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Structure and Properties of Heat-resistant Polymers

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The influence of the chemical structure of heat-resistant aromatic polymers on their physical properties is discussed mainly in relation to mechanical properties. Methods for determining the heat resistance of polymers and their mechanical performance are described, and the calculation of the principal physical characteristics from the chemical structure of the repeating unit is explained. A detailed account is given of the effect of chemical structure on the glass point of heat-resistant aromatic polymers and on relaxation transitions within the temperature range of the vitreous state. A list of 131 references is included.

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I. INTRODUCTION

The multitude of scientific publications appearing during recent years are testimony to the attention paid by specialists to the synthesis and the properties of heat-resistant polymers. A widely used route to such polymers is the synthesis of various polyheteroarylenes. Saturation of the polymer chain with aromatic ring systems and ladder-like fragments leads to increases in both skeletal and kinetic rigidity of the macromolecules, and hence to significant rises in the glass point and in the modulus of elasticity, with improvements in the strength and other properties of the polymer systems.

We attempt to summarise published information on the effect of the chemical structure and the supermolecular structure of the broad class of polyheteroarylenes and certain other heat-resistant polymers on their various physical properties, including mechanical (relaxation and strength), electrical, etc. properties. Special attention is paid to the nature of the heat resistance of polymers. These problems have recently been dealt with in several monographs [1-7] and reviews [8-10]. The present Review, therefore, will discuss the most recent research results, not covered in the above publications.

II. CHARACTERISTICS OF THE HEAT RESISTANCE OF POLYMERS

Before discussing results we must examine the very concept of the "heat resistance of polymers". According to one definition [11] "heat resistance is the ability of a polymer to retain at high temperatures the hardness necessary for the performance of articles made from it". In practice heat resistance is often measured in terms of certain temperatures, at which deformation of the polymer by a strictly defined amount occurs under a specified load (e.g Vicat or Martens heat resistance). With such a measure it is not always borne in mind that actual softening† of a material (i.e. loss of heat resistance) may take place not only at the glass point, determined under certain mechanical conditions, but also at any point within a range of temperatures if other stresses are applied.

In this connection Korshak [1,2] understands by heat resistance the "limiting temperature at which a polymer loses its mechanical strength under the influence of a particular load". It is very significant that this limiting temperature is influenced not only by the magnitude but also by the duration of the mechanical stress. Small stresses acting for a long time may produce the same breakdown of the material as do large stresses, when softening or fracture takes place rapidly. The same applies also to the temperature: fracture or softening occurs after a longer time at a comparatively low temperature than at a comparatively high temperature under otherwise similar conditions. The heat resistance of a plastic, i.e. retention of shape and integrity by the solid, can therefore be characterised physically either by a time [12] (under specified mechanical and thermal conditions),

†Since the softening of a material may present two different aspects—softening of a solid (i.e. an abrupt decrease in Young's modulus) and the appearance of fluidity—the concept of "softening temperature" requires refinement. If the decrease in Young's modulus is important, the softening temperature of a vitreous polymer coincides with the glass point, and that of a crystalline polymer with the melting point. If, however, the appearance of fluidity is significant, the softening temperature is usually defined as that at which a substance in a capillary begins to flow under its own weight, and then coincides with the pour point (in the absence of degradation). If a solid polymer (vitreous or crystalline) undergoes chemical degradation when heated, its softening temperature coincides with the beginning of intense thermal degradation.

by a maximum performance temperature (with a definite mechanical constraint acting for a specified period), or by a maximum permissible stress (acting under specified temperature and time conditions).

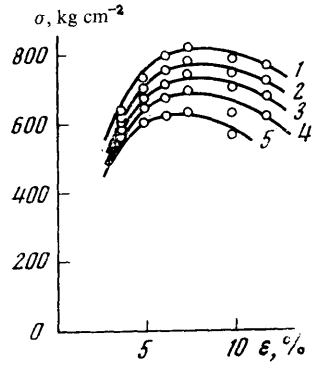


Figure 1. Isochronous dependence of stress σ on deformation ϵ for a polyimide of anilinefluorene and oxy-4,4′-diphthalic dianhydride (POI-10) at 130°C for different relaxation times t_r (min): 1) 1; 2) 3; 3) 10; 4) 60; 5) ∞.

If the conditions of service of the material require that its deformation should not exceed a specified value, the heat resistance will be characterised by the time of retention of shape t_{sh}, during which deformation under load (under certain temperature conditions) does not exceed this specified value. If, however, the stress in a material must not fall (owing to relaxation) below a required value, the heat resistance will be characterised by the time t_r during which this condition is satisfied (under specified temperature conditions).

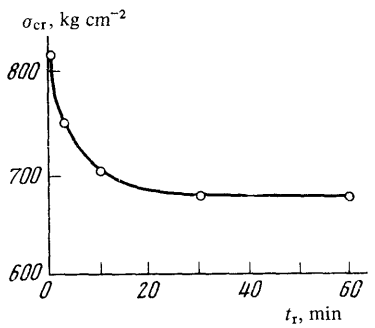


Figure 2. Dependence of σ_{cr} on t_r for POI-10 at 130°C.

To determine the maximum stresses that can be retained in a polymer for a specified time after the beginning of relaxation it is necessary to plot the stress σ against the deformation ϵ, when each curve corresponds to a definite duration of relaxation, i.e. is an isochronous dependence. Such relations usually pass through a maximum (Fig. 1). This maximum stress σ_{cr} depends significantly, of course, on the duration t_r of relaxation, as is illustrated by Fig. 2 for the polyimide of anilinefluorene and the dianhydride of the 3,3′,4,4′-tetracarboxylic acid of diphenyl ether. The dependence of σ_{cr} on t_r shows a monotonic decrease and conforms closely to Kohlrausch's equation.

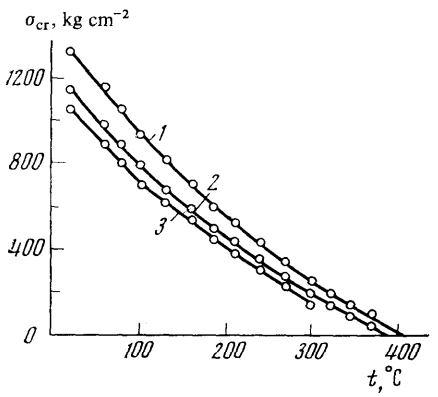


Figure 3. Temperature dependence of σ_{cr} for POI-10 after different relaxation times: 1) 1 min; 2) 60 min; 3) ∞.

From this equation we can determine the relaxation parameters, among which the most interesting is the maximum stress $\sigma_{cr,\infty}$ produced in a polymer by the completion of relaxation. It is a structural characteristic of the material, depending only on the chemical structure and the supermolecular structure. The temperature dependence of σ_{cr} determined for different relaxation times provides a complete description of the heat resistance of the polymer material (Fig. 3). These graphs also enable the period t_r of retention of the relaxing stress to be determined as a function of lg σ_{cr}. When the times are short these relations are linear (Fig. 4) and are described by the equation

$$t_r = A\sigma_{cr}^{-(\alpha_0 - \kappa T)} e^{U/RT}, \qquad (1)$$

where A, α_0, κ, and U are parameters of the material, R is the universal gas constant, and T is the absolute temperature. A more complicated relation applies for longer relaxation times [12]. The temperature dependence of $\sigma_{cr,\infty}$ and the dependence of t_r on σ_{cr} have since been used by several workers in assessing the influence of the chemical structure of a polymer on its heat resistance (see below).

Lengthy experiments are required to characterise heat resistance by the measurement of stress relaxation throughout the ranges of possible temperatures and deformations for each polymer. Such a determination should therefore be reserved for assessing the heat resistance only of the most promising individual representatives of a given class of polymers. More rapid assessment can be made by a widely used method [13-16] in which stress relaxation is examined under non-isothermal

conditions. For this purpose prismatic monolithic specimens of the polymer are placed between the working plates of a relaxometer and are deformed a certain amount, after which the temperature is raised linearly with time. In fixed specimens under such conditions, of course, compressive stresses arise as a consequence of the tendency to thermal expansion. With rise in temperature the stress increases to a certain limit, after which it falls as a result of accelerating relaxation, to reach zero at the glass point. By imposing different initial deformations on a specimen, we can obtain a series of such relaxation curves, each with its maximum (Fig. 5).

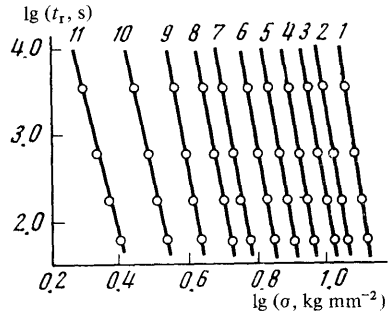


Figure 4. Dependence of lg t_r on lg σ_{cr} for POI-10 at various temperatures (°C): 1) 20; 2) 60; 3) 80; 4) 100; 5) 130; 6) 160; 7) 185; 8) 210; 9) 240; 10) 270; 11) 300.

The geometrical locus of these maxima delimits the region of stresses and temperatures within which the polymeric material remains effective, i.e. preserves heat resistance. The curve bounding the region of effectiveness obeys the equation

$$\ln \frac{\sigma}{\sigma'_\infty} = \frac{U_{r,0} - \gamma_r \sigma}{RT}, \qquad (2)$$

where $U_{r,0}$ is the initial activation energy of relaxation, and γ_r and $\sigma'_\infty = E\alpha\tau_{r,0}$ are parameters of the material, in which E is the Young's modulus, $\tau_{r,0}$ the pre-exponential factor in the temperature dependence of the stress-relaxation time, and $\alpha = \beta K$ the rate of deformation due to thermal expansion, β being the rate of temperature rise with time and K the coefficient of linear thermal expansion.

Experiment shows that, with a rate of heating of ~1.50 deg min^{-1}, the curve bounding the performance region almost coincides with the temperature dependence of σ_{cr} (Fig. 2) determined at a relaxation time t_r = 5 min. At longer relaxation times the bounding curves will, of course, be displaced to lower temperatures, but not very greatly (as in Fig. 3).

A thermomechanical method is also widely used for assessing the heat resistance of polymers. It is noteworthy that, over quite a wide range of molecular weights, many heat-resistant polymers do not exhibit rubberlike elasticity, passing directly from a vitreous solid to a viscous fluid when heated. In this case the temperature dependence of deformation (the thermomechanical curve) was described[17,18] in terms of Maxwell's model of a viscoelastic material. With a non-linear rise in temperature with time

$$T = a/(b - t), \qquad (3)$$

where a and b are constants, the thermomechanical curve will be represented by the equation

$$\varepsilon = \frac{\sigma a R}{E\tau_{r,0}U_r} e^{-U_r/RT}, \qquad (4)$$

in which ϵ is the relative deformation, σ is a constant stress, $\tau_{r,0}$ and U_r are parameters characterising the relaxation properties of the polymeric material, and E is the Young's modulus.

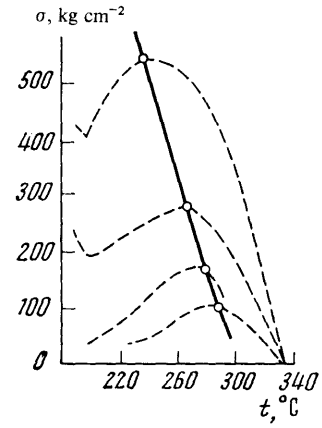


Figure 5. Performance range of polyamide of terephthalic acid and anilinephthalein.

