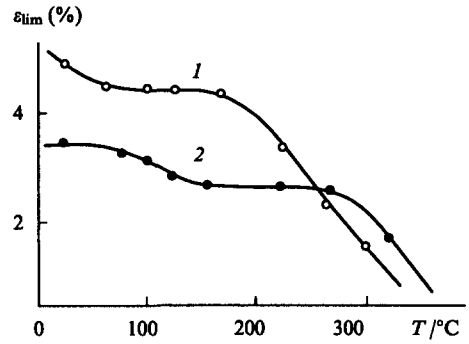


Figure 29. Temperature dependence of the limiting deformation ε_{lim} up to which linear viscoelastic behaviour is retained for PBO (curve *1*) and polyimide (curve *2*).

rate of the relaxation process is limited by the rate of reaction of the relaxators. The same conclusion has been reached[41] in the analysis of the relaxation behaviour of polybenzoxazole.

The results of the analysis in the form of parameters of the relaxation process and the correlation coefficient r are presented in Tables 9–11.

These data make it possible not only to follow the temperature variation of the parameters of the relaxation processes but also to reach definite conclusions about the changes in the process mechanisms and about the relaxation transitions within the temperature range of the glassy state. We shall therefore consider them in greater detail.

We shall compare the values of all the parameters and the correlation coefficients r when the memory functions $T_1(\tau)$ and $T_3(\tau)$ are used. It can be readily shown (Tables 9 and 10) that all

Table 7. Kinetic parameters of the stress relaxation process for POD determined using the memory functions $T_1(\tau)$ and $T_2(\tau)$.

T/°C	Function $T_1(\tau)$						Function $T_2(\tau)$[a]		
	E_0 /GPa	$\frac{m_1 k_B}{S_0}$	r	β	$10^2 k^*$ /min^{-1}	n	E_0 /GPa	$\frac{m_2 k_B}{S_0}$	r
20	2.9144	1265	0.9976	0.4	1	3.50	2.6158	428	0.9843
70	2.7504	1660	0.9931	0.8	1	2.25	2.5313	631	0.9627
120	2.6444	1670	0.9996	0.4	1	3.50	2.4394	579	0.9888
170	2.6049	1617	0.9966	0.6	1	2.67	2.3929	601	0.9753
220	2.5228	10945	0.9960	0.2	0.1	6.00	2.2933	613	0.9946
270	2.7575	299728	0.9986	0.2	0.001	6.00	2.2376	175	0.9903
300	1.8074	272	0.9934	0.3	1	4.33	0.9532	52	0.9762

[a] At 220 °C, the parameter a was 40.3, whilst at the remaining temperatures it was 0.05; the parameter $\gamma = 0.5$ at all temperatures.

Table 8. Kinetic parameters of the stress relaxation process for polyimide determined using the memory functions $T_1(\tau)$ and $T_2(\tau)$.

T/°C	Function $T_1(\tau)$						Function $T_2(\tau)$[a]		
	E_0 /GPa	$\frac{m_1 k_B}{S_0}$	r	β	$10^2 k^*$ /min^{-1}	n	E_0 /GPa	$\frac{m_2 k_B}{S_0}$	r
20	3.3259	694	0.9999	0.6	1	2.70	2.6984	223	0.9846
70	3.1109	608	0.9998	0.3	1	4.30	2.4561	172	0.9928
120	3.2992	83	0.9856	0.2	10	6.00	2.5816	249	0.9473
170	2.9620	10375	0.9974	0.2	0.1	6.00	2.6770	583	0.9925
220	3.0221	727	0.9934	0.5	1	3.00	2.4791	233	0.9720
270	2.9483	493	0.9973	0.8	1	2.25	2.1603	149	0.9724
320	4.6264	33	0.9988	0.2	10	6.00	2.1391	60	0.9575

[a] At 220 °C, the parameter a was 40.3, whilst at the remaining temperatures it was 0.05; the parameter $\gamma = 0.5$ at all temperatures.

Table 9. Parameters of the memory function $T_1(\tau)$ for PBO.

T/°C	E_0 /MPa	10^2k^* /min^{-1}	n	$\frac{m_1k_B}{S_0}$	r
22	2574	1	4.33	1533	0.999
100	2336	1	6.00	1975	0.999
125	1986	1	6.00	2118	0.998
150	1829	1	6.00	1517	0.995
175	2007	0.1	6.00	4520	0.998
200	2476	0.1	2.25	2462	0.999
210	2361	1	6.00	286	0.999
220	2522	1	2.25	230	0.996
230	834	1	2.25	222	0.998

Table 10. Parameters of the memory function $T_3(\tau)$ for PBO.

T/°C	E_0 /MPa	10^2k^* /min^{-1}	n	$\frac{m_3k_B}{S_0}$	r
22	2562	1	4.33	1605	0.999
100	2330	1	6.00	2047	0.999
125	1981	1	6.00	2194	0.998
150	1838	1	6.00	1524	0.995
175	1999	0.1	6.00	3508	0.998
200	2440	0.1	2.25	2513	0.999
210	2361	1	6.00	292	0.999
220	2412	1	2.25	236	0.996
230	796	1	2.25	224	0.998

Table 11. Parameters of the memory function $T_2(\tau)$ for PBO.

T/°C	E_0 /MPa	a	$\frac{m_2k_B}{S_0}$	r
22	2348	0.0403	770	0.989
100	2184	0.0403	826	0.987
125	1857	0.0306	1565	0.997
150	1673	0.0306	1049	0.999
175	1520	0.0209	616	0.997
200	1438	0.0306	137	0.997
210	1304	0.0403	71	0.990
220	1060	0.050	42	0.974
230	332	0.050	38	0.978

Note. The parameter γ was 0.05 at all temperatures.

the parameters and the values of r determined with the aid of the memory functions $T_1(\tau)$ and $T_3(\tau)$ are virtually the same. We may recall that the memory function $T_1(\tau)$ was obtained in the analysis of a unilateral nth order reaction of the relaxators, while the memory function $T_3(\tau)$ was found taking into account the reversible interaction. Consequently, when account is taken of the impossibility of the interconversion of relaxators and non-relaxators, there is no appreciable change in the process kinetics at least for the times t during which the experiment was performed (up to 6 h). This conclusion is in full agreement with the analogous conclusion in another study.[35]

It is seen from the tables that the correlation coefficients r are very large and approach unity when the memory function $T_1(\tau)$ or $T_3(\tau)$ is employed. When the memory function $T_2(\tau)$ is used (Table 11), the correlation coefficients are significantly lower in the range of comparatively low and high temperatures than the values of r obtained with the aid of the functions $T_1(\tau)$ and $T_3(\tau)$. In the range of moderate temperatures (from 125 to 200 °C), the correlation coefficients are very high when the function $T_2(\tau)$ is employed [approximately the same as those obtained with the aid of the functions $T_1(\tau)$ and $T_3(\tau)$]. Hence one may conclude (from the standpoints considered) that in the temperature ranges 22–100 °C and 210–230 °C the rate-limiting stage of the stress relaxation process is the interaction of the relaxators and their conversion into a nonrelaxing material.

In the temperature range 125–200 °C, the rates of interaction and diffusion of the kinetic units become comparable, as a result of which the relaxation process is described with approximately the same accuracy by all the memory functions. One may note that the correlation coefficients r obtained when the memory function $T_2(\tau)$ is used becomes actually higher than the value of r obtained with the aid of the $T_1(\tau)$ and $T_3(\tau)$ memory functions. This temperature range, in which both mechanisms operate at equal rates, is transitional. The occurrence of a distinct relaxation transition in this temperature range for PBO has been described;[4] for example, the temperature variation of σ_c for PBO has a characteristic form (Fig. 7): along the first section in the range 22–100 °C, the critical stress depends only slightly on temperature, in the range 100–200 °C, a sharp decrease in σ_c is observed, while in the range 200–230 °C the decrease becomes less marked.

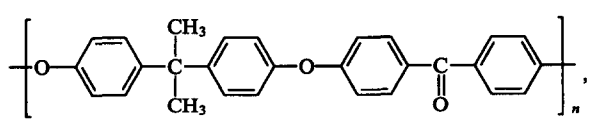
In the region of the T_{as} transition, the mechanism of the relaxation process changes (Tables 9–11). The rate constant for the interaction of relaxators increases in this range, but the number of relaxators m_1 increases and there is also a sharp increase in the number of kinetic units m_2 participating in the diffusion process. As a result of all these factors, the rates of interaction of the relaxators and of the diffusion of kinetic elements become comparable. With increase in temperature, the rate of interaction of the relaxators increases while the number of relaxators becomes small and changes only slightly with increase in temperature. The same may be said also about the diffusion process.

Another example of the application of the above approach to the analysis of the relaxation behaviour of polymers is the study of the relaxation processes of polyketones subjected to hydrostatic extrusion.[42]

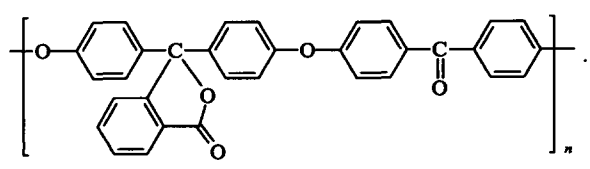
Numerous aromatic polyketones, including cardo-polyketones, have now been described. These polymers are amorphous or partly crystalline and they are preformed by injection moulding or by pressing. The principal physicomechanical parameters of the polymers are regulated by varying the parameters of the synthesis.[43]

The possibilities for regulating the structures and properties of these polymers by mechanical treatment have been investigated.[42,44] One of the promising methods for such treatment is hydrostatic extrusion, which makes it possible to achieve large plastic deformations of the polymers without disruption.

The results of studies of the hydroextrusion process and the structures and physicomechanical properties of the extruded materials — poly(aryl ether ketone) (PAEKN) and poly(aryl ether ketone) based on phenolphthalein (PAEKP) — have been published.[42]



PAEKN



PAEKP

The polymers were synthesised by nucleophilic substitution of an activated aromatic halogen.

Table 12. Parameters of the memory functions $T_1(\tau)$ and $T_2(\tau)$ obtained in fitting the experimental $\sigma(t)$ relations for PAEKN and PAEKP.

λ	T/°C	Function $T_1(\tau)$						Function $T_2(\tau)$					
		r	$10^{-2}\sigma_0$ /MPa	$10^{-2}\sigma_\infty$ /MPa	$10^2 k^*$ /min^{-1}	n	$\frac{m_1^* k_B}{S_0}$	r	$10^{-2}\sigma_0$ /MPa	$10^{-2}\sigma_\infty$ /MPa	$10^2 a$	$10^2 \gamma$	$\frac{m_2^* k_B}{S_0}$
PAEKN													
1.0	–	–	–	–	–	–	–	–	–	–	–	–	–
2.2	20	0.993	2	0.7	0.1	6.0	1.59	0.992	1.5	1.1	6	4	3.50
2.4	20	0.999	2.8	1.3	1.0	6.6	1.888	0.994	2.1	1.4	4	5	3.17
2.8	20	0.991	3.3	1.8	1.0	4.3	2.27	0.981	2.5	1.9	5	5	4.03
2.5	215	0.990	3.4	2.3	0.001	2.25	3.17	0.974	3.1	2.8	4	5	10.25
PAEKP													
1.0	–	0.950	0.70	1.29	1.0	6.0	0.35	0.945	0.62	0.54	5	4	8.19
1.8	170	0.993	1.38	0.79	1.0	4.3	2.34	0.991	1.13	0.90	4	5	5.00
2.6	170	0.965	1.35	0.72	1.0	6.0	2.13	0.981	1.09	0.87	10	3	5.00
1.8	180	0.982	0.78	0.44	10.0	6.0	2.27	0.967	0.66	0.56	4	5	6.55
2.6	180	0.982	1.00	0.66	10.0	3.5	2.28	0.962	0.80	0.66	5	5	5.58
4.0	180	0.997	1.66	0.67	0.01	3.0	1.68	0.988	1.35	1.07	4	5	4.88
6.0	180	0.993	2.14	1.33	10.0	4.3	2.64	0.978	1.69	1.35	5	5	4.95
1.8	190	0.994	1.17	0.57	0.01	1.0	1.93	0.978	0.98	0.81	4	5	5.81
2.6	190	0.929	0.87	0.55	10.0	6.0	2.67	0.933	0.71	0.57	4	5	4.98
6.0	190	0.947	1.64	0.93	100	6.0	2.33	0.907	1.14	0.91	5	5	4.96

Note. For the memory function $T_1(\tau)$, the quantity k^* is proportional to the rate constant for the interaction of the relaxators; the time-dependent factor of the memory functions, $m_1^* k_B/S_0$ and $m_2^* k_B/S_0$, are proportional to the number of microheterogeneities in the specimen.

