RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

December 1964

U.D.C. 541.64:541.66.092.2/.4

ADVANCES IN THE SYNTHESIS OF THERMOSTABLE POLYMERS

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CONTENTS

I. Introduction 609

II. Dependence of thermal stability on structure of monome unit 610

III. Dependence of thermal stability on structure of polymer chain 615

IV. Dependence of thermal stability on reactivity of macromolecule 619

V. New thermostable polymers 624

I. INTRODUCTION

Great interest has recently been shown in thermostable polymers. This has arisen from the needs of aviation, radio engineering, rocket technology, and other fields which demand the use of increasingly thermostable materials.

Polymers employed in electrical insulation and as working parts in various machines and equipment must operate at high temperatures for a long time and still maintain their mechanical properties. However, the prolonged action of a high temperature has a harmful effect on polymers, causing them to break down both by the direct action of temperature and by the rapid occurrence at elevated temperatures of chemical reactions with oxygen, water, and other chemical reagents.

It must first be noted that the actual concept of thermal stability is quite indefinite, so that different authors frequently use the term in different senses. We shall define thermal stability by the temperature at which polymers still retain their shape and their characteristic set of mechanical properties. In a definite sense thermal stability corresponds to the melting point or softening point of the polymers.

The mechanical strength of polymers varies with temperature as shown in Fig. 1. Thus the thermal stability at zero load will correspond to the softening point of the polymer. The greater the load the lower must be the temperature at which the polymer would retain the required strength. In order to specify the thermal stability of a polymer completely, therefore, the load at which it has been determined must be known. Consequently there must be a direct link between the thermal stability, conceived as the limiting temperature at which the polymer still withstands a given load, and the softening point of the polymer, which relation can in general be expressed by the formula $\tau = bt_{sft}$, where τ is the thermal stability (°C), t_{sft} the softening point (°C), and $b = 1 - \sigma_\tau/\sigma_0$, in which σ_τ and σ_0 are the loads (kg cm^{-2}) at the respective temperatures τ and 0°.

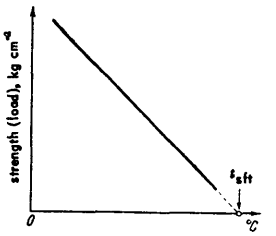


Fig. 1. Temperature dependence of strength of polymer.

A similar formula was proposed by Ratner *et al.*[8], who considered various aspects of its application in detail. These workers describe different methods of testing and estimating the thermal stability of polymers.

Thermal stability is also very widely taken to mean the ability of a polymer to maintain unchanged its engineering properties and structure at high temperatures. It depends on the strength of the bonds between atoms in the polymer molecule and the readiness with which the molecule undergoes various reactions, primarily those involving degradation.

Polymers are specified also by such concepts as heat--resistance or deformation temperature, which are defined with respect to special standards. A very convenient characteristic for comparing the operational properties of polymers may be the temperature at which 50% of their initial strength is lost.

Interest in this important branch of polymer chemistry is continually increasing, as is shown in the numerous papers, reviews, and monographs which have been published[1-10]. Our aim in the present review is to examine and summarise information published recently on the dependence of the thermal stability of polymers on their structure, and on this basis to give an overall picture of the present state of the problem.

II. DEPENDENCE OF THERMAL STABILITY ON STRUCTURE OF MONOMER UNIT

Examination of the dependence of thermal stability on the structure of the macromolecule is one of the most important aspects of the broad problem of studying the relation between the structure of a polymer and its properties. From this point of view both the structure of the monomer unit and that of the macromolecule as a whole are significant, as is also the interaction between the polymer molecules, which determines the structure of the polymer comprising these macromolecules. We shall therefore describe separately the effects which may be attributed to the structures of the monomer unit, the macromolecule, and finally the polymer as a whole, paying special attention to the behaviour of the polymer at high temperatures.

The structure of the monomer unit is the most important factor determining the melting point of a polymer. Fig. 2 illustrates the temperature ranges within which lie the melting points of polymers of various classes. It clearly shows differences between each type of polymer. Melting points below 0° are found only in the polymeric vinyl ethers, hetero-chain polyesters, and polysiloxanes. The higher we rise on the temperature scale, the fewer polymers we find remaining on the diagram. The majority of polymers melt below 200°, and only such groups as polyphenylenes, polyarylates, polybenzimidazoles, some polysiloxanes, polychelates, polypyromellitimides, and polypyrazoles include members which melt above 300°. In nearly all these cases the monomer unit contains a ring: *i.e.* they are cyclo-chain polymers. The presence of various rings in the macromolecular chain in such polymers confers on it great rigidity, and results in strong intermolecular forces, which are responsible for the high melting point.