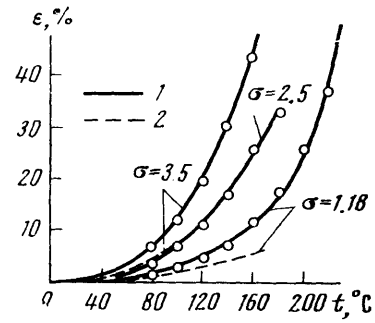
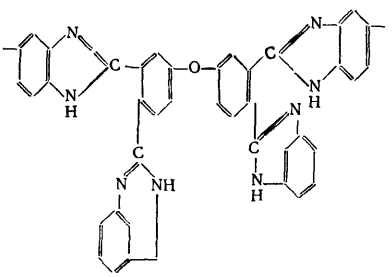


Figure 6. Thermomechanical curves (σ in kg mm^{-2}) for polyester of isophthalic acid and phenolphthalein having different structures: 1) fibrillar; 2) globular.

Fig. 6 shows thermomechanical curves obtained when films of a globular and a predominantly fibrous polyester of isophthalic acid and phenolphthalein are subjected to uniaxial extension. Only slight deformation is possible in the former polymer, but quite large deformation in the latter, which can thus pass into a viscous fluid under the

influence of mechanical stress. Experiments and calculations showed that the activation energy of relaxation U_r is rather larger for a globular than for a fibrous structure.

The relative simplicity of the relaxation process is indicated by the adequate description of the transition from solid to viscous fluid by Maxwell's method, i.e. by means of a single relaxation time that depends on temperature and stress. Softening in other heat-resistant systems, e.g. in various polybenzazoles, does not take place by one simple mechanism[19]. Fig. 7 shows thermomechanical curves (plotted as lg ϵ against $1/T$) for the polybenzimidazole



Since the relation is non-linear, relaxation is not described in this case by the usual temperature dependence of a single relaxation time.

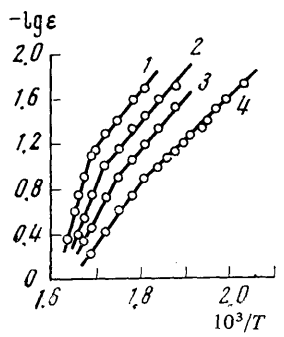


Figure 7. Thermomechanical curves for polybenzimidazole determined under different stresses (kg cm^{-2}): 1) 100; 2) 200; 3) 300; 4) 400.

In characterising the mechanical performance of polymers in general and their heat resistance in particular we must bear in mind the occurrence of several transitions at lower temperatures in addition to the main relaxation corresponding to transition from a vitreous solid into a state of rubberlike elasticity or of viscous flow. They are not revealed by the usual dynamic (mechanical and electrical) test methods but by examination of the relaxation properties of polymers under static conditions. Heat-resistant rigid-chain polymers are the most suitable subjects, since they exist in a vitreous state over an extremely wide temperature range, within which forced rubberlike elasticity develops: in other words, such polymers do not soften over a wide temperature range and do not exhibit brittle fracture.

These relaxation transitions were discovered earlier by Lazurkin[20] in a study of the temperature dependence of the limit of forced rubberlike elasticity for several polymer glasses and by Bartenev[21,22] in an investigation of the temperature–time dependence of strength for several systems over a wide temperature range. Transition from one substate to another entailed a change not only in its durability but also in its stress dependence. Thus, even before reaching the brittle point, the region of the vitreous state can be subdivided into at least two substates, in which different types of relaxation processes occur.

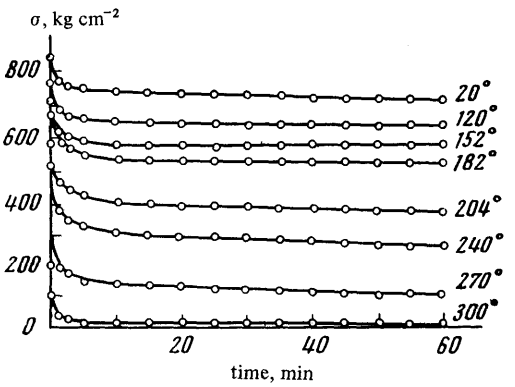


Figure 8. Stress-relaxation curves for polyester of terephthalic acid and phenolphthalein (ϵ = 4.4%).

Relaxation transitions detected by static methods of investigation are also very clearly developed in heat-resistant polymers. They have been studied[12,14,15,23] by examining the relaxation of stress at constant deformation under isothermal conditions. This yields a series of relaxation curves—the time dependence of stress—each corresponding to a certain chosen temperature. Fig. 8 shows that the relaxation curves are quite close together at low temperatures, and begin to shift rapidly down towards low stresses only after a certain temperature has been reached. A clearer idea of the temperature dependence of relaxation properties can be obtained from several properties, of which the simplest and most convenient is the relative decrease in stress after a specified relaxation time

$$\beta = \frac{\sigma_d - \sigma_t}{\sigma_d}, \qquad (5)$$

where σ_i is the stress on completion of deformation and σ_t the stress after relaxation for a certain time (e.g. 1 h).

The temperature dependence of $1/\beta$ is very characteristic (Fig. 9): it remains constant over a wide temperature range, after which it drops sharply, and then decreases smoothly with rise in temperature, to reach unity at the glass point. This means that the range of the vitreous state for a given system can be subdivided into two regions, differing in the temperature dependence of the relaxation parameters. At the lower temperatures the rate and extent of relaxation are relatively insensitive to temperature. The higher-temperature region shows a

sharp acceleration of relaxation processes, which is typical of many of the polymers studied earlier, not possessing high-glass points.

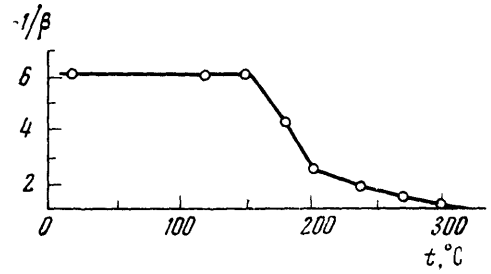


Figure 9. Temperature dependence of β^{-1} for polyester of terephthalic acid and phenolphthalein.

Without discussing the mechanism of the transition from one substate to the other, we note that such transition must be taken into account for an objective assessment of the heat resistance of a polymer. The glass point is usually regarded as the upper temperature limit of heat resistance: i.e. it is assumed that the polymer can be used right up to this temperature. This may be valid under very small loads for very short times. But even that is not the point. If a polymer material is functioning under variable temperatures, its transition from one substate to another, involving a sharp acceleration of relaxation processes, may lead to a complete loss of performance at temperatures far below the glass point. This is apparent, for example, in an abrupt increase in the coefficient of friction and in the seizing of moving parts[24]. Thus the zone of stable performance lies in the temperature range corresponding to the first substate, in which the rate of relaxation is insensitive to temperature. The real temperature range within which heat resistance is maintained therefore extends only to a temperature far below the glass point.

The above features are evident when the heat resistance of polymers is investigated by the measurement of stress relaxation. Prolonged creep tests under various loads must also be made for a more detailed assessment of the mechanical properties of heat-resistant polymers and for a comparison of their deformation behaviour under load. The isochronous stress–deformation curves obtained from these tests enable the rigidity of the systems to be judged more objectively[25].

III. CHEMICAL STRUCTURE AND PROPERTIES OF HEAT-RESISTANT AROMATIC POLYMERS

Before discussing the effect of the chemical structure of heat-resistant polymers on their properties, we must consider briefly the processing of such systems. Heat-resistant polymers whose glass point lies considerably below the temperature at which they begin to decompose can be processed[26] by the usual methods of injection moulding at high temperatures. The properties of monolithic specimens of poly(phenylene sulphide) have been reported[27]: specimens obtained by injection moulding possess moderate breaking stress (770 kg cm^{-2}), and extremely slight deformability (ϵ_r = 3%), but a considerable bending modulus of elasticity (E = 42 200 kg cm^{-2}); the maximum temperature limit to the performance of poly(phenylene sulphide) is assumed[27] to be 260°C.

Application of the usual methods of injection moulding and hot extrusion to process into monolithic articles highly heat-resistant polymers, in particular polyheteroarylenes, is made extremely difficult by the intensity of the accompanying thermal degradation and cross-linking. However, monolithic articles can be obtained from such polymers if processing is conducted below the limiting temperature at which thermal degradation takes place. By using high pressures and extruding at a temperature a few dozen degrees below that at which loss in weight begins we can obtain monolithic specimens from such heat-resistant systems as polytriazoles and polypyrazoles[28], polyphenylenes[29], aromatic polyimides[30–32], etc. This enables us to examine the effect of the chemical structure of polyheteroarylenes on their mechanical properties, in particular to specify the effect of the heterocycle.

If the heterocycle occupies a comparatively small volume, as e.g. in the case of poly(oxydi-*p*-phenylene–1,3,4-oxadiazole), appreciable crystallisation may occur, which in turn will tend to extend the performance range. With a more bulky ring system, e.g. poly(oxydi-*p*-phenylene–4-phenyl-1,2,4-triazole), the kinetic rigidity of the chain is increased, but crystallisation does not take place, the former factor tending to increase the performance range, and the latter to diminish it. Although the two effects are mutually competitive, experience shows that, with polyoxadiazoles and polytriazoles, crystallisation leads to a greater extension of the stress and temperature limits within which the polymer is effective. Competition between two processes—degradation and cross-linking—also occurs, however, if the polymer undergoes physical changes during processing. Cross-linking may have a favourable influence, promoting consolidation of the specimen at temperatures below the softening point (under the influence of high pressures). Thus the processing of poly-*p*-phenylene-1,2,3-triazole at 360°C yields monolithic specimens, whose performance range extends far above the processing temperature (Fig. 10).

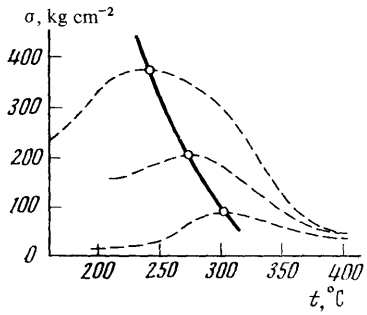


Figure 10. Performance range of poly-*p*-phenylene–1,2,3-triazole.

An especially interesting heat-resistant polymer is polyphenylene, from which monolithic specimens have also been obtained[29]. Although thermo-oxidative degradation occurs at ~400°C, monolithic polyphenylene is able

to function at far higher temperatures (Fig. 11). Moulded polyphenylene remains effective under a stress of 200 kg cm^{-2} at 300°C. Raising the temperature to 400°C lowers the working stress to 80 kg cm^{-2}, and even at 600°C the stress in monolithic polyphenylene is not completely relaxed to zero: i.e. performance is maintained at this temperature, but only under very small stresses.

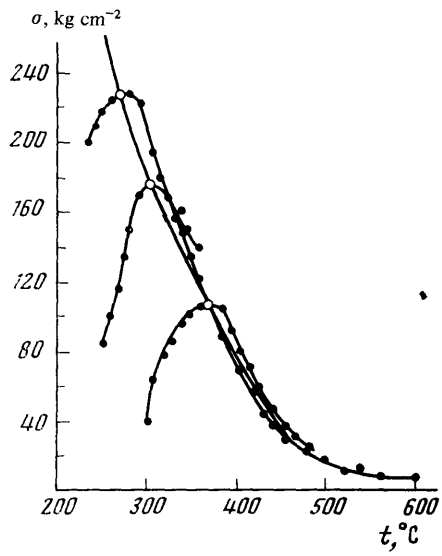


Figure 11. Performance range of polyphenylene.