The stress relaxation curves were determined for the initial and hydroextruded specimens, hydroextrusion being performed up to different degrees of extension λ and at different temperatures T_e (however, always below the glass transition temperature T_g).

For a detailed description of the kinetics of the relaxation processes, the $\sigma(t)$ relations were fitted with the aid of the memory functions $T_1(\tau)$ and $T_2(\tau)$. These memory functions were also used to characterise the relaxation properties of an aromatic polyketone based on isophthalic and terephthalic acids.[11] The results of the calculations are presented in Table 12.

Analysis of the parameters of the above memory functions shows that the Boltzmann equation with the memory function $T_1(\tau)$ reproduces best the course of the stress relaxation, although in a number of instances the correlation coefficient r is also fairly close to unity when the memory function $T_2(\tau)$ is used. With increase in λ the quantities σ_0 and σ_∞ as a rule increase. The most significant increase in σ_0 and σ_∞ is characteristic of extruded PAEKN specimens, which have a semi-crystalline structure. The increase in $m_1^* k_B/S_0$, observed for the deformed polymer, indicates an increase in the number of relaxators in the material, the rate of interaction of which in the extruded specimens is on the whole higher than in the cast materials. This is entirely reasonable provided that the relaxators are understood as different kinds of microheterogeneities, which are converted into nonrelaxing structures faster the higher the level of the internal stresses (the latter naturally increases on deformation).

Thus hydroextrusion improves the elastic and relaxation characteristics of aromatic polyketones. In this sense, the most promising material is PAEKN, which is capable of undergoing a structural transition from the amorphous to a partially semi-crystalline modification during the deformation process.

IV. Low-temperature relaxation processes and transitions in heat-resistant polymers

Much attention is devoted nowadays to the analysis of the mechanisms of the relaxation transitions in aromatic polymers, because these transitions influence significantly the macroscopic properties, which depend on the mobility of the structural elements. Questions of both methodological (methods used for the measurements, the presence of impurities in the monomers analysed) and structural (deliberate alteration of the chemical structure of the repeat unit in the macromolecule for a more clear-cut identification of the mechanisms of the transitions) natures arise in such an analysis. In the dynamic mechanical analysis of heat-resistant aromatic polymers, it is necessary to take into account the fact that many of them contain highly polar groups capable of retaining firmly the solvent with which they are in contact either during synthesis or during the preparation of film materials from solution. The presence of residual solvent promotes the appearance of additional losses and failure to take this into account may lead to erroneous interpretations of the transition mechanism.

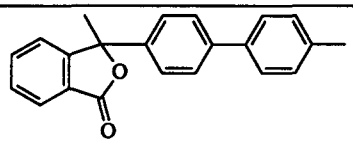
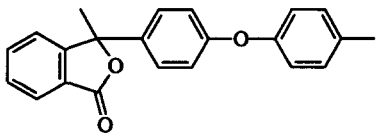
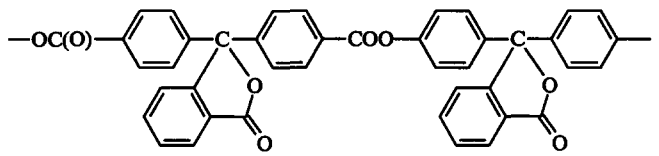
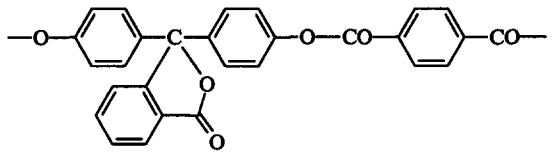
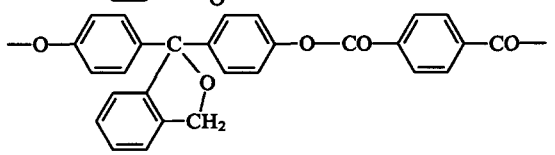
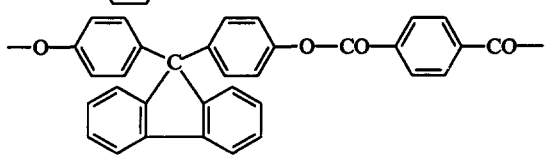
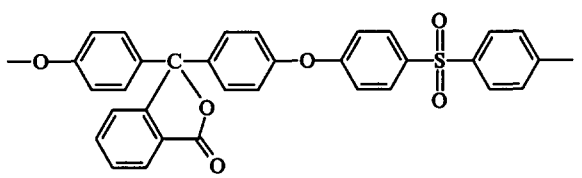
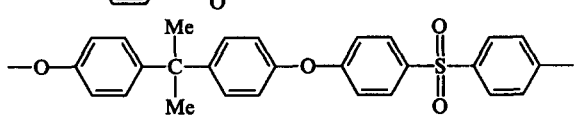
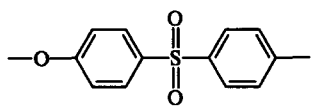
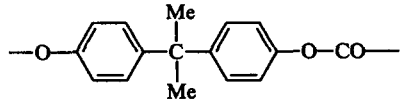
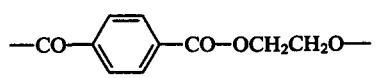
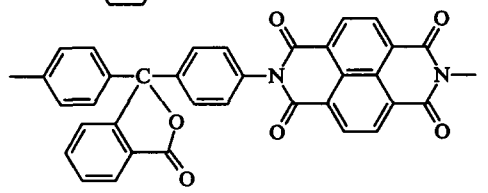
The low-temperature relaxation transitions in heat-resistant polymers have been investigated by numerous workers.[45–61] Attention was especially concentrated on the temperatures and mechanism of the β-transition. The mechanism of the β-transition has been associated with loss of water in the case of polyimides[46] and, in another study,[47] with the interplanar slip in the crystalline regions.

The influence of residual solvents and moisture on the nature of the relaxation transitions has been studied in detail[51,52] in relation to the polyimide obtained from naphthalene-1,4,5,8-tetracarboxylic acid and anilinephthalein. The diffuse maxima of the loss factor tan δ, which appear on the plot of temperature variation of tan δ for this polyimide, are smoothed out on heat treatment, which eliminates moisture and residual solvents.

It is sometimes assumed that hinge atoms or groups, positioned between aromatic rings, are responsible for the relaxation transitions in aromatic polymers. In order to answer more exactly the questions of the influence of such groups, a specially synthesised series of polyarylenephthalides have been investigated.[51] In this series, polyesters are replaced by polyethers and further by polyphenylenes (Table 13). In other words, particular hinge groups are 'taken away' in succession from the polymers as far as the complete elimination of all types of such groups.

Fig. 30 presents the temperature variations of E' and tan δ for a series of such polyheteroarylenes (polymers **1**–**3** in Table 13).

Table 13. The chemical structures and β-relaxation and glass transition temperatures for a series of heat-treated heat-resistant polymer films.

Compound	Formula of polymer unit	T_β /°C[a]	Frequency at T_β /Hz	T_g /°C	Frequency at T_g /Hz
1		−96	107	420	79
2		−93	104	270	85
3		−75	104	340	74
4		−67	111	305	75
5		−70	92	255	64
6		−70	88	330	64
7		−88	99	254	76
8		−76	115	177	99
9		−82	87	227	74
10		−70	133	145	103
11		−46	88	90	76
12		−120	119	–	–

[a] Temperature at the β-peak maximum.

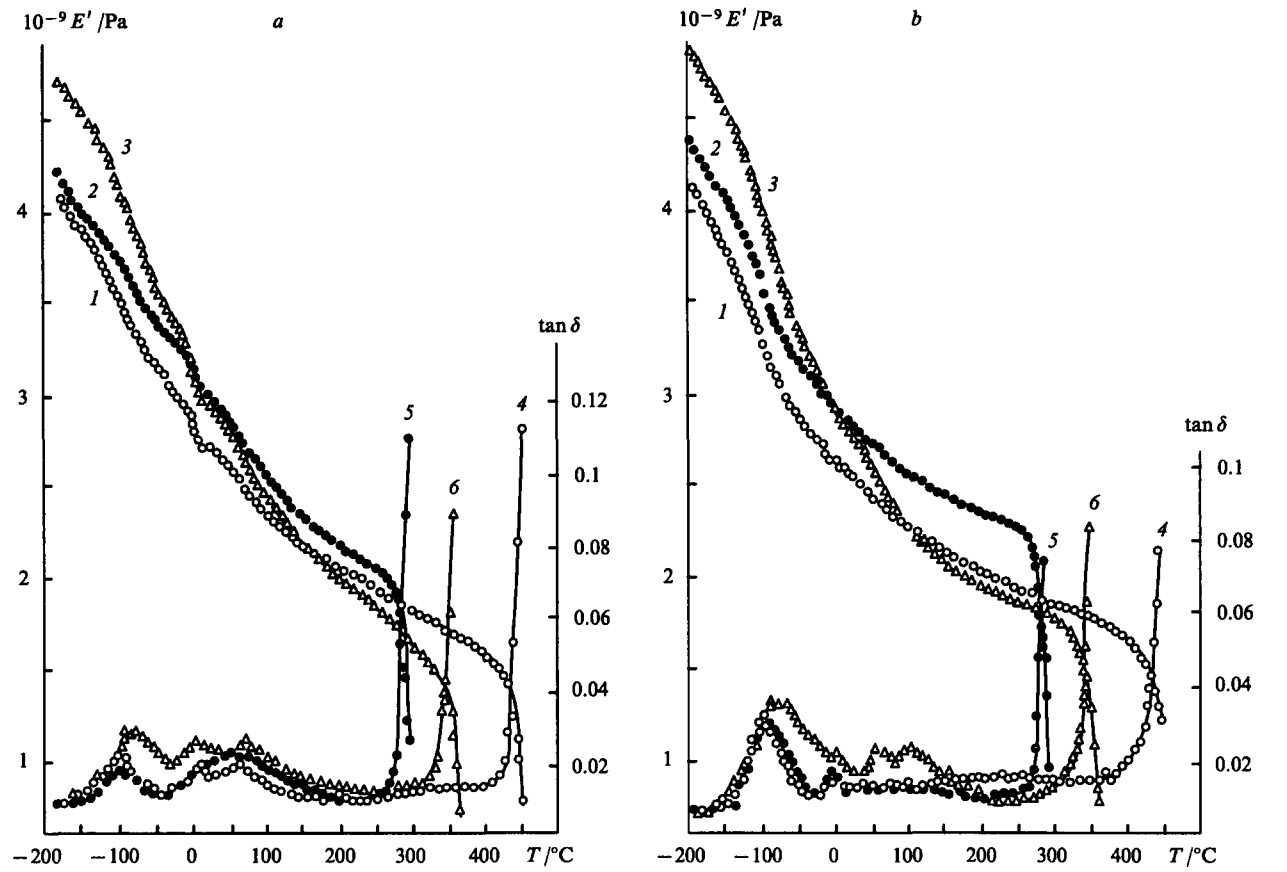


Figure 30. Temperature dependences of E' (curves 1–3) and tan δ (curves 4–6) for the initial (*a*) and heated (*b*) films of a series of polyheteroarylenes. Number of compounds in Table 13; (*1*) and (*4*), **1**; (*2*) and (*5*) **2**; (*3*) and (*6*) **3**.