In contrast to the above cyclo-chain polymers, ordinary straight-chain polymers, exemplified in the many poly-

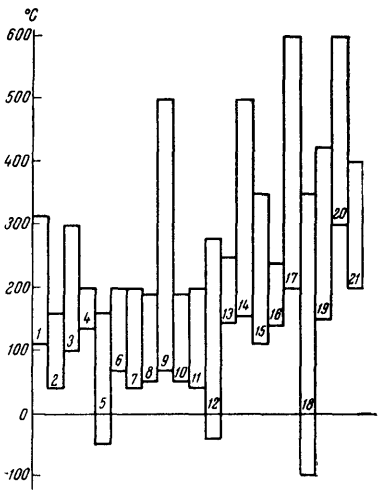


Fig. 2. Temperature ranges of melting points (softening points) for various classes of polymers:
1) polymeric hydrocarbons; 2) polymeric chlorinated derivatives; 3) polymeric fluorinated derivatives; 4) polymeric alcohols; 5) polymeric vinyl ethers; 6) polymeric vinyl esters; 7) polymeric acrylic esters; 8) polymeric dienes; 9) polyphenylenes; 10) polyethers; 11) polyacetals; 12) polyesters; 13) polycarbonates; 14) polyarylates; 15) polyamides; 16) polyerethanes; 17) polybenzimidazoles; 18) polysiloxanes; 19) polychelates; 20) polypyromellitimides; 21) polypyrazoles.

vinyl compounds, comprise monomer units consisting solely of individual carbon atoms extending in a linear chain $-CH_2-CHX-$. The great flexibility of such a chain and the weak intermolecular forces are responsible for the lower melting points of these and similar polymers.

The melting (softening) points of vinyl polymers depend on the number and nature of the substituents in the monomer unit, as well as on the structure of the chain itself (on stereoregularity, cross-linking, etc.), which will be considered in greater detail below.

The length of the monomer unit, the nature of the atoms it contains, and also the possibility of hydrogen bonding have a significant influence. Thus it has long been established with polyamides and polyesters that polymers in which the monomer unit contains an even number of methylene groups melt at higher temperatures than analogous compounds containing an odd number of atoms in the unit. Figs. 3 and 4 show the variation in the melting points[11] of polyesters of ethylene glycol and of eicosamethylene glycol with dicarboxylic acids containing even and odd numbers of methylene groups in the monomer unit. A similar pattern is observed with polyamides (Fig. 5).[12]

Replacement of a methylene group by an oxygen atom results at first in a rise in melting point, as is readily seen on comparing polyethylene with polyformaldehyde (m.p. 115° and 185° respectively). With a longer monomer unit, however, the melting points of both polyethers and polyesters fall. This is shown especially clearly by the polyesters of triethylene glycol, which melt below 0° (Fig. 6).[13]

In contrast, introduction of an amide grouping NHCO into a polymer chain produces a marked rise in the melting

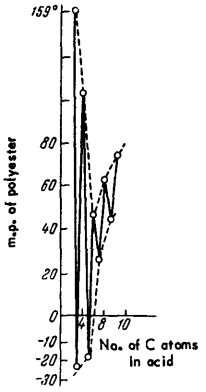


Fig. 3. Variation in melting point of polyesters of ethylene glycol.

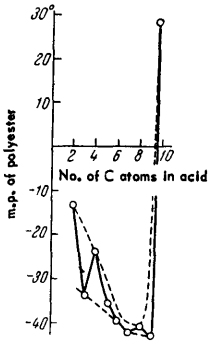


Fig. 6. Variation in melting point of polyesters of triethylene glycol.

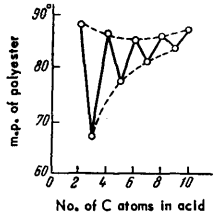


Fig. 4. Variation in melting point of polyesters of eicosamethylene glycol.

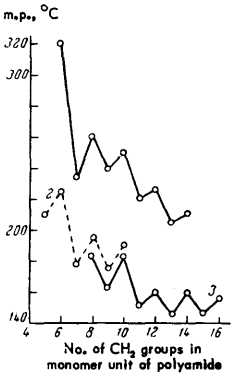


Fig. 5. Variation in melting point of polyamides of differing structure with number of methylene groups in molecules of the initial monomers:
1) polyamides from hexamethylenediamine and various dicarboxylic acids;
2) polyamides from ω-amino-acids;
3) polyamides from tetramethylene glycol and various diisocyanates.

points of the resulting polyamides, probably associated with a strengthening of the forces between the macromolecules.

The effect of substitution in the chain, as well as the general relationship between the melting points of hetero-chain polymers and their chain structure, may be traced by comparing hetero-chain polymers containing different hetero-atoms in the macromolecule.