The extrusion of heat-resistant polymers even at very high temperatures and pressures does not always yield true monoliths, since the extrusion temperature lies below the pour point. Despite this, such caked material is able to function in rigid structures. Thus the aromatic polyester Ekonol 301 is extruded under pressure to yield machinable monolithic material[33]. Articles made of Ekonol retain good mechanical and dielectric properties up to 315°C.

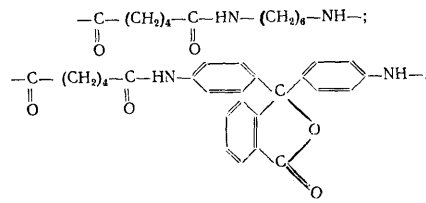
Mechanical properties under hydrostatic pressure have been studied[34] in connection with the problem of obtaining monolithic articles from rigid-chain polyimides at comparatively low temperatures. Under these conditions the polyimide exhibits large plastic deformations and collapses with formation of a neck, so that the polyimide can be processed by cold moulding. The application of hydrostatic pressure to polyimides may tend to raise the limit of forced elasticity and the elongation at rupture, and also to increase Young's modulus[35].

One route for obtaining heat-resistant plastics is the use of oligomers having reactive end-groups[36]. Fibres of a filler (e.g. graphite fibres) are impregnated with solutions of the oligomers and aromatic diamines, and then dried at a high temperature, after which the products are extruded. The resulting plastics possess good mechanical properties.

In the above processing methods the heat-resistant polymers are subjected to high temperatures and pressures, which is often undesirable and may lead to thermal degradation. This can be avoided by producing goods (in particular, films) from solution. In this connection the synthesis of the card type of heat-resistant systems has made a significant contribution to polymer science[37-41]. Such systems contain bulky side-rings, often possessing appreciable polarity, with one of the cyclic elements forming part of the main polymer chain. Thus without loss of heat resistance the polymer acquires good solubility in many readily available organic solvents, so that strong transparent films, whose properties will be described below, can be obtained. Enhancement of solubility can be achieved by the synthesis of "spiral-staircase" polymers containing ladderlike fragments[42].

The production of polymeric goods directly from monomers is currently a leading line of advance in polymer processing. The accompanying polymerisation or polycondensation results ultimately in formation of a finished article. This is sometimes the only possible method for heat-resistant systems, since many heat-resistant polymers do not possess fluidity. Morgan et al[43-45] have shown that it is entirely possible to process the monomers of pyrrones to give articles possessing adequate strength, elasticity, and several other valuable properties. Equimolecular mixtures of the monomers are compressed in a mould at temperatures up to 450°C for 1 h. In this way pyrrones have been obtained from pyromellitic dianhydride, benzophenone-3,3',4,4'-tetracarboxylic acid and biphenyl-3,3',4,4'-tetra-amine, etc. The optimum temperature, pressure, and time can be chosen to give specimens of maximum density, which in this case possess the greatest strength (up to 1475 kg cm^{-2}).

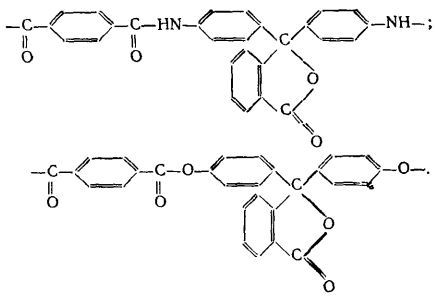
In assessing the effect of the chemical structure of heat-resistant polymers on their properties it must be borne in mind that a change in chemical structure quite often leads to a change in the state of aggregation (e.g. crystallisation), with significant changes in all the properties. The phase must therefore be taken into account. In order to examine the effect of chemical structure and state of aggregation on the mechanical properties of several polyesters and polyamides we shall compare the performance ranges of a few pairs of such polymers[46]. In the first pair of polyamides



the polymethylene segment in the amine component is replaced by an anilinephthalein residue. The performance regions of these polymers (Fig. 12) show that, although their softening temperatures are about the same, the polyamide based on an aromatic diamine withstands far greater stresses at all lower temperatures. Whereas polyhexamethylenadipamide is crystalline, while polyanilinephthaleinadipamide is amorphous, the latter forms a far more rigid monolith, capable of withstanding considerable mechanical loadings.

Comparison of the mechanical properties of an aromatic polyamide and an aromatic polyester in which the diol

residue has the same chemical structure as the diamine residue



permits assessment of the contributions by ester, peptide, and intermolecular (hydrogen) bonds in establishing the set of mechanical properties of the polymer over a wide temperature range. Fig. 13 shows that the curves bounding the performance regions of polyamides lie at considerably higher temperatures than the corresponding curves for polyarenecarboxylates. The largest displacement is found with polymers of aliphatic dicarboxylic acids, since hydrogen bonds continue to "function" at low temperatures, and undergo appreciable cleavage at high temperatures.

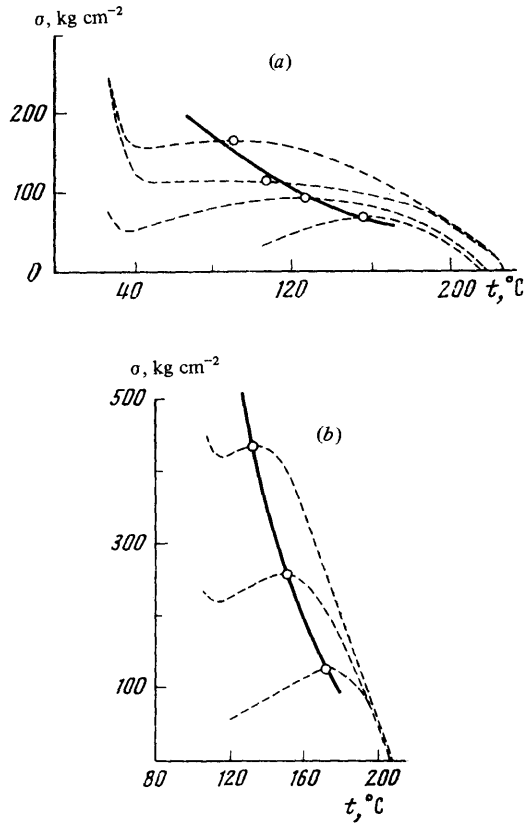


Figure 12. Performance ranges of: *a*) polyhexamethylenadipamide; *b*) polyamide of adipic acid and anilinephthalein.

A clearer idea of the effects both of chemical structure and of intermolecular interaction on the mechanical properties of such polymers can be obtained from the curves bounding the performance regions of polysebacamides and the corresponding polysebacates (Fig. 14). The polyamide formed by sebacic acid and anilinephthalein possesses the largest performance region. The bounding curve undergoes only a slight displacement to lower temperatures on passing to the analogous polyester, but a completely aliphatic polyester based on sebacic acid exhibits a sharp decrease in the mechanical stress limits. Thus the presence of intermolecular (hydrogen) bonds with a repeating unit of almost identical structure shifts the boundaries of the performance region only with respect to temperature, but changing the chemical structure (in the presence of hydrogen bonds) produces displacements with respect both to temperature and to stress.

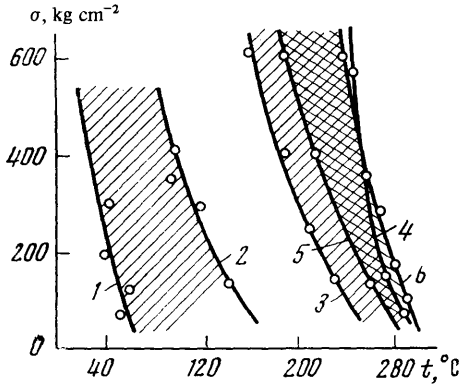


Figure 13. Curves bounding performance regions of various polyamides and polyesters: 1) polyester of sebacic acid and phenolphthalein; 2) polyamide of sebacic acid and anilinephthalein; 3) polyester of isophthalic acid and phenolphthalein; 4) polyamide of isophthalic acid and anilinephthalein; 5) polyester of terephthalic acid and phenolphthalein; 6) polyamide of terephthalic acid and anilinephthalein.

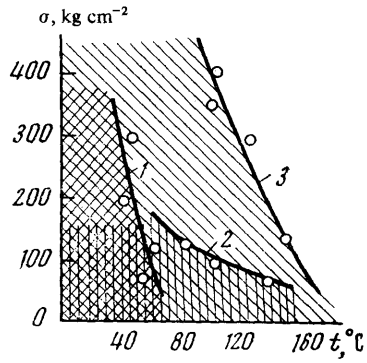
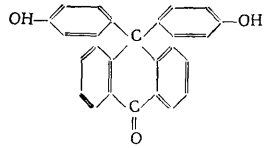


Figure 14. Curves bounding performance regions of polyamides and polyesters based on sebacic acid: 1) polyester with phenolphthalein; 2) polyamide with hexamethylenediamine; 3) polyamide with anilinephthalein.

The difference in softening point between aromatic polyamides and polyesters was used[47] to determine the energy of the hydrogen bonds as 6,6 kcal mole^{-1}. Special attention has been paid[48,49] to the influence of substitution isomerism on the properties of aromatic polyamides[50].

The above systems belong mainly to the group of card polymers containing bulky side-rings. The presence of such rings confers solubility on the polymers, but often prevents their crystallisation, especially if the rings are unsymmetrical. In some cases, however, the presence of a bulky side-ring does not prevent crystallisation, and polyarenecarboxylates based on 9,9-bis-*p*-hydroxyphenylanthrone



are interesting in this respect[51-53]. Like analogous polymers they dissolve readily in many of the usual organic solvents, from which strong, transparent films can be obtained. Such polyesters show a pronounced tendency to crystallise. The structure of poly(hydroxyphenylanthrone terephthalate) and its properties can be changed by varying the conditions of preparation[52]. The use of different methods of polycondensation (at high and low temperatures in solution, interfacial) or different conditions of high-temperature polycondensation (reaction temperatures, rates of heating and cooling of the reaction mass, concentrations of starting materials, nature of the solvent) enabled this polyester to be obtained in crystalline form, in amorphous form, and as a mixture of the two forms‡. The polyester of hydroxyphenylanthrone and terephthalic acid is obtained in the most crystalline form by polycondensation at 220°C in chlorinated biphenyl, 1,2,4-trichlorobenzene, nitrobenzene, and 1-chloronaphthalene. The structure of this polyester can be varied not only by changing the conditions of preparation but also by appropriate treatment—reprecipitation, heating in specially selected solvents—of the finished polymer. The crystallisation of aromatic polyesters based on hydroxyphenylanthrone is accompanied by a deterioration in their solubility.

The presence of an anthrone ring system in a polymer chain favours crystallisation of the aromatic polyesters, and thereby provides further opportunities for improving their heat resistance, and perhaps that of other classes of rigid-chain polymers. Examination of a monolithic, partly crystalline polyester of hydroxyphenylanthrone and terephthalic acid showed a peculiar influence of order on heat resistance. Determination of the performance region of this polyester showed[52] that relaxation processes accelerate sharply, i.e. the material begins to soften, at the same temperatures with a partly crystalline specimen as with the amorphous material (Fig. 15), which suggests that softening involves the amorphous part of the polymer.