Two principal sections may be seen on the temperature variation of the storage modulus E'. The loss factor maxima at −96, −93, and −75 °C for the heated polymer **1**, **2**, and **3** films and at −100, −95, and −80 °C for the initial films correspond respectively to a sharp decrease in the storage modulus. Thus, both in the presence and absence of hinge atoms and groups in the main chain, the β-transition is manifested for all the polymers in approximately the same range of temperatures. Consequently, these hinge groups are not responsible for the β-transition.

For all the polymers **1**–**3**, intense loss factor peaks are observed in the intermediate range −30 to 200 °C. Heat treatment at T_g for each polymer smoothes out these peaks to a large extent for polymers **1** and **2**, but does not affect appreciably their intensity for polymer **3**, containing a highly polar ester group in the main chain. The increase in the polarity of the polymer for the series of bridges between aromatic rings —, —O—, —COO— leads to an increase in the intensity of the intermediate peaks and influences significantly the relative height of the β-peak. Whereas for the heat-treated polymer **1** and **2** films the increase in the intensity of the β-process is caused mainly by the removal of the residual water and the solvent, for polymer **3**, with an ester group in the backbone, this is apparently associated with the redistribution of the intermolecular interactions, limiting the movement of the segments of the chain responsible for the low-temperature transition. Furthermore, the presence of a highly polar ester group in the main chain of polymer **3** intensifies the intermolecular interaction, expanding greatly the region of β-relaxation towards higher temperatures. For polymer **2**, containing an ether group in the main chain, this effect is much weaker. The introduction of the polar groups —O— and —COO— into the main chain lowers the glass transition temperature from 420 to 270 and 340 °C for polymers **2** and **3** respectively.

Thus the introduction of ether and ester groups into the main chain of the polymer expands and displaces the maximum of the β-peak towards higher temperatures, on the one hand, but reduces the glass transition temperature, on the other. The contributions of the —O— and —COO— groups to the shift are then directly opposed in relation to the β- and α-transitions.

It may be postulated that the limited rotation of the phenylene groups relative to collinear bonds is responsible for the β-relaxation. However, the observed behaviour cannot be accounted for by this simple mechanism. Indeed, since the hinge atoms and groups facilitate the movement of the phenylene rings (this leads to an increase in the flexibility of the chain and a decrease in T_g), the temperature of the β-transition should be lowered on introduction of the hinge groups. In fact, it increases (Fig. 30 and Table 13).

In the analysis of the mechanism of the β-transition, it is essential to take into account the fact that the polymer in the glassy state consists of a complex system of interacting macromolecules responsible for the existence of regions with different degrees of order and for the relaxation transitions in the main chain of the polymer. From this standpoint, the β-relaxation transition may be accounted for by the freeing of the mobility of large chain segments in the least ordered regions. With increase in temperature, the movement in the more ordered (or more cross-linked as a result of the impurities present in the polymers) regions is freed, such movement being characterised by a higher activation energy necessary to overcome the intermolecular interaction forces. On vitrification, the most ordered and cross-linked segments of the chain are freed. The relative contribution of the polymer chain segments ordered in different ways, taking into account intermolecular interaction, to the overall process involving the freeing of mobility may be determined, for example, in terms of the dynamic loss modulus. The presence of the crystalline

phase in the polymer expands the number of regions with different types of order in chain segments on the assumption that additional energy scattering mechanisms arise. The distribution spectrum of regions with differently ordered chain segments is determined primarily by the specific chemical structure of the chain, the molecular mass distribution, the presence of branches, the impurities present in the polymer, the method of preparation of the test specimen, and also the test conditions.

Even if the hinge atoms and groups are absent from the aromatic polymer, β-relaxation is nevertheless manifested. Hence follows the unambiguous conclusion that these are not the groups responsible for the β-transition.

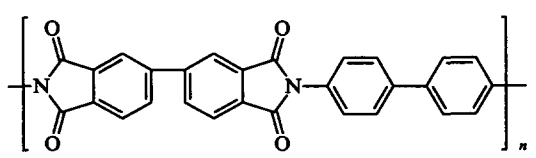
Most investigators associate the mechanism of β-relaxation with the freeing of the molecular mobility of the aromatic rings.[48-59] Approximately the same conclusion was reached by Eisenberg and Cavrol.[62] The results obtained in their study by means of dynamic mechanical analysis indicate that the β-transition in polyimides is associated with the rotation of rigid *p*-phenylene segments and the imide groups around the hinges. However, the authors [62] believe that the β-transition is manifested by a broad maximum at a positive temperature lower than the glass transition temperature.

The acoustic properties of poly(phenylene sulfide) have been investigated.[63] The β-relaxation in this polymer was observed in the temperature range from 193 to 223 K for an amorphous specimen (judging from the temperature variations of the mechanical loss factor). According to the ideas of Lukashov et al.,[63] the β-relaxation is associated with the vibrational motion of the phenylene groups in the main chain of the polymer. In the region of α-relaxation, poly(phenylene sulfide) exhibits two transitions due to the freeing of the segmental mobility at two levels of the supermolecular organisation of the polymer. Annealing of the polymer leads to an increase in the transition temperatures in the β-relaxation region.

The influence of flexible alkoxy-groups of different length, located in repeat units of rigid-chain polyesters, on the viscoelastic behaviour of these systems has been investigated.[64] The results of dynamic mechanical analysis have shown that these polymers have a complex relaxation spectrum. In order to explain the observed spectrum, the authors resort to the concept of different kinds of molecular motion in combination with structural rearrangements on heating. In certain cases, properties typical of liquid-crystal systems were observed.

The relation between the structure and relaxation properties of copolymeric poly(arylene ether ketones) has been investigated.[65] Different copolymers were synthesised by the partial substitution of hydroquinone in the polyetherketone by resorcinol or hexafluorobisphenol A. In the former case, the dynamic viscosity and the storage modulus for copolymers with a low resorcinol content increased with increase in temperature. The copolymers with a high content of resorcinol residues did not exhibit such unusual behaviour.

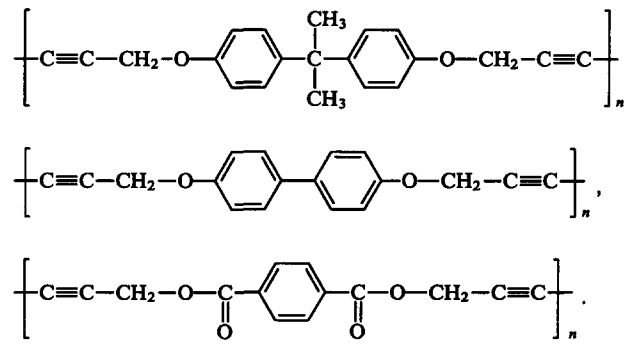
The thermal and thermooxidative stabilities, the coefficient of thermal expansion, the glass transition temperature, and the dielectric properties have been investigated in detail for the polyimide having the following structure:[66]



the glass transition temperature of this polymer is ~287 °C, its coefficient of thermal expansion is 6.98×10^6 K^{-1}, and the dielectric constant of films, measured after ageing at 50% humidity, amounts to 2.8–2.9 in the frequency range from 0.1 kHz to 1 MHz.

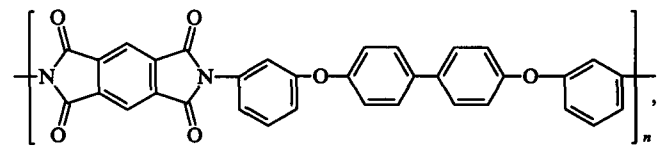
Relaxation properties have also been investigated for oriented systems (fibres and films) obtained from heat-resistant polymers. The relation between structure and mechanical properties for highly modular fibres of poly[2,5(6)benzoxazole] has been investigated.[67] It was found that the modulus of elasticity of the fibres increases from 91 to 133 GPa as a result of treatment of the fibre at 525 °C, while the deformation at break falls from 4.3% to 2.0%; the strength of the fibre remains unchanged under these conditions and is above 2.1 GPa. The increase in the modulus is attributed to the development of three-dimensional crystalline order in the fibre.

About all the technologically important fibres are manufactured from linear heat-resistant polymers, such as polyimides, polyoxadiazoles, aromatic polyamides, etc. The modulus and strength of such fibres, measured along the fibre axis, are determined by the strength of the covalent bonds in the chains of these polymers. It has been suggested [68] that the reduced strength and modulus at right angles to the fibre axis are associated with the weak (compared with chemical bonding) intermolecular interaction involving the formation of hydrogen bonds and dipole–dipole and dispersion interactions arising between the polymer chains in the fibre. An increase in compressive strength in the fibres may be achieved by cross-linking the macromolecules. The authors [68, 69] therefore prepared and characterised three linear polymers with two conjugated triple bonds in each repeat unit:



The third polymer — poly(dipropargyl terephthalate) — crystallises in the solid state on precipitation with water. The crystallisation is in this case the initial stage of the cross-linking process. Thus self-cross-linking fibres may be obtained by a wet method.

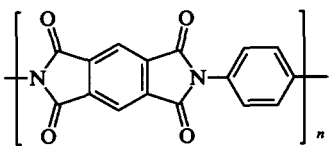
The dynamic mechanical properties and relaxation transitions of the new thermoplastic polyimide



have been studied.[70] The polyimide films were investigated directly after casting and after zone stretching in order to increase the degree of orientation.[71-73] The zone stretching of the polyimide leads to an increase in the modulus of elasticity over the entire temperature range investigated and is accompanied by an increase in the glass transition temperature and a decrease in the mechanical loss factor.[70]

The birefringence of fibres based on heat-resistant polymers has been studied.[74-79] A critical analysis of the results has been published.[80]

The influence of the thickness of the coating on the orientation of the chains and the order in polyimides has been investigated.[81] It was found by X-ray diffraction that substrate prepared polyimide films are oriented in such a way that the polyimide chains are preferentially arranged within the plane of the film. The degree of orientation then increases with increase in the content of the rigid polyimide, for example of the kind:



With increase in the thickness of the film, the average degree of orientation falls and the coefficient of volume expansion increases.

The strength and relaxation properties under stretching and compression conditions have been investigated for fibres based on poly-*p*-phenylenebenzobisoxazole and poly-*p*-phenyleneterephthalamide.[82]

V. The mechanism of the relaxation processes in heat-resistant polymers

The question of the mechanism of the relaxation processes arising on deformation of glassy polymers has attracted constant attention of investigators. The question of the possibility of comparatively large deformations in heat-resistant aromatic polymers has acquired particular interest, such a possibility of existing down to the temperature of liquid helium.

The mechanism of the relaxation process involving the viscoelastic strain recovery of a polyimide film after its preliminary deformation up to a specified elongation has been studied.[83] The viscoelastic strain recovery curves (the time variations of the deformation after the specimen has been freed) were fitted with the aid of the memory functions $T_1(\tau)$ and $T_2(\tau)$.

The Boltzmann equation for the viscoelastic strain recovery curves assumes the following form:

$$\varepsilon(t) = \varepsilon_0\left[1 - \int_0^t T_1(\tau)\mathrm{d}\tau\right] \quad (29)$$

or

$$\varepsilon(t) = \varepsilon_0\left[1 - \int_0^t T_2(\tau)\mathrm{d}\tau\right], \quad (30)$$

where ε_0 is the initial deformation at which the load is removed and the shrinking process begins at a constant temperature.

The experiments were performed[83] for a commercial PM polyimide film, which was stretched under creep conditions up to the deformation $\varepsilon_0 = 10\%$. The load was then removed and the contraction of the specimen was measured.