Korshak and Frunze showed [14,15] that a quite definite relationship exists between the melting points of polyamides and the chemical structure of the monomer unit. In the case of aliphatic polyamides these relations are so simple that they can be expressed by an empirical linear equation linking melting point with the hetero-chain parameter of the polyamides: $Y = aX + b$, where Y is the melting point of the polyamide, X the parameter, representing the ratio, expressed as a percentage, of the number of groups containing hetero-atoms to the number of methylene groups, while a and b are constants characteristic of each series of polyamides.

The above workers proposed regarding polyamides in this respect as copolymers of polyethylene and isocyanic acid HNCO, and showed that the relative arrangement of these components had no effect on the melting point of the polymers, which depended solely on the ratio $CONH/CH_2CH_2$, *i.e.* on the molecular percentage of amide groups in the polymer.

It was shown that this applied to other series of hetero-chain polymers — polyureas, polyurethanes, polyesters, polyanhydrides, etc. — as well as to polyamides (Table 1). In all these series a linear relation was found, illustrated graphically in Fig. 7. The melting-point graphs intersect at a point corresponding to the melting point of polyethylene, *i.e.* to zero content of amide or other groups.

As we shall show later, all the relationships become more complicated on introduction into the polymer chain of aromatic or hydroaromatic rings, hetero-atoms, or side-chains. Replacement of methylene hydrogen atoms by other atoms or groups has a great effect on the melting point of the polymer, both the nature of the substituents and their number and relative arrangement in the chain and in space being of great significance.

Introduction of one substituent into each monomer unit of an atactic polymer in most cases lowers the melting

TABLE 1. Equations relating melting point with the hetero-chain parameter of various groups of polymers[14,15].

Polymer group	Equation
Polyureas with an even number of methylene groups in the monomer unit	$Y = 8.4X + 110$
Polyamides with an even number of methylene groups in the unit	$Y = 7X + 110$
Polyamides as above, from other data	$Y = 7X + 125$
Polyamides from dicarboxylic acids with odd, and diamines with even, numbers of methylene groups	$Y = 6.2X + 110$
Polyamides from even dicarboxylic acids and odd diamines	$Y = 5.6X + 110$
Polyamides from odd dicarboxylic acids and odd diamines	$Y = 4.5X + 110$
Polyurethanes with an even number of methylene groups in the monomer unit	$Y = 3.5X + 110$
Polyamides with sulphide sulphur in the chain	$Y = 3X + 110$
Polyamides with ethereal oxygen in the chain	$Y = 1.9X + 110$
Polyanhydrides with an even number of methylene groups in the unit	$Y = -2.5X + 110$
Polyesters with an even number of methylene groups in the unit	$Y = -3X + 110$
Polyesters with an odd number of methylene groups in the unit	$Y = -3.6X + 110$
Polyanhydrides with an odd number of methylene groups	$Y = -3.6X + 110$

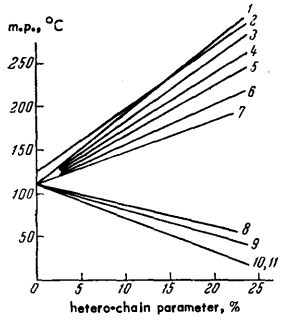


Fig. 7. Dependence of melting point on hetero-chain parameter for:
1) polyureas; 2) polyamides with an even number of CH_2 groups in the diamine and in the acid;
3) polyamides as (2), from measurements of the true thermodynamic melting points; 4) polyamides from even diamines and odd acids;
5) polyamides from odd diamines and even acids;
6) polyamides from odd diamines and odd acids;
7) polyurethanes; 8) polyanhydrides with an even number of CH_2 groups in the monomer unit;
9) polyesters from even glycols and even acids;
10) polyesters from odd acids and odd glycols;
11) polyanhydrides with an odd number of CH_2 groups.

point. Thus polyethylene melts at a higher temperature than poly(vinyl chloride), poly(vinyl acetate), and polystyrene, as is seen from Table 2.

We thus see that in most cases, with the exception of poly(vinyl fluoride), introduction of one substituent into the monomer unit of polyethylene lowers the softening temperature. However, a different situation is found with stereoregular polymers, which usually melt at higher temperatures than does polyethylene, as will be discussed in greater detail below.

In just the same way the presence of substituents in the molecules of polyamides, polyesters, and other polymers results in lower melting (softening) points, as is evident in

TABLE 2. Melting or softening points of polymers of type CH_2–CHX.

Polymer	Melting or softening point, °C
Polyethylene	115
Poly(vinyl chloride)	80
Poly(vinyl fluoride)	200
Poly(vinyl acetate)	70
Polystyrene	90
Polypropylene	80

the case of the polyesters of propylene glycol with various dicarboxylic acids[13]. These polyesters melt below 0°, as is shown in Fig. 8.

Introduction of two substituents may produce either a rise or a fall in the melting point of the polymers (Table 3).