‡In the discussion of structure formation in polymers the terms "crystallinity", "crystalline and amorphous parts", etc. must be employed with some caution, especially when applied to aromatic polymers having bulky side-chains. In such case it is better to speak of the ordering of the system, since polyesters of this type cannot be obtained in the usual crystalline form. However, we shall not enter into questions of terminology here, but use these terms with this reservation.

However, the maximum temperature limits of performance become much higher with weakly stressed, partly ordered specimens.

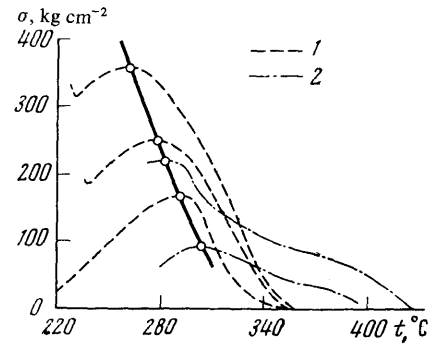
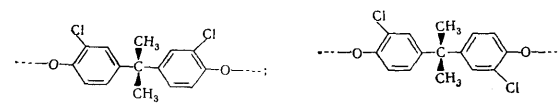


Figure 15. Performance ranges of monolithic specimens of polyester formed by hydroxyphenylanthrone and terephthalic acid: 1) amorphous specimen; 2) partly crystalline specimen.

Interesting results have been obtained[54,55] for the mechanical properties of aromatic polyesters of 3′,3″-dichloro-2,2-diphenylpropane-4′,4″-diol prepared by acceptor-catalysed polycondensation. The chlorine-35 nuclear quadrupole resonance spectra of such systems are characterised by comparatively narrow signals belonging to different crystallographic forms. The reason may be that the chlorine atoms in the diol permit in principle the existence of two rotational isomers.



whose presence in the polyester chain may lead to two isomeric types of macromolecules. Polyesters of this diol and terephthalic acid obtained under various conditions of acceptor-catalysed polycondensation (different reaction media, temperatures, etc.) exhibit several abnormalities of mechanical behaviour. The thermomechanical investigation of films reveal a transition, apparent in a rapid development of deformation at temperatures below the softening range and in the establishment of a plateau (Fig. 16). It was found that the increase in deformation was not due to the usual transition to a state of rubberlike elasticity.

Another interesting abnormality is evident in the determination of performance regions for monolithic specimens of such polyesters. The non-isothermal stress-relaxation curve under conditions of uniaxial compression passes not just through one maximum (as is usual) but through two maxima, which appear in the temperature range of the first increase in deformation on thermomechanical curves obtained at the corresponding stress. Detailed analysis of this phenomenon, based on nuclear quadrupole resonance and on the measurement of heat capacity, suggests[55] that all these anomalies may be due to a transition between

rotational isomers in the residue of the diol, with a consequent conversion of one isomeric form of macromolecule into the other. This transition is activated by mechanical stresses, since increase in stress lowers the transition temperature (Fig. 16).

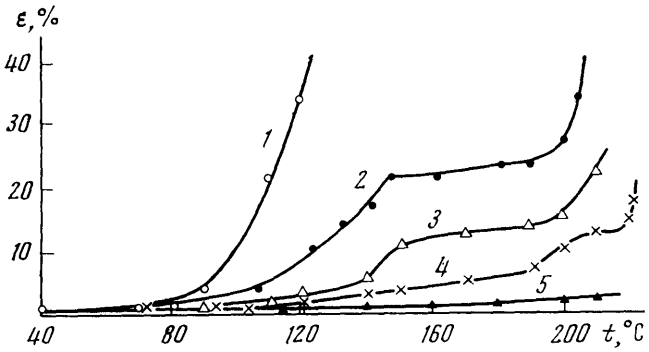


Figure 16. Thermomechanical curves obtained for polyester of 2,2-di-*m*-chlorophenylpropane-*pp'*-diol and terephthalic acid determined at constant tensile stresses (kg cm^{-2}): 1) 200; 2) 100; 3) 50; 4) 25; 5) 100 (repeat test).

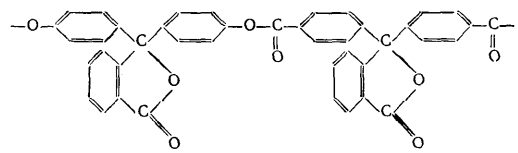
It appeared from the above considerations that the rotational isomers of aromatic polyesters of the dichlorodiphenylpropanediol were quite stable. This opens up the theoretical possibility of synthesising stereoregular polycondensed systems simply by varying the conditions. It also becomes obvious that the structure and properties of rigid-chain polymers can be most efficiently varied during synthesis, since the resulting macromolecular conformations are "frozen", remaining stable on subsequent treatment of the polymer[54,55]. Strength and deformation characteristics were published[56-58] for aromatic polyester films prepared in various media.

Strength cannot be fully assessed from the breaking stress, which merely provides a comparison of the strength properties of polymers differing in chemical structure. To obtain a more complete measure of the strength properties of polymers we must determine the parameters in Zhurkov's durability equation

$$\tau = \tau_0 e^{\frac{U_0 - \gamma\sigma}{RT}}, \qquad (6)$$

where τ_0 is the pre-exponential factor, U_0 the initial activation energy of fracture, γ a structure-sensitive parameter, and σ the constant stress. Numerical values of U_0 and γ were determined[17,59] by a modified thermomechanical method and by the application of Bailey's criterion to tests with uniaxial stretching at various temperatures. The initial activation energy of fracture was found to be low (U_0 = 30 kcal mole^{-1}) for globular polyesters of phenolphthalein with isophthalic and terephthalic acids. This indicates that the bonds between the globules forming a film or a monolithic body are fairly weak. The type of supermolecular structure of such systems has an appreciable influence also on the relaxation processes accompanying deformations remote from fracture. Greater rigidity at comparatively low temperatures and larger equilibrium stresses are obtained with a globular than with a fibrous structure. With rise in temperature the opposite situation is found, for the ease of rupture of the weak bonds between globules leads to premature breakdown of the material. Globular material is more homogeneous in structure, which results, in particular, in well defined temperature dependence of the relaxation parameters[60].

The effect of bulky side-rings in conferring solubility is confirmed by the synthesis of soluble, extremely heat-resistant polyesters of 4,4-diphenylphthalide-*pp'*-dicarboxylic acid with various diols (resorcinol, quinol, biphenyl-*pp'*-diol, etc.)[61]. Among them the polyester of this acid with phenolphthalein



is especially interesting, its performance range surpassing those of other aromatic polyesters with respect both to temperature and to stress at a given temperature. Thus the introduction of an additional bulky, polar ring not only improves the solubility but also extends the ranges of stresses and temperatures over which the polymer remains solid and able to function in rigid structures.

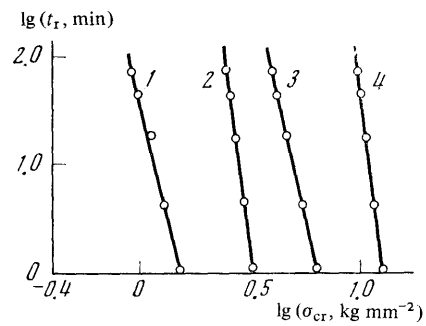
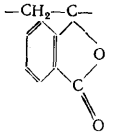


Figure 17. Dependence of lg t_r on lg σ_{cr} at 20°C for the polymers: 1) polyethylene glycol (M = 20 000); 2) poly(ethylene glycol sebacate); 3) polyester of sebacic acid and phenolphthalein; 4) polyester of terephthalic acid and phenolphthalein.

In concluding our account of the structure and properties of polyesters we must pay special attention to their relaxation properties, which largely determine the heat resistance. Measurement of these properties over a wide temperature range has enabled[62] the effect of chemical structure on heat resistance to be studied for a series of polyesters. Comparison of the relaxation parameters of the sequence from aliphatic polyethers to polyesters containing different numbers of aromatic rings in the repeating unit shows that, under otherwise similar conditions, an aromatic polyester (polyarylate F-2) retains the relaxing stress for a far longer period than any other polymer in this sequence (Fig. 17). As we pass

from polyethers to polyesters and as the latter become saturated with benzene rings the above relations shift regularly to greater critical stresses. Thus extension not only of the temperature ranges of mechanical performance but also of the range of working stresses themselves can in practice be achieved by controlled variation of the chemical structure of the polymer to increase the relative proportion of aromatic rings in the repeating unit.

Special importance must be attached to the presence of bulky (polar) groups, whose beneficial effect on solubility and heat resistance when in the side-chain is especially clearly demonstrated with cardlike carbon-chain polymers, an example of which is polymethylenephthalide[63,64]



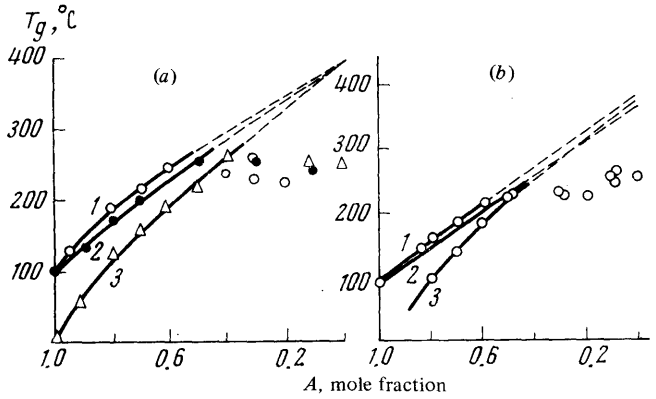


Figure 18. Dependence of glass point determined: *a*) by thermomechanical method; *b*) from performance regions on composition of copolymers [of methylenephthalide] with (*A*, mole fraction): 1) styrene; 2) methyl methacrylate; 3) methyl acrylate.

This polymer can usefully be regarded as a substituted polyethylene possessing incomparably greater heat resistance than either polyethylene itself or its other derivatives. Thus the glass point of polyethylene is −130°C, and that of polystyrene is 100°C, whereas thermomechanical curves suggest that polymethylenephthalide has a glass point of 300°C. However, this last polymer undergoes intense thermal degradation at these temperatures, so that the true softening temperature may be still higher. Calculation by means of Eqn. (8) gave a softening point of 390°C. Calculated and experimental softening points were tested by examining a series of copolymers with styrene, acrylonitrile, methyl methacrylate, methyl acrylate, and other monomers, which showed[64] a smooth rise to 250°C with increase in the methylenephthalide content (Fig. 18). Further increase produced no further rise in softening point of the copolymer, which remained constant in the range 220–250°C. The observed constancy of the softening temperature with variation in the composition of a copolymer is evidently due to thermal degradation at this temperature. The softening point of polymethylenephthalide itself can be determined only by extrapolating the composition dependence of the glass point of the copolymers to zero concentration *c* of the second comonomer, which yields a glass point lying in the range 370–380°C, in good agreement with the calculated temperature.