The fitting of the strain recovery curves by Eqns (29) and (30) demonstrated[83] that these curves are best fitted with the aid of the memory function $T_1(\tau)$ (Table 14). Consequently, from the standpoints considered, the relaxation process in the shrinkage of the specimen after loading is limited by the stage involving the interaction of the relaxators. The rate constant is then small (Table 14). When a load is applied at an elevated temperature, the quantity $k_B m^*/S_0$ is significantly greater than at room temperature.

If the mechanism of the relaxation processes described above is indeed associated with the formation and redistribution of microheterogeneities in the polymeric material, then analysis of positron annihilation in the relaxing specimen may provide an experimental confirmation of this mechanism, because it is precisely with the aid of this method that one can estimate the volumes and nature of the microcavities having dimensions comparable to or somewhat exceeding those of the repeat units of the heat-resistant polymers. The authors[83] therefore measured the annihilation spectra in both the initial polyimide specimen and in the prestretched specimen and also during its contraction after the removal of the load.

The measurements showed that the positron annihilation process in the polyimide differs significantly from that usually observed in the majority of polymers. The annihilation spectrum in the polymers is characterised by the presence, as a rule, of three or four components with average lifetimes from 10 ps to 4 ns.[84–86] However, a different structure of the spectrum was observed for the polyimide, which was found to have only one, and short-lived, component with $\tau_0 = 0.388$ ns (Fig. 31). The time distribution can be fitted satisfactorily by a single decay line, the slope of which defines the average lifetime.

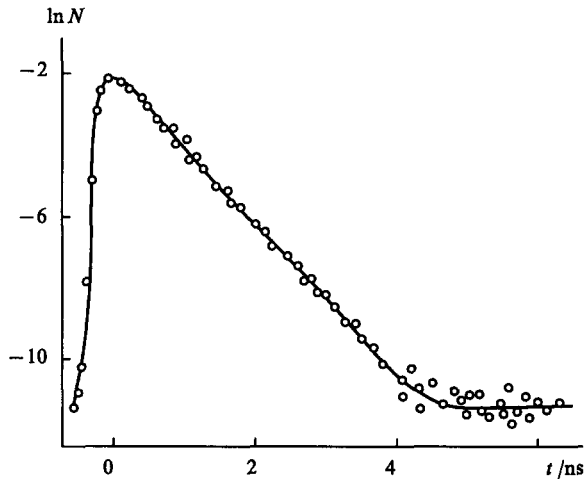


Figure 31. Spectrum of positron lifetimes in the initial polyimide film; N = number of counts in the channel.

The lifetime and the structure of the spectrum suggest that the annihilation in the polyimide occur in the positron state without the formation of a positronium atom of the kind characteristic of metals and semiconductors with a high mobility of electrons and an ordered crystal structure.

In this sense, the polyimide has an electronic structure unique for polymers, characterised by a high degree of uniformity of the electron density function.

In relation to interaction with positrons, the microstructure of the initial (undeformed) polyimide film is defect-free. However,

Table 14. Parameters of the memory functions $T_1(\tau)$ and $T_2(\tau)$ for the polyimide PM film at preliminary load application temperatures of 20 and 200 °C.

T/°C	Function $T_1(\tau)$[a]					Function $T_2(\tau)$[b]				
	r	ε (%)	$\frac{m_1 k_B}{S_0}$/s	$\frac{m_1^* k_B}{S_0}$	β	r	ε (%)	$\frac{m_2 k_B}{S_0}$/s	$\frac{m_2^* k_B}{S_0}$	a
20	0.984	26.648	22.440	1.045	0.7	0.848	6.771	118.045	1.266	0.0306
200	0.980	20.559	31.197	1.388	0.3	0.887	8.027	92.598	2.652	0.05

[a] k^* was 0.1 s at both temperatures. [b] $\gamma = 0.5$ at both temperatures.

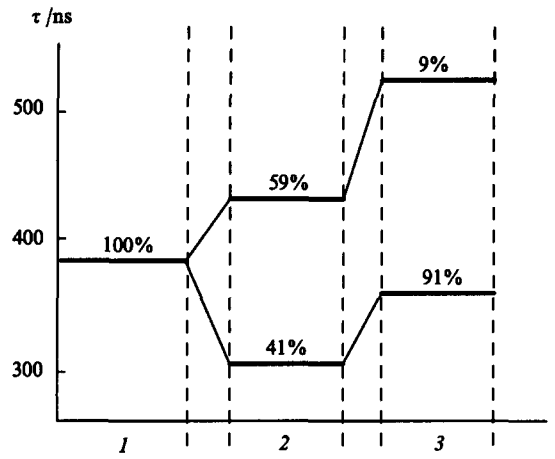


Figure 32. The lifetimes and intensities of the components in the spectra with polyimide the initial polyimide specimen (*1*) and polyimide specimens subjected to preliminary extension, measured for strain recovery durations of 1 h (*2*) and 24 h (*3*).

after deformation, the time aspects change (Fig. 32 and Table 15). Instead of the one component in the deformed specimen, two components are observed: with shorter (τ_1) and longer (τ_2) lifetimes. After strain recovery for 24 h at room temperature, an increase in the lifetimes of both components and a decrease in the intensity of the longer-lived one are observed. The nature of the changes occurring suggest that a rearrangement of the supermolecular structure of the polyimide occurs on deformation: the intermolecular bonds are broken and microdefects — free volumes sufficient to accommodate a positron — are formed. For the long-lived component, the time τ_2 should reflect in this case the changes in the average size, whilst the annihilation intensity I_2 should reflect the concentration of such defects. Similar changes in the spectra have been observed on formation and annealing of defects in metals and semiconductors. These changes are usually analysed with the aid of the positron capture model.[87] The model reflects qualitatively well changes in the time spectra of the polyimide during its deformation. The decrease in the lifetime of the 'short' component, associated with the annihilation in the defect-free part of the polymer, is due to the high rate of capture in the deformed specimen. After the partial contraction during the strain recovery process, the concentration of the defects falls and the lifetime τ_1 approaches that characteristic of the initial polymer. The intensity I_2 for the long-lived component, formed as a consequence of the annihilation of positrons on defects, also decreases under these conditions. The quantities calculated from the rate of capture spectra for the deformed and partially relaxed specimens are presented in Table 15. The increase in the lifetime τ_2 can be accounted for by the coagulation (the combination of small defects into larger ones) during strain recovery or by the rapid relaxation of the small pores and hence by the increase in the average capture radius.

Table 15. Characteristics of the positron annihilation spectra for polyimide film specimens.

Duration of strain recovery at 20 °C /h	τ_0 /ps	τ_1 /ps	τ_2 /ps	I_2 (%)	Rate of capture $10^{-9}k$ /s^{-1}
Initial specimen					
–	385±5	–	–	–	–
Deformed specimen					
1	–	294±30	440±17	59±5	0.60±0.15
24	–	361±10	531±30	9±2	0.12±0.05

The concentration of microdefects after partial relaxation falls by a factor greater than 7, whereupon the free volume induced by deformation diminishes, by a factor of 4.[83] The values obtained show that both processes take place — the fusion of the microdefects and the relaxation of the smallest defects — although the intensity of the latter is apparently greater.

Thus a one component spectrum is characteristic of the initial polyimide film. In the deformed specimen, at least two components are observed in the time spectra and are associated with the annihilation of positrons in the free state and the state corresponding to trapping in micropores, which arise on extension. During the relaxation of the structure, the lifetime increases and the intensity of the annihilation of the defective component diminishes. The results obtained with the aid of the positron capture model describe satisfactorily the observed changes in the time distribution and suggest that the structure of the free volume changes on relaxation not only as a result of the rapid recombination of the smallest pores but also as a consequence of the recombination of small pores with formation of long-lived large microcavities.

On the basis of the analysis, the following model of the annihilation of positrons and the mechanism of the relaxation process associated with the latter have been proposed:[83] before deformation, all the positrons are annihilated in the state corresponding to their enclosure in small traps with a binding energy slightly exceeding the thermal energy, while after deformation fairly extended regions appear (compared with the positron diffusion length) in which the concentration of small traps (~10 nm in size) appreciably diminishes with the simultaneous appearance of loosened regions with deep positron capture centres, in which the positron lifetimes are longer; relaxation takes place in such a way that the pores formed on deformation recombine and in addition increase in size as a result of fusion.

Consequently, having measured the lifetime of the positrons, it is possible to obtain data on the changes in the structure of the unoccupied volume occurring after the deformation of the polyimide film. However, in order to interpret the information obtained, it is necessary to study in detail the nature of the components of the complex annihilation time spectrum characteristic of the nonequilibrium state of the polymer. The problem formulated could not be solved with the aid of one of the positron methods[84,85] and for this reason a combined study has been carried out[88] of the annihilation of positrons in the deformed polyimide by measuring the lifetime of the positrons and the angular correlation of the annihilation emission.

Two series of experiments have been described.[88] In the first series, the polyimide film was subjected to uniaxial extension deformation by 20%. The film was then freed from the clamps and was allowed to relax freely. The lifetime spectra were recorded on a freely relaxing film at 1.5 h intervals. The parameters of the angular correlations were determined at 1 h intervals for 24 h.

In the second series of experiments, the stress relaxation process was investigated for the deformation $\varepsilon_0 = 20\%$. The characteristics of the angular correlations were determined for a film with fixed ends. The measurements were performed with the aid of a device which made it possible to deform specimens directly in the measuring chamber. At the same time the stress relaxation curves themselves (time variation of the stress) were recorded together with the strain recovery curves (time variation of the deformation).

The positron lifetimes obtained from the spectra are presented in Table 16 and in Fig. 33. In the structure of the time spectrum, fitted by three components, changes were observed, after deformation, in the annihilation characteristics, which then gradually relaxed to those characteristic of the initial polyimide specimen.

Three components were differentiated: the lifetime of the first short-lived (170–220 ps) component depended greatly on the relaxation time; the lifetime of the second component

Table 16. Variation of the annihilation characteristics of a polyimide film as a function of the duration of relaxation after 20% deformation.

Duration of relaxation /s	Lifetime			Angular correlation			
	τ_p /ps	τ_1 /ps	I_2 (%)	FWHM /mrad	Γ_1 /mrad	θ_p /mrad	I_p (%)
Unannealed specimen							
0	365	201	74.3	10.44	10.49	7.14	28.2
1	360	176	73.6	10.77	–	–	–
5	368	208	77.2	10.60	–	–	–
24	362	205	73.0	10.48	10.64	7.14	34.7
240	364	200	74.1	10.43	10.72	6.95	32.3
Annealed specimen							
0	368	220	76.3	–	–	–	–

Note. τ_p, τ_1, and I_2 are characteristics of the positron lifetime spectra quoted subject to errors of ±1, ±10, and ±1.5 respectively; FWHM is the full width at half maximum of the overall spectrum quoted subject to an error of ±0.05; Γ_1 is the FWHM for the first Gaussian quoted subject to an error of ±0.07; θ_p and I_p are the characteristics of the parabolic component of the angular correlation spectrum quoted subject to errors of 0.07 and 1.5 respectively.

(388 ±10 ps) was independent or depended only slightly on the state of the specimen, but appreciable changes in the intensity of this component were observed; the characteristics of the third component did not change during the experiment.

Experiments involving the measurement of the angular correlation (together with the measurement of the lifetime of the positrons) have also been performed.[88] Being unable to analyse in detail the results of these measurements we shall only note that, in the experiments with fixed ends (under the conditions of stress relaxation), an increase in the unoccupied volume after deformation and its subsequent slow relaxation, occurring as a result of the decrease in the concentration of micropores, are well manifested.