The polymer chain can be made rigid, and free rotation about single bonds hindered, by introducing various atoms and groups into the macromolecule. Thus polytetrafluoroethylene melts at 330°, in contrast to polyethylene (m.p. 115°), although the forces of intermolecular interaction are almost the same in these two polymers. The potential barrier preventing free rotation about C–C bonds was found to be far higher in hexafluoroethane than in ethane itself (4550 and 3000 cal respectively). If it is assumed that similar potential barriers remain in the polymers, these concepts can be used, according to Billmeyer[16], to explain the high melting points of fluorinated polymers as a result of greater rigidity of the polymer chain caused by the screening effect of the densely packed fluorine atoms.

The higher melting points of polymers obtained from branched α-alkenes compared with those of linear α-alkenes

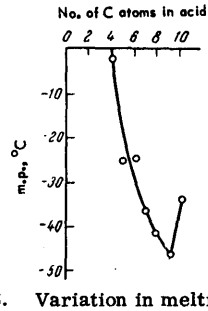


Fig. 8. Variation in melting point of polyesters of propylene glycol.

TABLE 3. Melting points of polymers of type CH_2–CX_2.

Polymer	Melting or softening point, °C
Poly(vinylidene chloride)	185
Poly(vinylidene fluoride)	170
Poly(methyl methacrylate)	125
Poly-α-methylstyrene	160
Polymethacrylonitrile	115

can also be explained by the increased rigidity of the polymer chain produced by the introduction of substituents, whose presence hinders free rotation about the carbon–carbon bonds. In the case of atactic polymers, the increase in rigidity of the polymer chain accompanying introduction of substituents is usually balanced by a decrease in interchain interaction caused by the accompanying breakdown in molecular symmetry and in dense packing.

Cyclo-chain polymers containing carbocyclic or heterocyclic rings in the chain are usually distinguished by high thermal stability. Table 4 gives melting (softening) points for series of cyclo-chain polymers, and includes for comparison melting points of structurally analogous polymers not containing rings. The introduction of *p*-phenylene groups into a polymer chain always results in a rise in melting point (see Table 4).

An increase in cohesive forces also cannot explain the improved thermal stability of the polymers in this case, since the increment in the energy of these forces for a phenyl group is almost the same as for six methylene groups (determined by comparing melting points and latent heats of vaporisation of aromatic and aliphatic compounds containing the same number of carbon atoms). Moreover, the crystal structure of poly(ethylene terephthalate) indicates that the distances between atoms of neighbouring macromolecules are the usual van der Waals distances. The considerable rise in melting point of polymers produced by introducing an aromatic ring into the chain must be due to the rigidity of the chain, and probably associated also with conjugation.

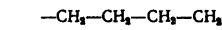
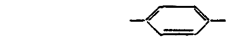
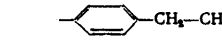
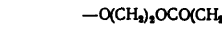
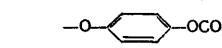
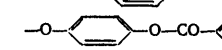
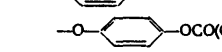
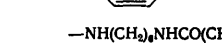
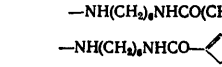
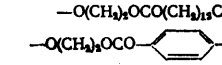
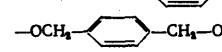
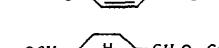
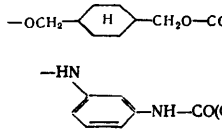
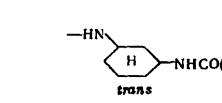
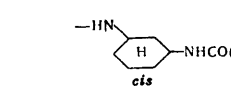
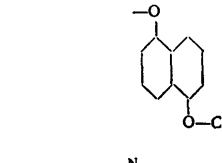
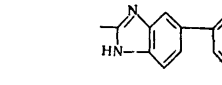
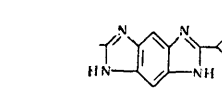
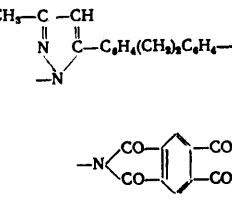
The effect of aromatic rings in a chain on the thermal stability of polymers can be seen especially clearly in a novel class of polymers, the polyarylates. Comparison of the softening temperatures of polyarylates of adipic acid with those of the corresponding polyarylates of terephthalic acid, which have been synthesised and investigated by Korshak and Vinogradova [10], has shown that replacement of aliphatic by aromatic (terephthalic) acid residues in the polyester chain raises considerably the softening point of the polyarylates. For example, the softening point of the polyarylate of quinol with adipic acid is 225°, whereas poly(quinol terephthalate) does not melt below 500° (Table 4). Polyarylates of adipic acid possess higher softening points than do the corresponding polyarylates of sebacic acid, probably owing to the diminished rigidity of the polymer chains in the latter case, resulting from the lower concentration of aromatic rings.

Introduction of 1,5-naphthylene and *pp'*-biphenylylene groups into the polymer chain also produces a rise in melting point compared with the corresponding polymers containing only one benzene ring (Table 4).