Thus the presence of card groups in a carbon-chain polymer leads to a sharp increase in heat resistance, as in heterochain polymers. In such systems the heat resistance exceeds the thermal stability, and the latter thus limits their performance. This has extremely important practical consequences. With a large margin of heat resistance present, the polymer can be modified by copolymerisation, plasticisation, etc. without danger of lowering its actual softening temperature. In particular, the quantity of plasticiser or the concentration of phthalide groups on copolymerisation with other monomers can be varied within wide limits. Nevertheless, the introduction of even a small quantity of phthalide segments into an ordinary carbon-chain polymer leads to a considerable improvement in its heat resistance.

Polyimides currently form one of the most important classes of heat-resistant polymers, since they form the basis of plastics, films, fibres, coatings, and other objects which retain their performance at high temperatures. Aromatic polyimides when heated often pass from a vitreous state directly into a viscous fluid, but in several cases they may develop rubberlike elasticity, as do polymers having flexible macromolecules. A characteristic of heat-resistant systems is that the range of such elasticity is displaced significantly to higher temperatures, which its upper limit determined by the intensity of thermal degradation and cross-linking. Furthermore, the modulus of rubberlike elasticity is substantially greater for heat-resistant systems than for flexible-chain polymers. Polyimides may yield either non-softening rigid polymers or softening polymers having normal Young's moduli of 50–100 kg cm^{-2}, depending on the proportion of flexible units in the polymer chain[65]. The thermomechanical properties of several polyimides were explained[66] by the formation of a labile network, whose presence was especially apparent above 250°C.

Determination of the temperature range of rubberlike elasticity from the thermomechanical curve without further verification of the reversibility of deformation may lead to substantial errors. The presence of a plateau on this curve is a necessary but not a sufficient condition for the development of rubberlike elasticity, since it may be due to thermal degradation and several other secondary processes: verification of the reversibility of deformation in the region of the plateau is therefore absolutely necessary. Fig. 19 shows thermomechanical curves, determined on uniaxially stretched films[31], for polyimides of oxy-*pp'*-dianiline and oxy-4,4'-diphthalic acid (curves *1* and *1'*) and of anilinephthalein and sulphonyl-4,4'-diphthalic acid (curves *2* and *2'*). The broken curves represent the properties of the polymers subjected to a constant stress, whereas the full (primed) curves apply to periodic loading. Fig. 19 shows that part of the deformation in the region of the plateau is reversible (rubberlike elasticity), while part is irreversible (viscous flow). The former polymer (curve *1*) possesses a wide range of rubberlike elasticity (280–500°C). Curve *1'*, determined under a variable load, shows that the modulus of rubberlike elasticity $E = \Delta\sigma/\Delta\epsilon$, where $\Delta\sigma$ is an increment of stress and $\Delta\epsilon$ the

consequent increment of reversible deformation, increases continuously with rise in temperature (from 30 to 100 kg cm^{-2} from 300 to 430°C). The specimen does not exhibit rubberlike elasticity above 460°C, which, like the increase in the modulus, is attributed to chemical cross-linking. A similar modulus (20 kg cm^{-2}) was observed in the transition zone for the second polyimide. The specimen had an extremely high glass point and hence a narrow range of rubberlike elasticity (430–470°C), bounded by the intensity of degradation and cross-linking.

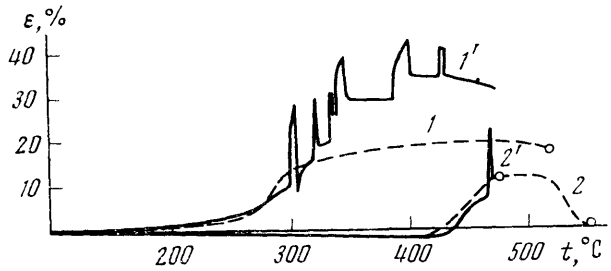


Figure 19. Thermomechanical curves for polyimide films.

Many types of aromatic polyimides are roughly equivalent in thermal stability, from which follows the conclusion of practical importance that the range of the state of rubberlike elasticity can be extended significantly by lowering the glass point either by introducing oxa, carbonyl, etc. groups into the polymer chain or by diminishing the number of fused rings. We again stress that, despite the sharp drop in glass point, the thermal stability remains almost undiminished; thus there is no direct link between the glass point and the temperature at which loss in weight begins. Rubberlike elasticity is exhibited not only by polyimides but also by other heat-resistant polymers, e.g. polybenzoxazoles[67]. The thermal stability of these systems is also little affected by the introduction of oxa, thia, or carbonyl groups into the main chain.

When the thermomechanical properties of these polymers are determined in the presence of small mechanical stresses, the glass points are often close to the decomposition temperatures. The former can conveniently be sought by making thermomechanical tests with comparatively large stresses. This lowers the glass point considerably, but a plateau is still formed on the thermomechanical curve because of the high moduli of rubberlike elasticity, and it is easy to determine both the glass point and the pour point T_{fl}. The true temperatures of these points can be determined by plotting T_g and T_{fl} against stress and extrapolating to zero stress. This procedure enables glass and pour points to be found when they lie above the decomposition temperatures of the polymers.

On the whole the introduction of "hinge" atoms into the repeating units of polybenzoxazoles, polyimides, and other heat-resistant polymers permits control not only of the glass point but also of strength and deformation properties. A suggested classification of polyimides was based[68,69] on the presence and site of hinge bonds. The resulting classes differed in physical properties. A physical model shows[69] that the rearrangement and introduction of "flexible" bonds, allowing for interaction between chains through transverse groups, controls the number of degrees of freedom of such a system. This classification can be applied also to other systems[70,71]. The introduction of various hinge groups—oxa, thia, carbonyl, peptide, carboxylate, etc.—not only enhances the deformability of heat-resistant systems but also facilitates their fabrication into monolithic articles by hot extrusion, injection moulding, etc. to yield polymeric materials having excellent mechanical properties[5]. However, the main advantage of many aromatic polymers—their high heat resistance—is in considerable measure lost.

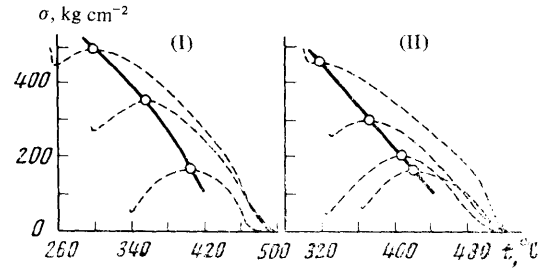
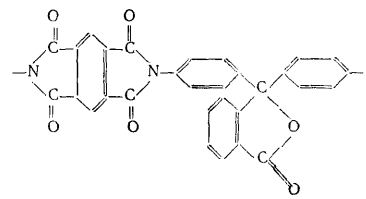
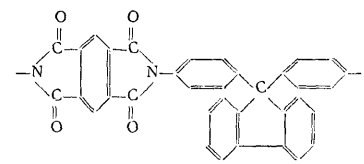


Figure 20. Performance ranges of monolithic specimens of polypyromellitimides (I) and (II).

More detailed consideration of this problem in relation to aromatic polyimides shows that, on introduction of the above groups, the heat resistance of the polymers will differ little from that of aromatic polyesters, aromatic polyamides, and other polyheteroarylenes. The performance ranges of monolithic specimens of the polyimides



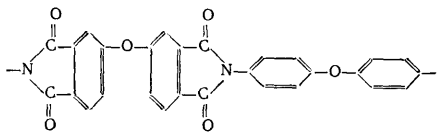
(I)



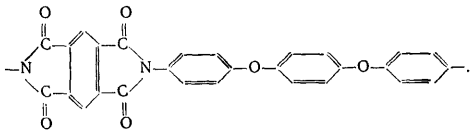
(II)

which do not contain the above groups, are extremely wide with respect both to temperature and to stress (Fig. 20)[32]. Thus at 300°C these plastics can function under a load of 500 kg cm^{-2} for a short time, and at 400°C they withstand 200 kg cm^{-2} (most structural plastics are completely devoid of performance at this temperature, owing both to degradation and to softening or flow). The maximum performance limits for the polyimides (I) and (II) are respectively 490 and 515°C. To compare the performance of these polyimides with that of polyimides containing "hinge" groups and also of several traditional polymers, we plot on the same diagram (Fig. 21) the curves bounding the performance regions of these systems.

The heat resistance of the polymeric materials increases significantly as the main polymer chain becomes saturated with aromatic rings and with other heterocycles. Some of the solid polyimides represented on Fig. 21 are not true monoliths (Nos. 9–11), and their performance ranges might be extended further if true consolidation of the material were achieved. The heat resistance can be improved also by crystallisation. Not only the number but also the relative arrangement of rings is no less important for the heat resistance of polyimides and other systems [31,32,72]. With identical numbers of imide rings, benzene nuclei, and all other groups and elements, the heat resistance is enhanced by a greater degree of ring fusion. Thus the polyimide



is considerably less heat-resistant than is



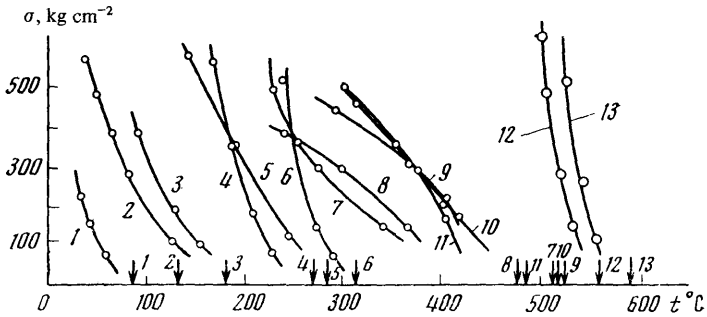


Figure 21. Curves bounding the performance regions of representatives of various polymer series: 1) poly(methyl methacrylate); 2) poly(2,2-diphenylpropane-*pp'*-diol carbonate); 3) poly(propane-2,2-di-*p*-phenylene isophthalate); 4) poly(phenolphthalein isophthalate); 5) polyimide of oxy-*pp'*-dianiline and oxy-4,4'-diphthalic acid; 6) polyamide of isophthalic acid and anilinephthalein; 7) polypyromellitimide of oxy-*pp'*-dianiline (amorphous); 8) polypyromellitimide of *p*-diphenoxybenzene-*p'p''*-diamine; 9) polypyromellitimide of oxy-*pp'*-dianiline (partly crystalline); 10) polypyromellitimide of 9,9-diphenylfluorene-*p'p''*-diamine; 11) polypyromellitimide of 3,3-diphenylphthalide-*p'p''*-diamine; 12) sodium silicate glass; 13) potassium silicate glass. The arrows indicate the softening points of the polymers. Specimens 5, 7, and 8 were obtained by formation from a preliminary polymer (polyamino-acid).

In conclusion we again direct attention to the possibility of obtaining extraordinarily heat-resistant organic polymers (polyimides). In this respect they approach quite closely to inorganic glasses, which many authors [73] now regard as polymeric in structure. Fig. 21 includes curves bounding the performance regions of two inorganic glasses, which are displaced to higher temperatures than the corresponding curves for polyimides based on anilinefluorene and on anilinephthalein, but not so greatly. In the preparation of polymers capable of functioning at high temperatures it must be borne in mind that the upper temperature limit of their performance may be governed not by loss of heat resistance (softening) but by the beginning of intense thermal degradation, i.e. loss of thermal stability. In several cases, therefore, it may be important to determine the thermal stability rather than the heat resistance.