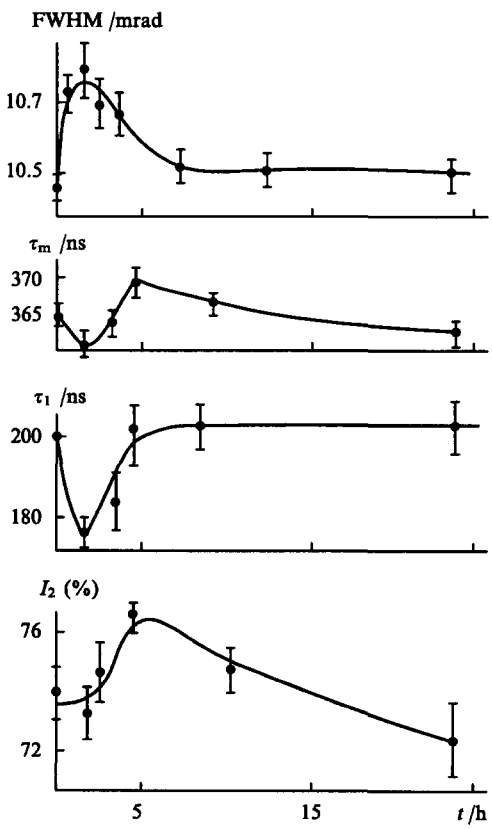


Figure 33. Dependence of the characteristics of the positron lifetime spectra on the relaxation time of a free polyimide film. For legend, see Table 16.

Overall, the changes in the macroparameters and microparameters of the polyimide films during the stress relaxation and strain recovery processes after deformation have been revealed by the positron diagnostic method. Nonmonotonic changes in the characteristics of the positron lifetime spectra and the angular correlations of the annihilation photons were observed during the strain recovery period. Two regions corresponding to changes in the positron-sensitive properties of the polyimide, associated with rapid and slow relaxation processes, were differentiated and differences were observed in the nature of the relaxation of the microporous structure of the polymer as a function of the deformation and strain recovery conditions. The observed effects are due to the formation of regions with local freeing of the molecular mobility.

All these experimental facts show that, during the stress relaxation process, the microporous structure of the polymer is rearranged, which is expressed by redistribution of the dimensions of the micropores and their fusion with one another. In this connection, it is of interest to compare the data obtained by the positron diagnostic method with the results of curve fitting with the aid of memory functions (Table 17). In the case of stress relaxation in the linear region of the mechanical behaviour, the correlation coefficient r, obtained using the memory function (19) is close to the value found with the aid of the memory function (18) and amounts to approximately unity. Consequently, the interactions of the relaxators and the diffusion of the microheterogeneities in the specimen take place at approximately the same rate. The fluctuation volume δ is 25.6 Å^3 per repeat unit of the polymer on ~20% deformation.

Under the conditions of stress relaxation and the recovery of the dimensions of the specimen, the quantities $m_1^* k_B/S_0$ and $m_2^* k_B/S_0$, proportional to the number of microheterogeneities in the specimen, are approximately the same after the removal of the load; on the other hand, $m_2^* k_B/S_0 > m_1^* k_B/S_0$ which indicates a greater number of active microheterogeneities participating in their diffusion in the material. The rate constant for the interaction of the relaxators in the case of stress relaxation is significantly lower (in the linear region of mechanical behaviour) than in the strain recovery relaxation process.

Since the concepts 'relaxator' and 'micropore' are comparable, one may conclude that the relaxation parameters obtained are in good agreement with the microstructural characteristics determined by the positron annihilation technique. During the relaxation of a free film, more favourable conditions are created for the diffusion of micropores and the formation of large and stable packing defects.

Table 17. Results of the fitting of the stress relaxation and strain recovery curves for polyimide film specimens using the memory functions $T_1(\tau)$ and $T_2(\tau)$.

Function $T_1(\tau)$							Function $T_2(\tau)$					
E_0 /MPa	k^* /min^{-1}	β	n	$\frac{S_0}{m_1 k_B}$ /min^{-1}	$\frac{m_1^* k_B}{S_0}$	r	E_0 /MPa	a	γ	$\frac{S_0}{m_2 k_B}$ /min^{-1}	$\frac{m_2^* k_B}{S_0}$	r
Stress relaxation												
2600.7	10^{-4}	0.2	6	$1.84 \cdot 10^{-5}$	2.26	0.987	2177	0.0113	0.5	$3.88 \cdot 10^{-4}$	3.79	0.993
Strain recovery												
–	10^{-2}	0.7	2.3	$1.84 \cdot 10^{-3}$	2.55	0.998	–	0.05	0.5	$6.0 \cdot 10^{-3}$	4.77	0.978

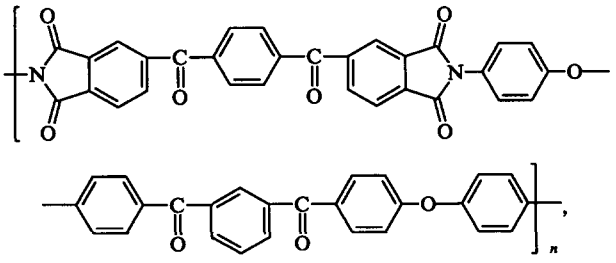
We shall now consider the results of a study designed to analyse the mechanisms of the deformation and relaxation in heat-resistant polymers capable of crystallising and of giving rise to a liquid crystal state.

Wierschke et al.[89] carried out a theoretical study of the moduli for single poly-*p*-phenylenebenzobisthiazole chains. The study was carried out by the molecular orbital method within the framework of the AMI semiempirical approximation. As a result of the investigation of rigid-chain polymers containing different heteroatoms in the repeat unit, it was found that the charge distribution and the nature of the bonds change on deformation. The moduli of elasticity of the chains obtained in this way were found to be greater than the quantities measured for the real materials. This is attributed both to the presence of heterogeneities in them and to the inadequacies of the computational method itself, which systematically predicts unduly high moduli. These have been mentioned by Shoemaker et al.[90] The results of the study by Wierschke et al.[89] permit a comparative analysis of the influence of the chemical structure of heat-resistant polymers on the rigidity of their chains and their mechanical properties.

The moduli of elasticity of the crystalline regions were measured by X-ray diffraction for poly(ether ketone), poly(ether ketone), and poly(*p*-phenylene sulfide).[91] This permitted a further study of the way in which the mechanical properties are related to the conformation of molecular chains and also to the intermolecular interaction in these polymers.

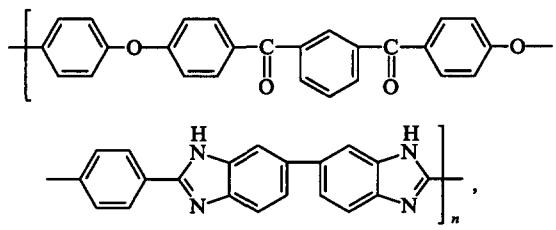
The crystallisation and morphology (which depends on the content of the *meta*- and *para*-isomers) of poly(aryl ketone ketones) have been investigated.[92] The poly(aryl ketone ketones) were synthesised from diphenyl ether and terephthalic and isophthalic acids. The polymers of this type have two different crystal structures. The addition of the *meta*-isomer diminishes the equilibrium melting point and the rate of crystallisation but increases the flexibility of the chains and the capacity for recrystallisation.

The transition in the crystal phase of the thermoplastic polymer with T_g = 216 °C[93]



has been investigated.[94] It was shown that this polyimide is semi-crystalline and may contain one or two crystalline phases. The mechanical properties of the polyimide films depend significantly on the type and level of crystallinity. Crystallinity promotes a significant increase in the modulus compared with the amorphous polymer, but reduces the capacity for deformation. Its extensive strength depends on the crystal form.

The mechanical properties of different heat-resistant polymers have been studied.[95–100] Among many heterocyclic polyethers, poly(arylene ether benzimidazole) exhibits the greatest strength. This was demonstrated by tests on nonoriented films of this material.[101] The influence of molecular mass on the mechanical properties of heat-resistant polymers



synthesised from 1,3-bis(4-fluorobenzoyl)benzene and 5,5′-bis-[2(4-hydroxyphenyl)-benzimidazole], has been investigated.[102] With decrease in molecular mass, the glass transition temperature and the temperature corresponding to 5% weight loss also diminish. However, the molecular mass does not influence (in the range investigated) the strength of these films and their moduli of elasticity.

Information about the structures and properties of rigid-chain aromatic polymers in the liquid-crystalline state may be found in a review.[103] Among other investigations in this field, we may mention the study[104] in which the mechanism of the plastic deformation in thermoplastic and thermosetting polyimides and their interpenetrating networks was studied.

VI. Networks, blends, and composites based on heat-resistant polymers

Prepregs based on epoxy-resins have been investigated with the aim of reducing brittleness.[105] The prepregs were modified with aromatic and heat-resistant thermoplastics. The epoxy-resins include systems based on the diglycidyl ethers of bisphenol A and bisphenol F, triglycidyl-*p*-aminophenol, and tetraglycidyldiaminophenylmethane. A poly(ether sulfone), polysulfone, and polyimide were chosen as the modifying thermoplastics. It was shown that the brittleness of the epoxy-resins and their relaxation behaviour depend significantly on the type and amount of the modifying agent. The results of dynamic mechanical analysis showed that the modification has only an insignificant influence on the shear modulus and the glass transition temperature. It is noteworthy that, in explaining the results obtained for the initial resins and the composites based on them, the authors[105] did not take into account the chemical interaction between the epoxy-resin and the heat-resistant aromatic polymers.

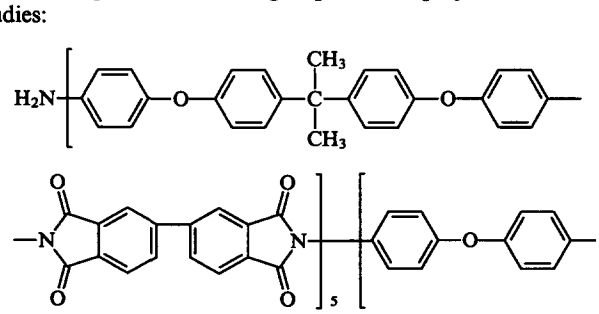
Materials based on epoxy-resins, modified with different amounts of a polyetherimide, have been obtained.[106,107] The mechanical properties of these materials have been studied in detail.[108] Attention was concentrated on the breakdown rigidity and the rate of liberation of energy. These characteristics increased with increasing content of the polyetherimide as the modifying agent. The authors were able to attain a decrease in the

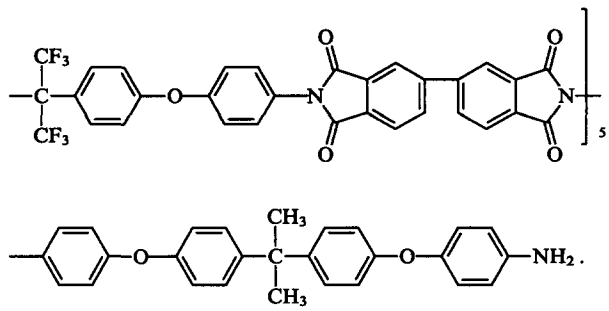
brittleness of the materials by introducing the poly(ether imide). Under these conditions, the mechanical behaviour is influenced significantly by, for example, parameters such as the initial length of the crack and phase separation processes. Different methods for the reduction of the brittleness of epoxy-resins by the introduction of a second component, which forms an independent phase during the curing process, were proposed in this connection.[109-114]

Mention may be made of yet another study[115] in which the relaxation behaviour of epoxy-resins with added polyetherimide was investigated in detail by means of dynamic mechanical analysis. It was found that the curing temperature and the composition of the blend influence significantly the storage modulus E', the loss modulus E'' and the mechanical loss factor $\tan\delta = E''/E'$. The quantity E' depends only slightly under these conditions on the content of the polyetherimide in the region of the glassy state. The opposite behaviour occurs in the region of transition from the glassy to the rubbery state: E' increases with increasing content of the poly(ether imide) and the glass temperature shifts under these conditions to the high temperature region. In the rubbery state, E' diminishes with increasing content of the poly(ether imide), which indicates a decrease in the degree of crosslinking. The loss factor $\tan\delta$ decreases with increasing content of the polyetherimide and the $\tan\delta$ maximum shifts at the same time towards higher temperatures with increasing curing temperature. The presence of only one maximum indicates the compatibility of the components.