It is interesting that hydrogenated aromatic rings also raise the melting point, sometimes to a greater extent than do aromatic rings, as can be seen from Table 4. Various heterocycles are also extremely effective, their introduction into the macromolecule greatly raising the melting point of the polymers (Table 4), which include polybenzimidazoles, polypyrazoles, polypyromellitimides, etc.

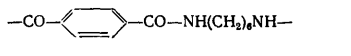
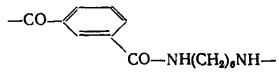
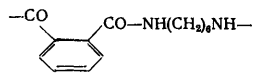
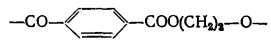
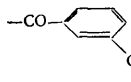
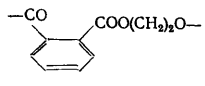
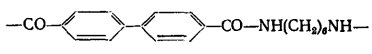
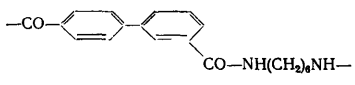
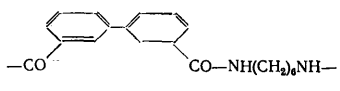
The examples which have been cited show that *para*-substituted rings very greatly raise the melting points of polymers. Rings which are substituted in *ortho* and *meta* positions have quite different effects. Their presence usually results in lower melting points, as is seen from the examples in Table 5, and it also diminishes the crystallinity.

TABLE 4. Effect of the presence of rings in the chain on the melting points of polymers.

Monomer unit	Melting or softening point, °C	Ref.
	115	17
	530	18
	380	19
	45	20
	264	21
	225	22
	500	23
	172	22
	235	23
	350 (decomp.)	11
	80	23
	330	11
	238	24
	290	25
	258	11
	300	26
	165	26
	250	26
	630 (decomp.)	27
	600	28
	500	28
	280	29
	400	30,31

Korshak and Vinogradova [23] showed that the softening temperature of a polyarylate depends on the relative arrangement of functional groups both in the acid and in the diol. Polyesters of acids and diols having their functional groups in the *para* positions have higher softening

TABLE 5. Effect of substitution isomerism in the ring on the melting points of polymers.

Monomer unit	Melting or softening point, °C	Ref.
	350	11
	150	11
	50	11
	256	11
	103	11
	63	11
	360	11
	140	11
	142	11

points than polyesters of initial components with *meta*--oriented functional groups. Thus polyarylates formed by resorcinol with terephthalic and isophthalic acids soften considerably below the corresponding polyarylates of quinol; the polyarylates of these acids with 2,2-diphenylpropane-*pp'*-diol, hexaphenylxylene-*pp'*-diol, and naphthalenediols also support this generalisation[23,27,32].

The energy of free rotation, or the energy required to surmount the potential barrier opposing rotation, is about 1–5 kcal mole^{-1}, which is of the same order as the energy of cohesion. Potential barriers to rotation about single C–C bonds adjacent to a double C=C bond are lower than in saturated molecules[33,34]. Thus introduction of double bonds into a polymer molecule increases its flexibility, which is shown in a lowering of the softening point of the polymer. On the other hand, the presence of conjugated double and triple bonds makes the molecule rigid and raises the softening point[35]. Thus "carbyne",[36] which is a linear polymer with a system of conjugated triple bonds $(C{\equiv}C)_x$, is unchanged by temperatures up to 2300°. Polyvinylene[37] $(CH{=}CH)_x$, obtained by the dehydrogenation of poly(vinyl alcohol), is unchanged by heating up to 800°.

The strength of the bonds between atoms in the monomer unit is of great significance for the thermal stability of polymers. Table 6 gives data on the stabilities of bonds between individual elements. Elements whose bonding energy exceeds 37 kcal mole^{-1} are able to form polymers. With lower values formation of homo-chain polymers is not observed, as is evident from the example of nitrogen and

TABLE 6. Energy of bonds between like atoms[38].

Bond	Bond energy, kcal mole^{-1}	Bond	Bond energy, kcal mole^{-1}
C—C	80.0	Sb—Sb	42.0
S—S	63.0	Ge—Ge	39.2
P—P	53.0	As—As	39.0
Se—Se	50.0	N—N	37.0
Te—Te	49.0	O—O	34.0
Si—Si	45.0		

oxygen. This capacity is most clearly developed with carbon, which is distinguished by the highest bonding energy.

A very different situation is found with hetero-chain polymers, and the number of elements capable of forming them is much greater. Table 7 gives bond energies which are typical of hetero-chain polymers. It is seen that these values are quite considerable, and in many cases exceed the bond energies of homo-chain polymers. In most cases, therefore, hetero-chain polymers are hard, durable substances of high melting point.