Considering in greater detail the relaxation properties[30] of block specimens of one of the most important aromatic polyimides—the polypyromellitimide of oxy-*pp'*-dianiline—we note that the properties of its films have been studied in some detail[6], but different views are held on several of its principal physical properties. Results for the glass point are especially contradictory, for temperatures of 250, 380, and >500°C have been found [6,66,74]. The temperature dependence of the parameter α in Eqn. (1) for block specimens of this polymer shows (Fig. 22) two relaxation transitions (at 270 and 400°C), which may be due to devitrification. Extrapolation to $\alpha = 0$ yields [12] $T_g = 520$–530°C. However, this polymer exhibits a tendency to crystallise, which may be responsible for the break in the temperature dependence near 400°C.

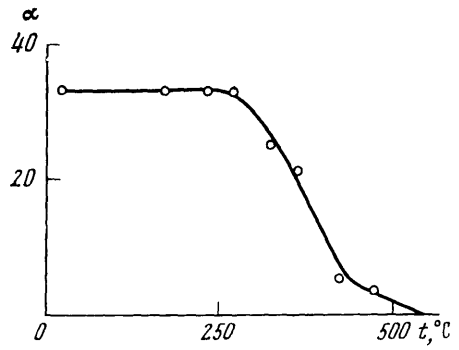


Figure 22. Temperature dependence of α for block specimens of the polypyromellitimide of oxy-*pp'*-dianiline.

The temperature dependence of $\sigma_{\infty, cr}$ exhibits a similar pattern: Fig. 23 shows that this critical equilibrium stress remains approximately constant over a wide temperature range, after which it decreases smoothly with rise in temperature. The curve bounds the region of stresses and temperatures in which the solid polymeric material can function under conditions of stress relaxation for a long time. With the above polypyromellitimide this region is quite large with respect both to temperature and to stress, although polyimides having a card structure are able to operate under far larger stresses at the same temperatures (cf. Figs. 23 and 20).

Investigation of the effect of chemical structure on the properties of polyimides must take into account their possible tendency to crystallise. This tendency varies in complicated fashion with the rigidity of the chain [75–77],

which is determined by the presence of aromatic nuclei: increase in the content of such rings initially prevents crystallisation, and at a certain content the tendency to crystallise becomes minimal; but after this the strengthening of intermolecular interaction intensifies the tendency, leading to an infusible polymer. The crystallisability is significantly affected by the position of the aromatic ring in the chain and by the presence of a solvent [75,76].

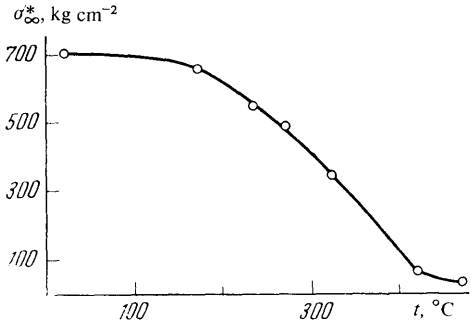


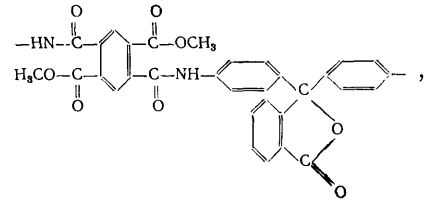
Figure 23. Temperature dependence of σ^*_∞, cr for block specimens of the polypyromellitimide of oxy-*pp'*-dianiline.

Close attention has recently been paid to the hydrolytic stability of polyimide films. Keeping such a film in water produces a rapid fall in tensile strength and in elongation at break. This phenomenon is characteristic both of polyalkyl-imides (based on pyromellitic dianhydride) and of completely aromatic systems. With the former the elongation at break falls rapidly from 200 to 100–40% after immersion in water at 70–100°C for 50–100 h. [78] A film of poly(oxy-*pp'*-dianiline pyromellitimide) [79] exhibits the same peculiarities, although the quantity of water absorbed is about 4%, compared with 0.4% for polyalkyl-imides.

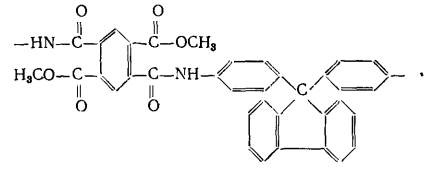
It is possible [80] to restore the strength and deformation properties of Kapton polyimide film after they have been sharply reduced by hydrolysis in distilled water at 100°C. The tensile strength of 1860 kg cm^{-2} and elongation of 62% of the initial film had fallen to 1050 kg cm^{-2} and 6.3% after standing in water at 100°C for 12 days. Heat-treatment of the hydrolysed film at 224–310°C for a few hours increases the tensile strength to 1700–1800 kg cm^{-2} and the corresponding elongation to 38–51%. Thus the amino-acid units formed by hydrolysis are recyclised, rapidly in the early stages and slowly in the later stages; this occurs not only in the solid state [81,82] but also in solution [83].

In this connection it is very important, in the two-stage formation of polyimides and other polymers, that cyclisation of the initial polymer should be as complete as possible. The presence of uncyclised units not only diminishes the heat resistance but also sharply decreases the hydrolytic stability and impairs several other properties. It is thus very important to determine the optimum conditions for cyclisation. It was shown in the case of poly(3,3-diphenylphthalide-*pp'*-dicarboxylic hydrazide) that its cyclisation to polyoxadiazole takes place rapidly at temperatures below the glass point of the polyhydrazide [84,85]. Chemical cyclisation is accompanied here by considerable contraction of the repeating unit. Passage through the glass point makes possible, of course, full development of the mobility of the polymer chain, as a result of which the intramolecular cyclisation is considerably accelerated.

In other cases cyclisation is rapid even in the vitreous, solid state, as has been shown for the polyimides resulting from cyclisation of the alkoxycarbonylated polyamides



(III)



(IV)

Detailed examination has shown [86] that, although the glass point of (IV) is 290–300°C, the polymer has undergone intense cyclisation over the range 150–250°C. With certain other polyimides rapid cyclisation takes place above the glass point of their polyamino-acids [87,88]. However, these workers themselves [87,88] admit that the polyamino-acid contained a large quantity of solvent (*NN*-dimethylformamide), which not only lowered the glass point of the system but also changed the whole kinetics of cyclisation. Calculations based on Eqn. (8) gave glass points of these acids considerably higher than the published temperatures [87,88].

Thus heat-resistant aromatic systems can undergo rapid and extensive cyclisation in the solid phase either above the glass point of the initial polymer or in the vitreous state. Both the rate and the extent of cyclisation are determined, not by the physical state of the system (vitreous or rubberlike elastic), but mainly by the chemical structure, which governs the kinetics of the process and the need for a particular contraction of the repeating unit on formation of an intramolecular ring.

The properties of heat-resistant polymer films can be modified by synthesising mixed systems, which often tend to change the structure and improve the mechanical properties of the films. The properties of polyheteroarylenes can be modified by preparing polyamide-imides, whose solutions are more stable (in contrast to solutions of polyamino-acids); stable films can be obtained from them without heat-treatment [89]. The preparation and properties of polyamide-imides and polyester-imides of ordered structure have been described [90–93]. The latter polymers, because of the introduction of an ester group into the dianhydride component, possess several specific properties and characteristics of their state of aggregation. The macromolecules show well defined spontaneous orientation as a consequence of a conformational transition into a more ordered state, occurring in the region of the glass point of the polymer (210–230°C), where the molecular units become sufficiently mobile. The transition is accompanied by the appearance in unoriented films of an axial (in some cases axial-planar) texture with its axis perpendicular to the surface of the film. Polyester-imides undergo extensive crystallisation when heated to

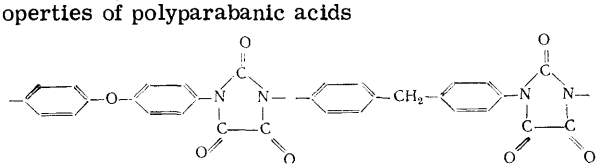
350–380°C. Drawing these polymers at temperatures near the glass point yields a typical amorphous texture, which, together with the spontaneous orientation effect, indicates that considerable order is present in the amorphous state. Further heating enables highly crystalline structures to be obtained, which are stable up to 420–450°C. X-Ray diffraction showed that increasing the number of phenyl rings in the diamide component merely increased the parameter c of the unit cell, without affecting the relative arrangement of the macrochains. The characteristic behaviour of polyesterimides is explained by enhanced rigidity of the macromolecules and interaction between phenyl rings, leading to a non-spherulitic type of crystallisation[91–93]. Films of polyimides and polyamidoimides are able to withstand ultraviolet radiation[94].

Other mixed heat-resistant systems of interest are polyamidoquinoxalines[95] and polybenzoxazolimides, whose mechanical properties have been reported in detail[96]. The tensile strength of films of these polymers lies in the range 1600–2200 kg cm^{-2}, and the elongation at rupture between 5% and 40%. The mechanical properties of films are significantly affected by the solvent in which the polymer had been dissolved. Evaporation of different solvents will yield films possessing appreciably different properties, probably because of differences in structure formation.

The properties of aromatic polymers, including polyimides, can be modified by the introduction of perfluoroalkylene segments[97,98], which is a more efficient method of lowering the glass point than is the introduction of ether links. The glass point can be varied within quite wide limits by changing the length of the perfluoroalkylene chain. Films, monolithic articles, and fibres possessing satisfactory mechanical properties have been obtained from modified polyimides. The glass point can be raised also by the introduction of card groups[10,99], their effect being most marked in an aliphatic chain (e.g. in aliphatic polyesters). Introduction of a card group, of course, increases both the skeletal rigidity of the chain and its kinetic rigidity, because of the large bulk of the group. Hence the significant rise in the glass point in comparison with the initial polyesters.

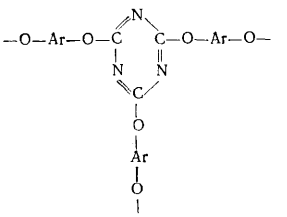
Heat resistance can be improved by cross-linking linear polymers, e.g. polyamidoquinoxalines, containing functional side-groups[100]. The system thereby loses its fluidity, and when filled possesses enhanced strength, which is maintained at very high temperatures. The strength of heat-resistant polymers can be increased by drawing and heat-treating them in a swollen state. Application of this procedure to poly-*m*-phenylenisophthalamide leads to significant increases in Young's modulus, tensile strength, and (with moderate degrees of drawing) elongation at break[101]. A very appreciable improvement in mechanical properties can be achieved by choosing optimum drawing conditions (type of solvent, temperature, duration of drawing, etc.).

A recent paper[102] has described the preparation and properties of polyparabanic acids



which possess high glass points (290–300°C), are readily processed into monolithic articles by stamping or extrusion, and form very strong films possessing good dielectric properties preserved at high temperatures.

An interesting investigation on the preparation and properties of heat-resistant aromatic polymers has been concerned[103,104] with polycyanates, obtained by the polycyclotrimerisation in mass of dicyanates of various aromatic diols. This reaction produces a network



of high regularity resulting from the enhanced selectivity of cyclotrimerisation of O–C≡N groups[103,104]. Polycyclotrimerisation is characterised also by a high conversion of such groups, reaching 98–99%. All these features lead to the formation of systems having a very dense network and possessing increased resistance to mechanical impacts and several other interesting properties[105]. The network systems exhibit not only increased resilience but also appreciable signs of structural order, with almost constant packing coefficients of the macromolecules in the networks close to the mean value (k = 0.681) for amorphous monolithic polymers[15]. Thus three-dimensionally cross-linked aromatic polymers are similarly ordered systems to amorphous and slightly crystallised linear polymers. The heat resistance of such networks is limited by the temperature at which their degradation begins; for many of them the limit is 300–350°C.