In order to improve the compatibility of the components, one may use a chemical reaction between them.[116] This possibility has been implemented in relation to poly(ether ketones). Poly(ether ketones) reacted with polycarbonate, affording the corresponding block copolymers. Despite the fact that the initial components [the poly(ether ketone) and the polycarbonate] were incompatible, the block copolymers based on them were found to be homogeneous and exhibited one α-transition. The moduli of elasticity of the block copolymers were greater than those calculated assuming additivity.

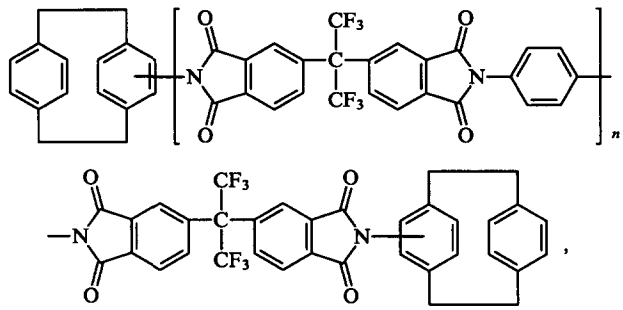
The preparation of blends of heat-resistant polymers with thermoset resins is an effective procedure for improving the mechanical properties of composites. Two approaches to the improvement of the mechanical properties of composites have been described.[117-119] The first provides for the preparation of 'thermoplastic polymer–thermoset polymer alloys'. The second is associated with the preparation of a system in which thin sheets of heat-resistant thermoplastic polymers serve as spacers in the initial composition with the thermoset polymer. The results of the application of both approaches to the improvement of the mechanical properties of composites have been published.[120-122] The diglycidyl ether of resorcinol and polyimide oligomers with the following terminal amino-groups were employed in the above studies:





The application of these approaches made it possible not only to improve the mechanical properties of composites but also to facilitate the performance of thermosetting systems.

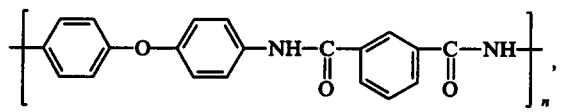
Graphite-reinforced plastics based on the cyclophane resins



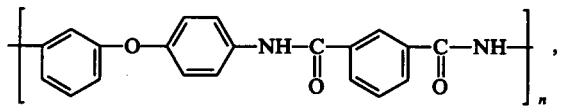
have been investigated.[123] The structure of these resins gives rise to a high thermal stability and glass transition temperature and promotes effective cross-linking via their end groups. An effective procedure for the improvement of the mechanical relaxation properties involves also the preparation of semi-interpenetrating polymer networks, in which the linear component is a copolymer based on polyimide.[124]

Analysis of the results of the above studies shows that the most promising ways of improving the mechanical properties of heat-resistant polymers and of developing new types of the latter consists in the synthesis of network systems comprising aromatic oligomers, using, for example, the polycyclotrimerisation reaction, and the preparation of networks with the aid of chemical reactions between oligomers (for example, epoxy oligomers) and heat-resistant aromatic polymers containing in the main chain reactive groups, which can interact chemically with the reactive groups of the oligomer. In certain cases, it is possible to obtain satisfactory mechanical properties without the employment of chemical reactions between the components of the blend. The results of a series of studies, with which we shall deal briefly below, confirm this conclusion. The mechanical behaviour of binary blends of poly(ether sulfone) and poly(phenylene sulfide),[125] poly(ether sulfone) and poly(ether ketones),[126-130] poly(ether ketone) and poly(ether imide),[131,132] polyamidoimide and an aromatic polyamide,[133] polyimides with different types of chemical structure,[134,135] polybenzimidazole and polyimides,[136-142] polybenzimidazole and polyarylate,[143] and poly(ether ketones) and poly(ether sulfone) [144] has been investigated.

We shall consider in greater detail the results of a study [145] in which binary blends based on two aromatic polyamides

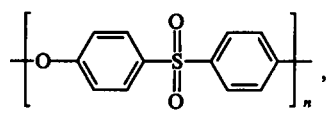


D

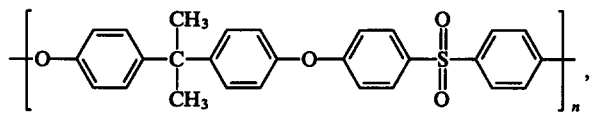


E

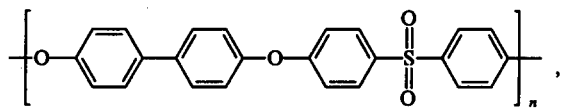
and three poly(ether sulfones)



F



G



H

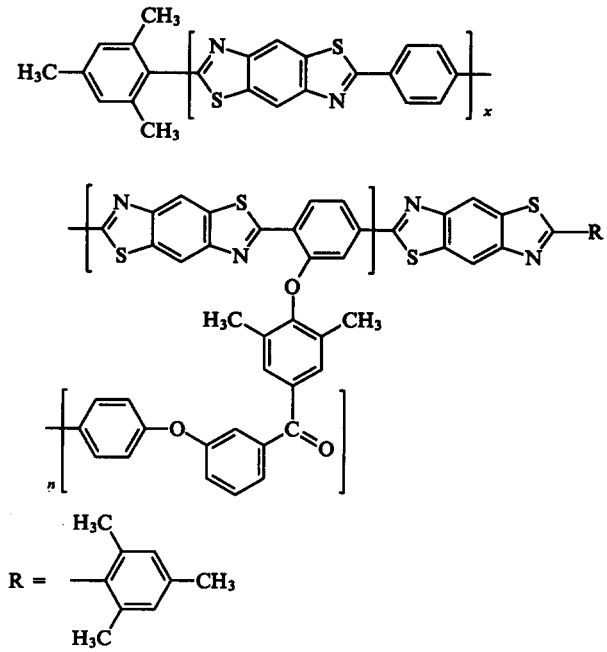
were investigated.

Films made of blends of these polymers were obtained by casting from solutions in *N,N*-dimethylacetamide and *N*-methyl-2-pyrrolidone. These films were investigated by dynamic mechanical analysis, differential scanning calorimetry, and IR spectroscopy; the ultimate mechanical characteristics were also measured. The principal result of this study was the observation of crystallisation induced by the presence of the second component, which entails an increase in the heat resistance of the systems, particularly after their annealing. Test results were achieved for blends based on compounds **D** and **F**. The initial films, for example those prepared from polymers **D** and **F**–**H**, were transparent, but after heat treatment they became opaque and their quality improved.

Thermotropic liquid-crystalline polymers are used nowadays to improve the mechanical properties of heat-resistant polymers. One of the methods of preparation of composites with a high strength and rigidity involves the blending of liquid-crystalline polymers with thermoplastics. There have been fairly numerous studies (see, for example, Refs 146–157) in which the improvement of the mechanical properties of heat-resistant polymer matrices was achieved by adding thermotropic liquid-crystalline polymers to them. Among the heat-resistant polymers, such studies have been performed for poly(ether ketone), poly(ether imide), poly(phenylene sulfide), and polycarbonate. The phenomenon of synergism is characteristic of certain blends of the above polymers and liquid-crystalline polymers.

A series of publications [156–158] have been devoted to the problem of mechanical anisotropy, which has been observed in blends of liquid-crystalline polymers with heat-resistant aromatic systems.

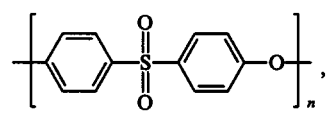
The studies [159–162] in which an approach to the preparation of molecular composites was proposed are of significant interest. A molecular composite consists of rigid-chain rod-like polymers, introduced into a polymer matrix, which is made up of a flexible-chain polymer with coiled macromolecules. The rigid-chain macromolecules then serve as strengthening elements of the composite. For example, a graft copolymer based on a rigid-chain polybenzobisthiazole (main chain) and a polyetherketone (side chain) has been synthesised.[163]



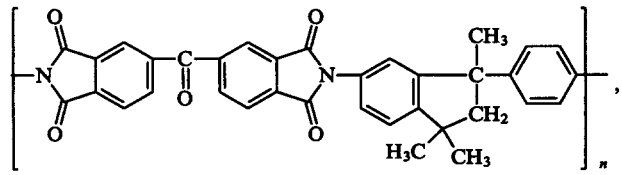
A detailed study of the relaxation properties of this system by dynamic mechanical analysis has been described.[164]

In estimating the relaxation properties, it is important to take into account the microphase separation process, which may occur when thermoplastics are blended with thermosetting systems and may also arise on hardening of the composite. The results of studies [109, 165, 166] in which composites based on blends of a polyethersulfone with an epoxy resin are instructive in this respect. Hardening results in the formation of a two-phase system, which promotes an improvement in the mechanical properties (a decrease in brittleness). Detailed measurements of the enthalpy relaxation have been made for such systems. Subject to a satisfactory fitting of the relaxation curves (for example, with the aid of the Kohlrausch–Williams–Watts function), such measurements can be used to predict the long-term behaviour of polymeric materials under ageing conditions.

Another example of a combined investigation of the relaxation properties may be found in a study [167] in which the behaviour of a blend of the poly(ether sulfone)



and the polyimide



was investigated. These polymers are compatible and their behaviour was investigated by differential scanning calorimetry, dynamic mechanical analysis, and rheological methods. For a polyimide content > 10% microphase layer separation occurred and was manifested by a sharp alteration of the rheological properties. The author also did not rule out the occurrence of a cross-linking process, which may be superimposed on the microphase layer-separation process.

VII. Conclusion

Analysis of the results of relaxation measurements for heat-resistant aromatic polymers permits a series of conclusions about the characteristic features of their mechanical behaviour. One of these conclusions, which at first sight may appear trivial, is that heat-resistant aromatic polymers are capable of withstanding for a long time much greater mechanical loads than traditional plastics in the region of not only high but also moderate and low temperatures. This conclusion is based on the results of measurements of stress relaxation and creep, which show that both processes are less marked than for the usual plastics. Therefore, in creating constructional materials which can be used not only at high but also at low temperatures and for large loads, preference must be given to heat-resistant aromatic polymers. At the same time, it has become evident that, in order to discover the advantages of one set of polymers over others, relaxation measurements are not only desirable but also essential.

One should bear in mind that, even within the class of heat-resistant polymers itself, the structure of the latter has an appreciable influence on their mechanical relaxation properties. For example, in terms of critical stresses, polyimide is superior to PBO; the rate of stress relaxation in polyimide is lower than in PBO. On the other hand, in the range of comparatively low temperatures, polyimide is inferior to PBO in terms of these features.

In dynamic mechanical analysis, heat-resistant aromatic polymers exhibit a series of relaxation transitions associated with the freeing of the molecular mobility of individual groups and segments. A study of the mechanism of these processes by synthesising and investigating a series of polymers in which different hinge atoms and groups are deliberately 'taken away' demonstrated unambiguously that the β-transition in these polymers is associated with the freeing of the molecular mobility of phenylene groups.

However, attention should be concentrated on the characteristics of the mechanical behaviour of heat-resistant polymers, which are manifested in the analysis of relaxation transitions under the conditions of static measurements of stress relaxation and creep. The essential feature of the transitions is that, within the range of the glassy state at temperatures greatly below the glass transition temperature, the relaxation processes are accelerated sharply and the critical stresses are reduced. These transitions play a significant role in an objective assessment of the mechanical workability of polymers. If the polymer is designed for use at variable temperatures and is to be subjected to appreciable mechanical loads, then, on heating to the transition temperature, the mechanical workability may be lost long before the glass transition temperature. The occurrence of these transitions is undoubtedly associated with the linearity of the mechanical behaviour, whereupon appreciable deformations result in a change of the relaxation parameters of the polymer.