From a study of polymers having inorganic chains Andrianov[39] concluded that an E–E' bond will be more stable with less ionic character in the bonds forming the main chain, *i.e.* the closer the mean electronegativity of the two elements forming the bond to the electronegativity of the carbon atom, which is 2.5. Table 8 gives electronegativity values for several elements.

Andrianov points out[39] that examples of organoelementary polymers having this structure are provided by the polyorganosiloxanes and the polyaluminoorganosiloxanes, whose chains are built up from alternating electropositive silicon and aluminium atoms and electronegative oxygen atoms, the mean electronegativity of the bond between these two elements approaching that of carbon. These chains reproduce the skeleton of the inorganic polymers — quartz and aluminosilicates — occurring in Nature; they are stable to heat and hydrolysis.

TABLE 7. Energy of bonds between unlike atoms[38].

Bond	Bond energy, kcal mole^{-1}	Bond	Bond energy, kcal mole^{-1}
B—O	119.3	C—N	66.0
B—N	104.3	As—O	64.5
Si—O	89.3	Al—C	61.6
B—C	89.0	C—S	61.5
P^{III}—O	81.7	Si—S	60.9
C—O	79.0	C—Si	57.6

TABLE 8. Electronegativities of elements in Groups III–VI of the Periodic System[39].

III	IV	V	VI
B —2.0	C —2.5	N —3.0	O —3.5
Al—1.5	Si —1.8	P —2.1	S —2.5
	Ge—1.8	As—2.0	Se—2.4
	Ti—1.6	V —1.9	Te—2.1
	Sn—1.7	Sb—2.1	Mo—2.1
	Zr—1.5		W —2.0
	Pb—1.6		

The stability of the bonds between substituents and main chain is also of great significance. Thus poly(vinyl chloride) is a polymer of relatively low thermal stability, since it readily eliminates hydrogen chloride. The same applies to poly(vinylidene chloride), poly(vinyl alcohol), and compounds of similar structure. These considerations apply also to the side-chains. Thus the higher thermal stability of Penton (a polymer of 3,3-bischloromethyloxetan) is explained by the fact that the carbon atom adjacent to the chloromethyl group carries no hydrogen atom, which would be necessary for the formation of hydrogen chloride.

The results considered above make clear the relationship which can be detected between the structure of the monomer unit and the properties of the polymer. However, this does not exhaust the problem of the link between thermal stability and polymer structure. Other factors also have a great influence, and will be considered later. These are the structure of the macromolecule itself and the various changes it undergoes at elevated temperatures.

III. DEPENDENCE OF THERMAL STABILITY ON STRUCTURE OF POLYMER CHAIN

Several structural features of the macromolecule are as important as the structure of the monomer unit, among them being the regularity of the chain, the presence of branching or cross-links between chains, the ability to crystallise, the strength of the intermolecular forces, and the flexibility of the macromolecule.

A regular alternation of monomer units in the macromolecule is a factor tending to raise the melting point. This is shown especially clearly when homopolymers are compared with copolymers: the latter always have lower melting points, since the disordered arrangement of monomer units impedes crystallisation and any ordering of the macromolecular chains in the mass of the polymer in general. Thus polyamides having a regular arrangement of monomer units, prepared by migration copolymerisation from bisoxazolones and diamines, have higher melting points than polyamides of similar composition but with a disordered arrangement of monomer units, obtained by polycondensation of the starting materials[40].

A still greater effect in raising melting point is obtained by stereoregular arrangement of the units in a chain, which ensures not only the accurate alternation of monomer units but also their regular spatial arrangement, as we observe in the case of stereoregular (isotactic and syndiotactic) polymers.

Table 9 gives examples of compounds of stereoregular and atactic structure which have high melting points. They illustrate well the considerable rise in melting point in stereoregular as compared with atactic polymers of the same composition. The former are crystalline even in the presence of bulky substituents, which do not interfere with crystallisation, in contrast to amorphous atactic polymers, in which the ability to crystallise is often completely absent owing to steric hindrance by the substituents. Crystallinity is an important factor tending to increase thermal stability. This question has been discussed in detail in the literature[41].

The presence of branching impedes crystallisation and ordering of the macromolecule. The classical example of this is polyethylene produced at high pressures, which melts at 105°, whereas low-pressure polyethylene melts

TABLE 9. Examples of high-melting stereoregular polymers.

Polymer	Melting or softening point, °C		Ref.
	cryst.	amorphous	
Poly-3,3-dimethylbut-1-ene	370	—	41
Poly-4,4-dimethylpent-1-ene	320	—	41
Poly-4,4-dimethylhex-1-ene	350	—	41
Poly-3-phenylbut-1-ene	360	—	41
Poly-o-methylstyrene	360	120	41
Poly-2,4-dimethylstyrene	310	180	41
Poly-2,5-dimethylstyrene	330	170	41
Poly-1-vinylnaphthalene	350	100	41
Polyvinylcyclohexane	300	—	41
Polyallyldimethylphenylsilane	300	—	42
Polydiallylmethylphenylsilane	400	—	42

at 138°.[17] The structural difference between them is that the former contains branched macromolecules, and the latter unbranched macromolecules. A fair number of examples of this kind are now known. It can probably be accepted as proved that the lower melting points of polymers obtained by radical polymerisation are due not only to their atactic structure but also to their inherently branched character.