Not only monolithic articles and films but also fibres retaining their performance at high temperatures can be obtained from heat-resistant aromatic polymers. Without considering in greater detail this special aspect, we note merely that information has been published on the properties of fibres based on aromatic polyamides and various irregular copolyamides[106] and that fibres have been obtained from alternating polyoxadiazolimides[107], polyamide–hydrazides[108–113], and adamantane[114] and other polymers[115,116], among which considerable interest attaches to poly-2,2′-octamethylene-5,5′-dibenzimidazole, obtained by interaction between biphenyl-3,3′,4,4′-tetraamine and derivatives of sebacic acid. This last polymer forms stable films and fibres, whose crystalline state is affected significantly by the solvent[116]. In particular, replacing the solvent (formic acid by acetic acid) changes the parameters of the unit cell. Experimental results obtained by X-ray diffraction, thermography, and infrared spectroscopy combine to indicate the formation of a crystalline solvate state, which considerably alters the physical properties of this polymer.

IV. RELAXATION TRANSITIONS

Relaxation transitions in polymers are usually detected from the temperature dependence of the tangent of the angle for mechanical and dielectric losses tan δ. Heat-resistant polymers are extremely interesting to investigate, since they exist in the vitreous or crystalline state over a wide range of temperatures, within which many transitions can be discovered. Study of the temperature dependence of tan δ is not only of scientific value for identifying relaxation transitions but also of considerable practical value as a method of quality control of the article

during processing. A still more complete picture is obtained by combining this method with differential thermal analysis. An instrument has been described[117] for the simultaneous determination of dielectric constant and losses, together with differential thermal analysis.

The appearance of particular relaxation transitions will depend on the previous thermal history of the specimens, their crystallinity, and other factors, as well as the method of investigation. It is interesting to trace the transitions in poly-(2,6-diphenyl-1,4-phenylene ether)[118], amorphous specimens of which exhibit a distinct maximum in the temperature dependence of E'' at ~230°C, which corresponds to the glass point. A slight maximum is observed at lower temperatures (~130°C), whose appearance is due to twisting vibrations of the phenylene groups. This transition is more clearly evident in the dilatometric curve, which shows a break near 120°C as the coefficient of cubical expansion increases. The temperature dependence of tan δ for dielectric losses reveals new transitions at 290, 340, and 485°C.

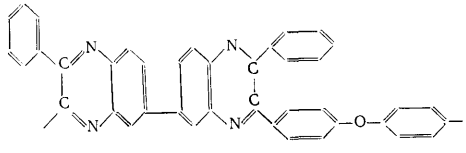
The influence of the previous thermal history on dynamic and static mechanical properties has been studied in detail on polyimides obtained by the cyclisation of polyamino-acids[119]. The temperature dependence of tan δ and that of Young's modulus vary with the rate of heating and the temperature at which cyclisation occurred. The presence of uncyclised units and the possibility of chemical cross-linking at very high temperatures lead to "post-cyclisation" over a certain temperature range during testing, with the appearance of additional peaks in the temperature dependence of tan δ. This applies also to the effect of water and of residual solvent, an aspect which must be discussed in greater detail.

Whether low-temperature transitions in polyimides are due to the molecular nature of the repeating units or to the presence of impurities (e.g. water) has been a matter of debate. A special investigation[120] has revealed three distinct maxima below 130°C in the temperature dependence of tan δ for polyoxy-*pp'*-diphenylenepyromellitimide containing no water: the first, γ-transition occurs at −123°C; the second, at 77°C, is attributed to β°-relaxation; and the third, very weak maximum at −27°C is due to residual moisture in the specimen. Even a small quantity of water (0.225%) changes the picture significantly: a blurred peak is observed from −123 to +77°C, probably owing to the superposition of all the above relaxation processes. Detailed analysis[120] of the temperature dependence of tan δ for samples with different water contents has shown that the transition at −27°C is actually due to the presence of water in the polyimide.

Serious attention must therefore be paid to the importance of removing solvent residues in the investigation of the dynamic mechanical properties of heat-resistant polymers, since its presence may not only distort the temperature dependence of tan δ but also lead to chemical changes at high temperatures. Hence special methods have been developed[121] for examining dynamic mechanical properties, involving attempts at the complete removal of residual solvent. The product of the polycondensation of napthalene-1,4,5,8-tetracarboxylic acid with biphenyl-3,3',4,4'-tetra-amine underwent irreversible chemical changes involving the formation of chemical cross-links, "postcyclisation", etc. even after complete removal of residual solvent[121]. However, the low-temperature peak of tan δ (at −100°C) remained in all cases, so that these irreversible changes do not suppress the mobility of the kinetic units apparent at low temperatures.

The use of dynamic methods to investigate relaxation transitions yields conclusions in several cases as to the mechanism of the relaxation processes accompanying orientation, shrinkage, etc. Thus three temperature regions are found in which a Kapton film shrinks at a maximum rate[122]: the first maximum is observed near 90°C whatever the degree of preliminary drawing at room temperature; a second maximum appears in the region of 200°C only with films that have been stretched by 25%; and the third maximum near 350°C applies to films that are 40% oriented. Each of these maxima occurs roughly at the temperatures of maxima in tan δ for mechanical and electrical losses. Hence the rapid shrinkage after these temperatures have been reached is due to an increase in the molecular mobility of the polyimide macromolecules. Thus a comparative investigation of the temperature dependence of tan δ and of other (static) characteristics—Young's modulus, rate of shrinkage, etc.—may provide valuable information on the establishment of the set of mechanical properties or of polyimides, which has been made for aliphatic and aromatic polyimides[123].

A fundamental investigation of transitions in heat-resistant aromatic polymers was made[124] on a long series of amorphous polyquinoxalines, among which that having the structure



was examined in greatest detail by a variety of methods. Polymers of this type can occur in three isomeric forms, which was regarded[124] as preventing their crystallisation. A single sharp maximum is observed in the temperature dependence of tan δ, E'' and ϵ'', corresponding to vitrification of the polyquinoxalines, the maximum in the dielectric measurements being displaced several tens of degrees to higher temperatures. A weak, additional peak near 210°C is attributed to impurities; in any case, it cannot be explained by the thawing out of the motion of phenyl groups, since it appears even in their absence. The temperature dependence of the heat capacity also showed a transition (vitrification), which was confirmed by dilatometric measurements. Analysis of experimental results obtained by various methods suggested that the appearance of mobility in polyquinoxalines was due not to torsional vibrations but to deformation of the polymer chain itself, which had the form of a tape. The flexibility of such a tape depends on the presence of particular heteroatoms in the main chain.

The most significant transition in a heat-resistant polymer is that involving softening or vitrification. It is therefore extremely important to be able to calculate the glass point T_g solely from the chemical structure of the repeating unit. It was suggested initially[125] that use could be made of the relation

$$\lg T_g = \frac{d}{M}\sum_i K_i' + A', \qquad (7)$$

in which d is the density of the polymer, M the molecular weight of the repeating unit, $\Sigma K_i'$ is its effective volume, comprising the effective volumes of the atoms and groups of atoms forming the unit, and A' is a parameter representing a given series of polymers. This equation holds

well for several series (aromatic polyesters and polyamides, polymethacrylates), Numerical values of K_i' and A' can be found from the original paper [125].

Table 1. Increments K_i^* for various atoms and types of intermolecular interaction.

Atom or interaction	Conventional symbol	Value
Carbon	K_C^*	10.739
Oxygen in side-group	$K_{O,s}^*$	3.925
Oxygen in main chain	$K_{O,m}^*$	−5.244
Hydrogen	K_H^*	−1.248
Nitrogen in side-group	$K_{N,s}^*$	9.520
Nitrogen in main chain	$K_{N,m}^*$	2.185
Chlorine	K_{Cl}^*	7.242
Silicon	K_{Si}^*	19.570
Hydrogen bond	K_h^*	7.333
Dipole-dipole*	K_d^*	7.333
Symmetry coefficient**	K_p^*	10.500

*The coefficient K_d^* is introduced in all cases in which a hydrogen atom is replaced by any type of radical other than phenyl. This rule does not extend to polyisoprene and polychloroprene. When two hydrogen atoms are replaced by identical radicals, the value 0.5 K_d^* is introduced.
**The coefficient K_p^* is introduced if all the aromatic rings in the main chain are substituted in the *para*-position.

Later a general scheme of calculation was proposed [126], applicable to polymers of any series. The glass point was determined from the relation

$$\lg T_g = \frac{\sum_i K_i^*}{N_A \sum_i \Delta V_i} + A, \qquad (8)$$

where $\sum_i K_i^*$ is an additive quantity having the dimensions of a volume and connected with the packing coefficient k and the coefficient α_G of cubical expansion, $\sum_i \Delta V_i$ is the van der Waals volume of the repeating unit, comprising the volumes ΔV_i of all the component atoms, $A = 1.435$ is a parameter of linear polymers of any chemical structure, and N_A is Avogadro's number. The quantities K_i^* occurring in ΣK_i^* are characteristic of each element and each type of intermolecular interaction, and are listed in Table 1. With their values known, it is easy to calculate the glass point of a polymer by means of Eqn. (8) provided that its chemical structure is known. It is first necessary to find [15,127] the van der Waals volume of the repeating unit. Calculated and experimental glass points show good agreement [126] for many polymers of the most diverse structure. Fig. 24, in which the theoretical dependence of the glass point on $\sum_i K_i^*/N_A \sum_i \Delta V_i$ has been drawn, and experimental values have been plotted, confirms that formula (8) holds over a very wide temperature range.

It is thus theoretically possible to calculate the glass point of a polymer before it has been synthesised: the applicability of Eqn. (8) has been subjected to the most detailed verification on heat-resistant polymers. Use of the above scheme of calculation to predict glass points with the aim of synthesising polymers having specified properties has been applied [128] to heat-resistant systems containing fluorine. Other problems can also be solved by this means. Thus, knowing the increment K_d^* representing the effect of intermolecular interaction on the glass point, we can determine from Eqn. (8) the number of chemical groups in the repeating unit that are able to interact in this way and how many are excluded from interaction by steric hindrance. With aromatic polyimides, for example, only two of the four possible carbonyl groups enter into interaction. It is noteworthy also that carbonyl groups enclosed directly between aromatic ring systems are also incapable of intermolecular interaction because of steric hindrance, as has been demonstrated by an independent method [129].