Another characteristic feature of the relaxation behaviour of aromatic heat-resistant polymers is that, over a fairly wide temperature range within the region of the glassy state, the parameters of the relaxation processes are relatively insensitive to temperature. This temperature range confines the region of the stable workability of the polymers and it is desirable to take it into account when selecting a polymeric material for each specific task.

One of the significant features of the mechanical behaviour of aromatic polymers is their ability to develop large deformations (i.e. to undergo nonbrittle disruption) in the region of low and ultra-low temperatures. Even at the temperature of liquid helium, the deformation of aromatic polymers attains a large percentage value and relaxation processes are also manifested at these temperatures. Analysis of the mechanisms of deformation and relaxation with the aid of the positron annihilation method has shown (in relation to polyimide) that these polymers have a unique electronic structure and a very narrow size distribution of their pores. It may be that this is the cause of the surprising behaviour at low temperatures. Aromatic polymers also have another significant advantage over the usual ones (for example, Teflon) — they are capable of withstanding an enormous number of thermocycles over a temperature range from 200 °C to the temperature of liquid nitrogen without loss of mechanical strength.

Finally, many aromatic polymers contain in their chains functional groups (ester, amide, imide, etc. groups) capable of interacting with the functional groups of thermoset oligomers and of curing them. This property is used in creating composite materials based on traditional polymers (for example, epoxy resins), which are strengthened when heat-resistant polymers are introduced into them and lose their brittleness.

References

1. A A Askadskii, G L Slonimskii *Usp. Khim.* **43** 1688 (1975) [*Russ. Chem. Rev.* **43** 767 (1975)]
2. A A Askadskii *Struktura i Svoistva Teplostoikikh Polimerov* (Structure and Properties of Heat-Resistant Polymers) (Moscow: Khimiya, 1981)
3. A A Askadskii *Deformatsiya Polimerov* (Deformation of Polymers) (Moscow: Khimiya, 1973)
4. R B Banyavichyus, A V Ambrazyavichyus, A A Askadskii *Vysokomol. Soedin., Ser. A* **26** 2307 (1984)
5. R B Banyavichyus, A I Marma, A A Askadskii *Vysokomol. Soedin., Ser. A* **21** 1383 (1979)
6. A A Askadskii, Z S Vikhauskas, R B Banyavichyus, A I Marma *Vysokomol. Soedin., Ser. A* **25** 203 (1983)
7. A A Mavricheva, A A Askadskii, V E Gul' *Vysokomol. Soedin., Ser. A* **19** 2379 (1977)
8. A A Askadskii, T V Todadze *Mekh. Kompoz. Mater.* 713 (1980)
9. Yu S Kochergin, A A Askadskii, G L Slonimskii, A P Travnikova, E S Krongauz, V V Korshak *Vysokomol. Soedin., Ser. A* **19** 2543 (1977)
10. Yu S Kochergin, A A Askadskii, S N Salazkin, I A Bulgakova, V F Alekseev, S V Vinogradova, G L Slonimskii, V V Korshak *Vysokomol. Soedin., Ser. A* **20** 880 (1978)
11. R B Banyavichyus, A I Barauskas, A V Ambrazyavichyus, A A Askadskii *Vysokomol. Soedin., Ser. A* **25** 1436 (1983)
12. Z S Vikhauskas, R B Banyavichyus, A A Askadskii, A I Marma *Vysokomol. Soedin., Ser. A* **25** 2351 (1983)
13. M S Matevosyan, A A Askadskii, G L Slonimskii *Vysokomol. Soedin., Ser. A* **29** 761 (1987)
14. V V Korshak, G L Slonimskii, A A Askadskii, A L Rusanov, T V Lekae, M S Matevosyan *Vysokomol. Soedin., Ser. A* **31** 34 (1989)
15. V V Korshak, A L Rusanov, T V Lekae, K A Bychko *Vysokomol. Soedin., Ser. A* **29** 761 (1987)
16. A A Askadskii, Yu I Matveev, M S Matevosyan *Vysokomol. Soedin., Ser. A* **32** 2157 (1990)
17. Yu I Matveev, A A Askadskii *Vysokomol. Soedin., Ser. A* **36** 436 (1994)
18. A A Askadskii, S N Salazkin, K A Bychko, N G Gileva, M G Zolotukhin, G L Slonimskii, S R Rafikov *Vysokomol. Soedin., Ser. A* **31** 2667 (1989)
19. G L Slonimskii, E V Todadze, A A Askadskii *Vysokomol. Soedin., Ser. A* **23** 1305 (1981)
20. E B Trostyanskaya (Ed.) *Termoustoichivost' Plastikov Konstruktsionnogo Naznacheniya* (Heat Resistance of Construction Plastics) (Moscow: Khimiya, 1980)
21. D A Wigley *Mechanical Properties of Materials at Low Temperatures* (New York: Plenum, 1971)
22. T I Sogolova, M I Demina *Mekh. Kompoz. Mater.* 387 (1977)
23. I I Perepechko *Svoistva Polimerov pri Nizkikh Temperaturakh* (Properties of Polymers at Low Temperatures) (Moscow: Khimiya, 1977)
24. I I Perepechko, E B Voloshilov *Vysokomol. Soedin., Ser. A* **19** 1620 (1977)
25. R B Banyavichyus, Z B Migonene, A A Askadskii *Vysokomol. Soedin., Ser. A* **26** 2604 (1984)
26. V V Pustovalov, V S Fomenko, Z B Migonene, A A Askadskii *Vysokomol. Soedin., Ser. B* **32** 363 (1991)

27. A A Askadskii, Z B Migonene, P Yu Zhilyukas, S N Salazkin, A V Samoryadov, V A Sergeev *Vysokomol. Soedin., Ser. B* **32** 188 (1991)
28. M Yu Kantsel'son, G A Balaev, in *Polimernye Materialy. Spravochnik* (Polymer Materials. Handbook) (Leningrad: Khimiya, 1982) p. 317
29. G L Slonimskii *Zh. Tekh. Fiz.* 1979 (1939)
30. A P Bronskii *Prikl. Matem. Mekh.* (5) 5 (1941)
31. A A Askadskii, V G Dashevskii, Yu S Kochergin *Vysokomol. Soedin., Ser. B* **19** 500 (1977)
32. A A Askadskii *Mekh. Kompoz. Mater.* 403 (1987)
33. R J Gaylord, B Joss, J T Bendler, E A Di Marzio *Br. Polym. J.* **17** 126 (1985)
34. A A Askadskii, A L Blyumenfel'd, E G Gal'pern, A L Chistyakov *Vysokomol. Soedin., Ser. A* **30** 886 (1988)
35. A A Askadskii, G V Surov, V V Nemchinov, A L Blyumenfel'd, Z S Vikhauskas *Vysokomol. Soedin., Ser. A* **31** 1320 (1989)
36. A A Il'yushin, B E Pobedrya *Osnovy Matematicheskoi Teorii Termovyazkouprugosti* (Fundamentals of a Mathematical Theory of Thermoviscoelasticity) (Moscow: Nauka, 1970)
37. A E Yee, R G Bankert, K L Ngai, R W Rendell *J. Polym. Sci., Part B, Polym. Phys.* **26** 2463 (1988)
38. A A Askadskii, M P Valetskii *Mekh. Kompoz. Mater.* 441 (1990)
39. A A Askadskii, Yu I Matveev *Khimicheskoe Stroenie i Fizicheskie Svoistva Polimerov* (Chemical Structure and Physical Properties of Polymers) (Moscow: Khimiya, 1983)
40. A A Askadskii, R B Banyavichyus, Z S Vikhauskas, A I Marma, A L Blyumenfel'd *Vysokomol. Soedin., Ser. A* **30** 1684 (1988)
41. A A Askadskii, A I Marma, R B Banyavichyus, Z S Vikhauskas *Vysokomol. Soedin., Ser. A* **31** 2271 (1989)
42. A A Askadskii, V A Beloshenko, K A Bychko, V V Shaposhnikova, A V Samoryadov, O V Kovriga, S N Salazkin, V A Sergeev, V G Slobodina, Ya V Genin *Vysokomol. Soedin., Ser. A* **36** 1143 (1994)
43. B J Jensen, P M Hergenrother *Hegh Perform. Polym.* **1** 31 (1989)
44. A A Askadskii, T R Razmadze, S N Salazkin, V A Sergeev, A V Samoryadov, K A Bychko, O V Kovriga, T M Babchinitser, A Varada Radzhulu *Vysokomol. Soedin., Ser. A* **33** 1239 (1991)
45. M I Bessonov, M M Koton, V V Kudryavtsev, L A Laius *Polyimides: Thermal Stable Polymers* (New York: Consultants Bureau, 1987)
46. W J Wrasidlo *J. Macromol. Sci., Phys. B* **6** 559 (1972)
47. R M Ikeda *J. Polym. Sci., Polym. Lett. Ed.* **4** 353 (1966)
48. G M Bartenev, M M Koton *Dokl. Akad. Nauk SSSR* **305** 112 (1989)
49. G M Bartenev *Plaste Kautsch.* **36** 151 (1989)
50. G A Bernier, D E Kline *J. Appl. Polym. Sci.* **12** 493 (1968)
51. O G Nikol'skii, A A Askadskii, S N Salazkin, G L Slonimskii *Mekh. Kompoz. Mater.* 963 (1983)
52. O G Nikol'skii, A A Askadskii, G L Slonimskii *Mekh. Kompoz. Mater.* 901 (1980)
53. E Butta, S D Petris, M Pasquini *J. Appl. Polym. Sci.* **13** 1073 (1969)
54. T Lim, V Frosini, V Zaleckas, D Morrow, J A Sauer *Polym. Eng. Sci.* **13** 51 (1973)
55. J K Gillham, H C Gillham *Polym. Eng. Sci.* **13** 447 (1973)
56. M Kochi, H Shimada, H Kambe *J. Polym. Sci., Polym. Phys. Ed.* **22** 1979 (1984)
57. M Kochi, S Isoda, R Yokota, H Kambe *J. Polym. Sci., Polym. Phys. Ed.* **24** 1621 (1986)
58. J E Harris, L M Robeson *J. Appl. Polym. Sci.* **35** 1877 (1988)
59. R H Pater *Polym. Eng. Sci.* **12** 13 (1991)
60. R P Chartoff, T W Chin *Polym. Eng. Sci.* **2** 244 (1980)
61. Z Sun, L Dong, Y Zhuang, L Cao, M Ding, Z Feng *Polymer* **33** 4728 (1992)
62. M Eisenberg, B Cavrol *J. Polym. Sci., Part C* **35** 129 (1971)
63. A Lukashov, V Feofanov, J D Schultze, M Boehning, J Springer *Polymer* **33** 2227 (1992)
64. C Schrauwen, T Pakula, G Vegner *Makromol. Chem.* **193** 11 (1992)
65. Chul Joo Lee Tae Won Sohn, Byoung Chul Lim, Van Sik Ha, in *The 34th IUPAC International Symposium on Macromolecules (Book of Abstracts) Prague, 1992* Sec. 1, p. 286
66. F E Arnold, S Z Cheng, S L-C Hsu, C J Lee, F W Harris *Polymer* **33** 5179 (1992)
67. R J Young, P P Ang *Polymer* **33** 975 (1992)
68. S Dirikov, Z Chen, D Wang *Polym. Prepr. Am. Chem. Soc.* **33** 483 (1992)
69. X Wu, Y Feng, S Dirikov, in *Radiation Curing of Polymeric Materials. ACS Symposium Series 417* (Eds C Hoyle, J Kinstl) (Washington, DC: American Chemical Society, 1990) p. 194
70. Y Aihara, P Gebe *Polym. Prepr. Am. Chem. Soc.* **33** 471 (1992)
71. T Kunugi, C Ichinose, A Suzuki *J. Appl. Polym. Sci.* **31** 429 (1986)
72. D Grubb, F Keamey *J. Polym. Sci., Part B, Polym.-Phys.* **28** 2021 (1990)
73. T Kunugi, A Suzuki, M Hashimoto *J. Appl. Polym. Sci.* **26** 1951 (1981)
74. E J Roche, R F Van Kavelaar, G Pausson *Polym. Commun.* **30** 151 (1989)
75. A A Hamza, J J Sikorskii *Microscopy* **113** 15 (1978)
76. M J Pluta *Microscopy* **149** 97 (1988)
77. H H Yang, M P Chouinard, W J Ling *J. Polym. Sci., Polym. Phys. Ed.* **20** 281 (1982)
78. A W Harsthorne, D K Laing *Microscopy* **32** 11 (1984)
79. N Barakat, A A Hamza *Interferometry of Fibrous Materials* (Bristol: Adam Hilger, 1990)
80. M Pluta *Polymer* **33** 1553 (1992)
81. J-H Jou, P-T Huang, H-C Chen, C-N Liao *Polymer* **33** 967 (1992)
82. S A Fawas, A N Palazotto, C S Wang *Polymer* **33** 100 (1992)
83. A A Askadskii, S A Tishin, V V Kazantseva, O V Kovriga *Vysokomol. Soedin., Ser. A* **32** 2437 (1990)
84. A Z Varisov, Yu N Kuznetsov, E P Prokop'ev, A I Filip'ev *Usp. Khim.* **50** 1892 (1981) [*Russ. Chem. Rev.* **50** 991 (1981)]
85. P Kindl, G Retter *Phys. Status Solidi A* **104** 707 (1987)
86. B D Malhotra, R A Petrick *Eur. Polym. J.* **19** 457 (1983)
87. C K Hu, G R Gruzalski *Phys. Rev. B* **27** 1 (1983)
88. A A Askadskii, S A Tishin, M I Tsapovetskii, V V Kazantseva, O V Kovriga, V A Tishin *Vysokomol. Soedin., Ser. A* **34** (12) 62 (1992)
89. S G Wierschke, J R Shoemaker, P D Haaland, R Pachter, W W Adams *Polymer* **33** 3357 (1992)
90. J R Shoemaker, T Horn, P D Haaland, R Pachter, W W Adams *Polymer* **33** 3351 (1992)
91. T Nishino, K Nakamae *Polymer* **33** 736 (1992)
92. K H Gardner, B S Hsiao, R R Matheson, B A Wood *Polymer* **33** 2483 (1992)
93. J R Pratt, T L St Clair, M K Gerber, C R Gautreaux, in *Polyimides: Materials, Chemistry and Characterisation* (Eds C Feger, M M Khojastch, J E McGrath) (Amsterdam: Elsevier, 1989) p. 193
94. C R Cautreaux, J R Pratt, T L St Clair *J. Polym. Sci., Part B, Polym.-Phys.* **30** 71; 162 (1992)
95. D M White, T Takekoshi, F J Williams, H M Relles, P E Donahue, H J Klopfer, G R Toncks, J S Manello, T O Mattews, R W Shlueny *J. Polym. Sci., Polym. Chem. Ed.* **19** 1635 (1981)
96. J L Hedrick, J W Labadie *Macromolecules* **21** 1883 (1988)
97. J W Connell, P M Hergenrother *Polym. Prepr. Am. Chem. Soc.* **29** 172 (1988)
98. F W Harris, J E Korieski *Polym. Mater. Sci. Eng.* **61** 370 (1989)
99. J W Connell, P M Hergenrother *Polym. Mater. Sci. Eng.* **60** 527 (1988); *J. Polym. Sci., Part A, Polym. Chem.* **29** 1667 (1991)
100. J W Connell, P M Hergenrother *High. Perform. Polym.* **2** 211 (1990)
101. J D Smith, J W Connell, P M Hergenrother *Polym. Prepr. Am. Chem. Soc.* **32** 193 (1991)
102. P M Hergenrother, J D Smith, J W Connell *Polym. Prepr. Am. Chem. Soc.* **33** 411 (1992)
103. M Ballauff *GII* **36** (11) 1095 (1992)
104. B Z Jang, R H Pater, M D Soucek, J A Hinkley *J. Polym. Sci., Part B, Polym.-Phys.* **30** 643 (1992)
105. M Stangle, V Alstaat, H Tesh, Th Weber *Adv. Mater. Proceedings of the 12th International European Chapter Conference, Maastricht, 1991* p. 33
106. H H Chen, N R Schott *Polym. Prepr. Am. Chem. Soc.* **30** 457 (1990)
107. H H Chen, ThD, University of Massachusetts at Lowell, 1991
108. H H Chen, N R Schott *Polym. Prepr. Am. Chem. Soc.* **33** 498 (1992)
109. C B Bucknall, I K Partridge *Polymer* **24** 639 (1983)
110. R S Raghava *J. Polym. Sci., Part B, Polym.-Phys.* **25** 1017 (1987)
111. G R Almen, R K Maskell, V Molhorta, M S Sefton, P T McGrail, S P Wilkinson *SAMPE Symp.* **33** 979 (1989)