Cross-linked polymers have higher thermal stability. The formation of bridges between chains increases not only the thermal stability of the polymers but also the modulus of elasticity and the hardness, while diminishing the elongation at break. Table 10 gives the effect of the number of cross-links, formed on copolymerisation of styrene with divinylbenzene, on the glass temperature of the polymer[43].

Later work showed that the thermal stability of copolymers of styrene and *p*-divinylbenzene increases linearly at a rate approximately equivalent to 3.3 deg per 1% of divinylbenzene. Tensile strength and impact resistance increase with the first 5% of divinylbenzene, and then fall; hardness increases in proportion to the increase in concentration of divinylbenzene[44]. According to Rutovskii and Shur[45] the thermal stability of poly(methyl methacrylate) can be improved by copolymerisation with allyl methacrylate (Table 11).

TABLE 10. Glass points of styrene–divinylbenzene copolymers.

Divinylbenzene content	Glass point, °C
0	87.0
0.6	89.5
1.5	97.0

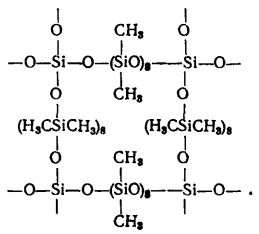
TABLE 11. Thermal stability of copolymers of the meacrylate and allyl meacrylate.

Allyl methacrylate content, %	Thermal stability according to Wieck, °C
0	116
10	141

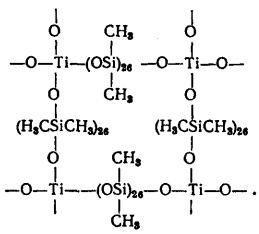
Recently Korshak and Vinogradova have established that the cross-linking of linear saturated polyarylates with formaldehyde and a novolak increases their thermal stability. Polyarylates obtained from isophthalic or terephthalic acid with 2,2-diphenylpropane-*pp'*-diol or phenolphthalein and *o*-allylphenol or the diallyl derivative of the diol readily underwent further hardening, both thermally and by copolymerisation with methyl methacrylate. The strengthened polyarylates are characterised by rubberlike elastic deformation over a wide range, and break down appreciably only at temperatures above 500°.[46-48]

A case of the improvement of the mechanical properties and thermal stability of polymers which has been known for a long time is the vulcanisation of rubber and other polymers by means of sulphur or a peroxide. Recently ionising radiation, has been successfully used for this purpose. Thus the γ irradiation of polyethylene increases its thermal stability to 250°.[50]

Andrianov and his collaborators[51] have synthesised regular polymers of three-dimensional structure from multifunctional oligomers containing unifunctional groups at the ends of branches, to which he assigns the structure



Condensation of ter- and quadri-functional oligomers also yields polyorganosiloxanes, as well as organoelementary siloxane polymers, of regular structure



The physical properties of polymers, such as softening and melting points, tendency to crystallisation, solubility, mechanical characteristics, etc., are directly linked with the structure of the polymer chain, being determined mainly by the stereochemical regularity of the macromolecule, its flexibility, and also the intermolecular forces. Interaction between polymeric molecules is responsible for the mechanical strength of the polymer and its thermal stability.

The intermolecular forces determining the thermal stability of polymers include dipole interaction, inductive forces, dispersion forces, and hydrogen bonds. Apart from dispersion forces, they all depend on temperature, becoming weaker as it rises. Intermolecular forces are of great significance, their strength determining to a considerable extent the limiting temperature which the polymer will withstand without breaking down.

The forces acting between molecules are electrical in nature. Non-polar molecules exhibit instantaneous dipoles, caused by the motion of electrons. Although the mean value of these dipole moments is zero, they are nevertheless able to polarise neighbouring molecules, inducing in them corresponding instantaneous dipoles. These interactions produce intermolecular forces of attraction, the so-called "dispersion forces". According to London[52] the potential energy of two identical molecules can be calculated from the formula

$$E = -\frac{3\alpha^2 I}{4r^6},$$

where E is the potential energy, α the polarisability, r the distance between the molecules, and I the ionisation potential.

In the presence of a permanent dipole, the molecule can polarise neighbouring molecules, producing additional forces of attraction, inductive forces. In this case the potential energy will be

$$E = \frac{2\alpha\mu^2}{r^6},$$

where μ is the permanent dipole moment.