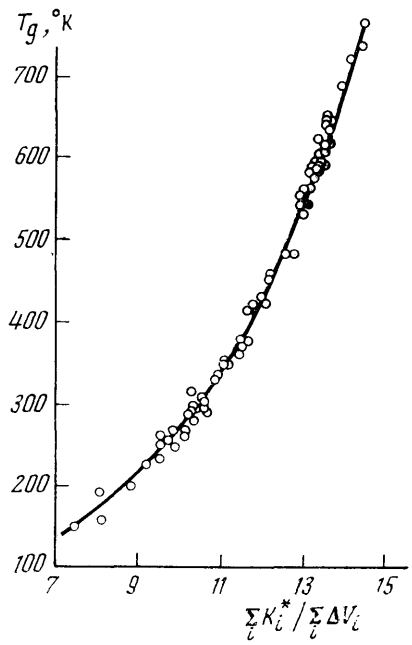
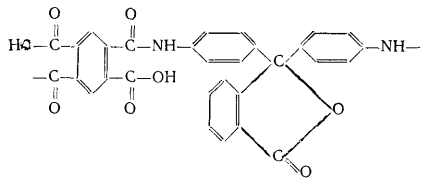
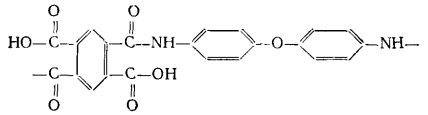
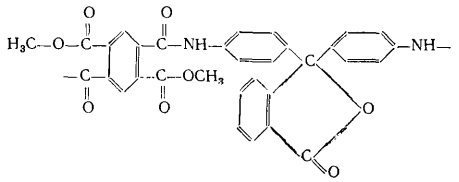
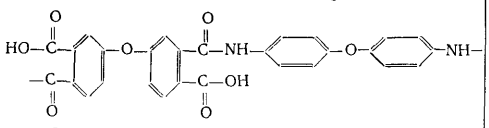
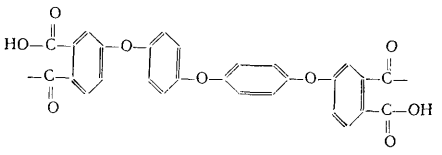
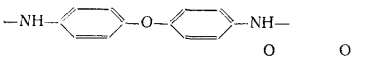
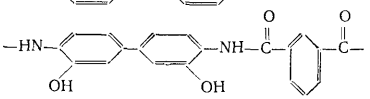
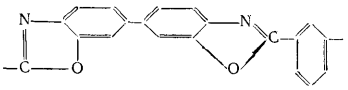
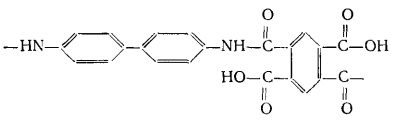
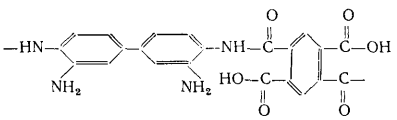
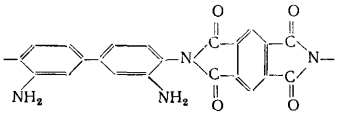
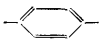


Figure 24. Dependence of T_g for a series of polymers on the ratio $\sum_i K_i^* / \sum_i \Delta V_i$.

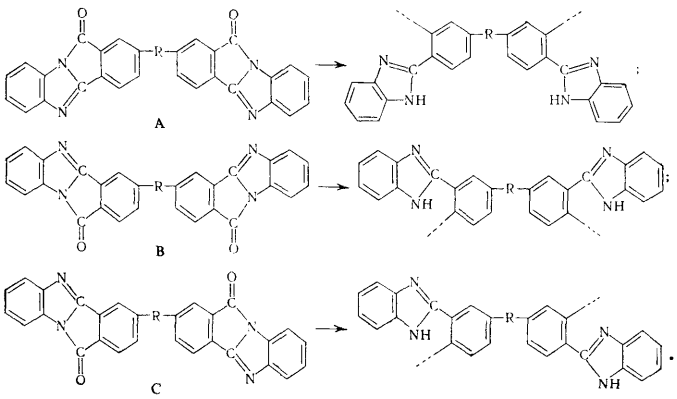
Another problem that can be solved by means of formula (8) is the calculation of glass points of polymers whose experimental determination presents great difficulties. Such are systems which undergo various types of chemical changes—thermal degradation, oxidation, cross-linking, cyclisation, etc.—when they are heated. This applies especially to heat-resistant polymers, in which such chemical changes may take place below the glass point. Table 2 gives calculated values for some of them, as well as for certain polyamide-esters, polyamino-acids, etc. that undergo rapid cyclisation.

Yet another use of the above scheme of calculation is to refine the chemical structure of a polymer whose glass

Table 2. Calculated glass points for polymers when experimental determination is difficult.

Polymer	$\sum_i \Delta V_i$, cm³ mole⁻¹	$\sum_i K_i^*$, cm³ mole⁻¹	T_g, °C (calc.)
	268.5	370.5	380±20
	208 8	266.6	242±15
	291.9	384.5	292±17
	259.7	310.3	154±13
	361.8	418.7	118±12
			
	180.7	232.0	251±16
	162.7	229.2	425±21
	203.6	271.9	316±18
	217.5	288.4	304±17
	194.3	285.8	532±24
	45.5	69.9	662±28
— [C≡C]—	14.8	21.5	493±23

point has been determined experimentally, as in a study [19] of the effect of chemical structure on the properties of polybenzazoles containing bulky substituents. These heat-resistant polymers may have an irregular arrangement of chains because of the possibility of geometrical (*cis–trans*) isomerism in the initial bisbenzoylenebenzimidazoles. With *meta*- or *para*-substitution the resulting polymers may in principle contain the structural units



It is difficult or almost impossible to determine the exact structure of such systems by the usual methods, so that the softening points of all the systems were calculated and compared with the experimental temperatures [19]. Experimental and calculated glass points showed good agreement when substitution occurred either in the *meta*-position or in *meta*- and *para*-positions. The first type of linking into chains may occur with the *cis*-isomer (A), and the second with the *trans*-isomer (B). Thus the polybenzazoles studied [19] evidently contain both structures and are mixtures of isomers. This is supported experimentally by the fairly wide melting range of the initial bisbenzoylenebenzimidazoles, despite their high purity. Analogous problems have also been solved [130].

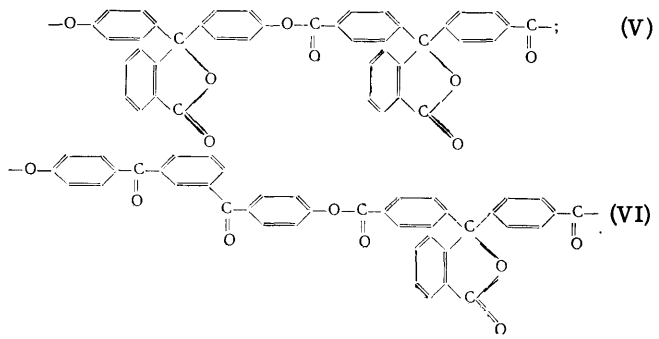
The chemical structure of a copolymer can also be determined by comparing calculated and experimental glass points. In several cases it is sufficient to apply formula (8), deduced on the assumption of approximately the same density of packing of macromolecules within monolithic amorphous systems. Differently constructed copolymers (random, block, various types of addition of units, etc.) may exhibit looser or denser packing of the macromolecules, which must be taken into account in the calculation. For this purpose Eqn. (8) can be rewritten

$$\lg T_g = \frac{k}{k_{av}} \cdot \frac{\sum_i K_i^*}{N_A \sum_i \Delta V_i} + A, \qquad (9)$$

where k is the actual packing coefficient and $k_{av} = 0.681$. Formula (9) will then give glass points higher or lower than the additive values depending on the composition, as is observed fairly often in practice. With copolymers not only the glass point but also the density must be determined experimentally, k calculated, and then T_g found from Eqn. (9). The chemical structure of the copolymer can be determined by comparing calculated and experimental glass points.

Furthermore, it is possible in several cases to estimate the contributions both of intermolecular and of intramolecular interactions to the glass point on passing from one copolymer to another. A series of copolymers and homopolymers was synthesised [129] from phenolphthalein,

3,3-diphenylphthalide-*p'p"*-dicarboxylic acid, and *m*-bis-*p'*-hydroxybenzoylbenzene. The homopolymers had the structures



(V)

(VI)

These polyesters, as well as all the copolymers, contained the same numbers of atoms and benzene residues, differing only in the numbers of attached phthalide rings. Passing from polymer (V) to polymer (VI) entailed not only diminished intermolecular interaction due to the phthalide ring but also a lower glass point because of diminished intramolecular interaction (steric factor). The contributions of each of these factors were estimated by means of formula (9), which for copolymers becomes

$$\lg T_g = \frac{k}{k_{av}} \cdot \frac{x_1\left(\sum_i \Delta V_i\right)_1 (\lg T_{g,1} - A) + x_2\left(\sum_i \Delta V_i\right)_2 (\lg T_{g,2} - A)}{x_1\left(\sum_i \Delta V_i\right)_1 + x_2\left(\sum_i \Delta V_i\right)_2} + A. \quad (10)$$

This showed that only half the difference $\Delta T = T_{g,1} - T_{g,2}$ was due to the decrease in the number of intermolecular bonds corresponding to the smaller number of phthalide groups, the rest being caused by rotation of a phthalide ring. The effective energy of intermolecular interaction in the presence of a phthalide ring was 9.4 kcal mole^{-1}.

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Comparison of the whole set of properties of heat-resistant aromatic polymers with those of ordinary polymers having relatively inflexible chains indicates that increasing the rigidity of the chain and saturating it with aromatic rings lead to the expected rise in the glass point, but this is accompanied by qualitative changes in all the other properties. Passing to heat-resistant aromatic polymers (e.g. various types of polyheteroarylenes) leads to a significant increase in the maximum mechanical stresses that the polymeric material is able to withstand in articles not only at high but also at ordinary temperatures. The explanation is not that the fixed test temperature lies at different distances from the glass point with different compounds: if this were the reason, application of the principle of corresponding states would yield the same tensile strength or limit of forced elasticity at the reduced temperature. However, this does not occur, since the temperature dependence of the forced rubberlike elasticity is indistinct at temperatures sufficiently below the glass point, and these relations cannot be superimposed merely by displacement along the temperature axis. Hence the reason for the increased strength lies in the actual nature of the polymer chain saturated with aromatic rings.

The difference between the mechanical properties of flexible-chain and rigid-chain aromatic polymers becomes especially clear in prolonged observations under conditions of stress relaxation. Such relaxation is considerably less marked with rigid-chain than with flexible-chain systems, which is responsible for the great difference in the mechanical stresses that these systems are able to withstand at a given temperature. Thus the synthesis of heat-resistant aromatic polymers not only extends the temperature range of performance but also increases significantly the mechanical stresses under which performance is maintained at lower temperatures.

Another characteristic feature of heat-resistant systems is an extraordinarily large optical stress coefficient C_σ, whose values for polyheteroarylenes exceed those for ordinary polymeric glasses (polystyrene, polymethacrylates, etc.) by factors of 10–1000. This means that even very small mechanical stresses cause large double refraction in them, which is of great practical importance, since the use of such materials in the photoelastic method enables the pattern of stress distribution to be obtained with extremely small deformations, i.e. under conditions under which Hooke's law is best obeyed.

The next interesting feature of heat-resistant aromatic polymers is a multitude of relaxation transitions, which plays a very important part in shaping the whole set of mechanical and other physical properties. In the Reviewers' opinion, especial interest attaches to the static methods that have been discovered for investigating the transitions, which largely determine the temperature ranges of performance, i.e. the heat resistance of the polymers.

Another curious feature of heat-resistant polyheteroarylenes is their capacity for considerable (10–20%) deformation at very low temperatures (down to that of liquid nitrogen) [5,6,72,131]. Hence heat-resistant aromatic polymers are able to satisfy a requirement for a polymeric material that is capable of non-brittle fracture not only at high but also at low temperatures.

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