112. J A Cecere, J L Hedrick, J E McGrath *SAMPE Symp.* **31** 580 (1986)
113. J A Cecere, J E McGrath *Polym. Prepr. Am. Chem. Soc.* **27** 299 (1986)
114. C B Bucknall, A H Gilbert *Polymer* **30** 213 (1989)
115. H H Chen, N R Schott *Polym. Prepr. Am. Chem. Soc.* **33** 495 (1992)
116. R J Kumpf, D Nerger, C Lautman, H Pielartzik, R Wehrmann *Polym. Prepr. Am. Chem. Soc.* **32** 280 (1991)
117. C B Bucknall, A H Gilbert *Polymer* **30** 213 (1989)
118. Eur. P. 0 311 349 (1989)
119. J E Masters, J L Courter, R E Evans *SAMPE Symp.* **31** 844 (1986)
120. H Kishi, N Odagiri, K Tobukuro, in *Proceedings of the 3rd European Symposium on Polymer Blends, Cambridge, 1990* A8
121. N Odagiri, H Kishi, T Nakae, in *Proceedings of the American Society for Composites, the 6th Technical Conference, 1991* p. 43
122. N Odagiri, H Kishi *Polym. Prepr. Am. Chem. Soc.* **33** 384 (1992)
123. J K Sutter, J Waters, M Schuerman *Polym. Prepr. Am. Chem. Soc.* **33** 366 (1992)
124. C L Leung, S Y L Kreisler, A L Landis *Polym. Prepr. Am. Chem. Soc.* **33** 508 (1992)
125. H Zeng, K Mai *Makromol. Chem.* **187** 1787 (1986)
126. C K Sham, C H Lae, D J Williams, F E Karasz, W J McKnight *Br. Polym. J.* **20** 149 (1988)
127. Q Guo, J Huang, T Chen *Polym. Bull.* **20** 517 (1988)
128. Q Guo, J Huang, T Chen, H Zhang, Y Yang, C Hou, Z Feng *Polym. Eng. Sci.* **30** 44 (1990)
129. Z Wu, Y Zheng, X Yu, T Nakamura, R Yosomiya *Angew. Makromol. Chem.* **171** 119 (1989)
130. Z Wu, Y Zheng, H Yan, T Nakamura, T Nozawa, R Yosomiya *Angew. Makromol. Chem.* **173** 163 (1989)
131. J E Harris, L M Robeson *J. Appl. Polym. Sci.* **35** 1877 (1988)
132. G Crevecoeur, G Groenincks *Macromolecules* **24** 1190 (1991)
133. K Yamada, T Mitsutake, M Takayanagi, T Kajiyama *J. Macromol. Sci., Chem.* **A26** 891 (1989)
134. R Yokota, R Horiuchi, M Kochi, H Soma, I Mita *J. Polym. Sci., Polym. Lett. Ed.* **26** 215 (1988)
135. I Mita, M Kochi, M Hasegawa, T Iizuka, H Soma, R Yokota, R Horiuchi, in *Polyimides: Materials, Chemistry and Characterisation* (Eds C Feger, M M Khojastch, J E McGrath) (Amsterdam: Elsevier, 1989) p. 1
136. L Leung, D J Williams, F E Karasz, W J McKnight *Polym. Bull.* **16** 457 (1986)
137. G Guerra, D J Williams, F E Karasz, W J McKnight *J. Polym. Sci., Polym. Phys. Ed.* **26** 301 (1988)
138. S Stankovic, G Guerra, D J Williams, F E Karasz, W J McKnight *Polym. Commun.* **29** 14 (1988)
139. G Guerra, S Choe, D J Williams, F E Karasz, W J McKnight *Macromolecules* **21** 231 (1988)
140. P Musto, F E Karasz, W J McKnight *Polymer* **30** 1012 (1989)
141. J Grobelny, D Rice, F E Karasz, W J McKnight *Macromolecules* **23** 2139 (1990)
142. D S Lee, G Quin *Polym. J.* **21** 751 (1989)
143. T Chung, P N Chen *Polym. Eng. Sci.* **30** 1 (1990)
144. R E Rigby *Polym. News* **9** 325 (1984)
145. S Nakata, M Kakimoto, Y Imai *Polymer* **33** 3873 (1992)
146. G Crevecoeur, G Groenincloc *Polym. Eng. Sci.* **30** 532 (1990)
147. G Kiss *Polym. Eng. Sci.* **27** 410 (1987)
148. K G Blizard, D G Baird *SPE 44th ANTEC (Proceedings of the Conference) Boston, 1985* Vol. 311, p. 301
149. A I Isaev, M Modic *Polym. Compos.* **8** 158 (1987)
150. K G Blizard, D G Baird *Polym. Eng. Sci.* **27** 563 (1987)
151. P Zhuang, J L White, T Kyu *Polym. Eng. Sci.* **28** 1095 (1988)
152. A Kohli, N Chung, R A Weiss *Polym. Eng. Sci.* **29** 573 (1989)
153. US P. 4 835 047 (1989)
154. A Mehta, A I Isaev *Polym. Eng. Sci.* **31** 971 (1991)
155. P R Subramanian, A I Isaev *Polymer* **32** 1961 (1991)
156. K G Blizard, T S Wilson, D G Baird *Int. Polym. Process.* V 58 (1990)
157. K G Blizard, D G Baird *Int. Polym. Process.* IV 172 (1989)
158. J P de Souza, H H Chen, D G Baird *Polym. Prepr. Am. Chem. Soc.* **33** 392 (1992)
159. US P. 4 207 407 (1980)
160. W F Hwang, D R Wiff, G I Benner, T E Helminiak *J. Macromol. Sci. Phys.* **B22** 231 (1983)
161. T Kyu, T E Helminiak *Polymer* **28** 2130 (1987)
162. C S Wang, I J Goldfarb, T E Helminiak *Polymer* **29** 825 (1988)
163. M Dotrong, M H Dotrong, R C Evers *Polym. Prepr. Am. Chem. Soc.* **33** 477 (1992)
164. U M Vakil, C S Wang, C Y-C Lee, M H Dotrong, M Dotrong, R C Evers *Polym. Prepr. Am. Chem. Soc.* **33** 479 (1992)
165. C D Breach, M J Folkes, J M Barton *Polymer* **33** 3080 (1992)
166. R S Raghava *J. Polym. Sci., Polym. Chem. Ed.* **25** 1017 (1987)
167. K Liang, J Grebowicz, E Valles, F E Karasz, W J McKnight *J. Polym. Sci., Part B, Polym. Phys.* **30** 465 (1992)