The mutual orientation of two dipoles is responsible for larger forces of attraction between the molecules. The mean value taken over all directions gives the increase in potential energy due to orientation forces calculated by means of the equation

$$E = \frac{2\mu^4}{3r^6RT}.$$

Walker[53] notes the following two important points about the above three expressions: (1) dispersion forces are independent of temperature, while depending on the number and strength of bonding of electrons, especially valency electrons; and (2) orientation forces are inversely proportional to the absolute temperature.

Since orientation forces vary with μ^4, their magnitude in polymers containing polar substituents should substantially affect the density of cohesive energy.

Intermolecular forces may be diminished in the case of a chemical structure which prevents the approach of certain atoms and groups to the corresponding atoms or groups in other molecules. Dispersion and orientation forces are inversely proportional to the sixth power of the distance, and therefore the energy of interaction of atoms or groups which are screened by inert groups is significantly lower.

Hydrogen bonds represent a special case of dipole interaction, in which the negative and the positive charge are arranged in such a way that the dipoles can approach very close together, which results in an increase in their energy of interaction.

Thus the stronger the forces of interchain interaction the greater the energy which must be supplied to destroy the order present in the polymer. It follows from the above that the magnitude of these intermolecular forces depends both on "specific" forces of attraction acting between groups in the polymer and on the geometry of the polymer molecules. A convenient measure of intermolecular interaction is the energy of cohesion of individual segments or structural units, calculated on the basis of an additive scheme in which a definite increment of cohesion energy is assigned to each chemical group of atoms.

Bunn[54] used these data to calculate cohesion energies for polymers (Table 12). In order to obtain greater clarity and to make it easier to compare forces of interaction between various groups, Mark[55] made calculations of molecular cohesion for a chain segment 5 Å long (Table 13).

Thus the energy of intermolecular interaction in various polymers (1–6 kcal mole^{-1}) is insignificant in comparison with the energy of a homopolar bond in the main chain (rupture of a single C–C bond requires energy of around 70–100 kcal mole^{-1}). At high degrees of polymerisation, however, the total energy of intermolecular interaction may exceed the energy of the valency bonds in the main chain, and then degradation will involve intramolecular cleavage at valency bonds. The data in Table 12 show that the specific cohesive force for a saturated hydrocarbon chain is small, whereas the presence of polar groups increases it. Simple hydrocarbon polymers, such as polyisobutene and natural rubber, are characterised by low values of specific molar cohesive energy, so that they have low softening points and are readily converted into elastic materials. The introduction of polar groups usually raises the softening point of polymers.

The opposite effect — the neutralisation or elimination of the polar influence of groups by the introduction of non-polar substituents into the molecule — can also be observed. For example, in the esterification of polyacrylic acid, containing strongly polar carboxy-groups, a lowering of the softening temperature of the polymers can be observed. The non-polar hydrocarbon chain neutralises the polar groups of the ester, the introduction of branched or cyclic alkyl groups affecting the softening point considerably less than does the presence of straight-chain alkyl groups of the same molecular weight in the macromolecular[54].

However, if the thermal stability of polymers is assessed only on the basis of the molar cohesion, several discrepancies are evident in Table 13: the high value of 3400 cal for the cohesion of poly(hexamethylene adipate) is consistent with its high melting point (264°); on the other hand, the cohesion energy of poly(ethylene terephthalate), with the same melting point, is considerably lower (1900 cal); while poly(ethylene adipate), in which the cohesion energy (1800 cal) is almost the same as in poly(ethylene terephthalate), melts at 50°; polystyrene, whose cohesion exceeds that of anid [probably a Russian polyamide fibre (Ed. of Translation)] (4000 cal), has m.p. 80°; Teflon and polymethylene have almost the same value for the intermolecular interaction, while their melting points differ markedly. Poly(methyl methacrylate) $CH_2.C(CH_3)(COOCH_3)$ and poly(ethyl acrylate) $CH_2.CH(COOC_2H_5)$ have the same composition and hence should possess the same cohesion; nevertheless, their thermal stabilities are different. Gutta-percha and rubber, which have the same chemical composition $CH_2.C(CH_3):CH.CH_2$ and the same cohesion, also differ in thermal stability (60° and 0° respectively), probably as a result of different steric positions of the substituent (*trans* and *cis*).

TABLE 12. Energy of cohesion of polymers.

Group	Molar cohesion energy, kcal mole^{-1}	No. of chain units in monomer unit	Mean energy per monomer unit, kcal mole^{-1}	Melting or softening point, °C
$-CH_2-$	680	1	680	136.5
$-CF_2-$	760	1	760	330
$-CHCl\cdot CH_2-$	3040	2	1520	80
$-CCl_3\cdot CH_2-$	3780	2	1890	200
$-C(CH_3)_2-CH_2-$	2680	2	1290	0
$-(CH_2)_{10}CONH-$	19 380	18	1076	149
$-(CH_2)_4CONH(CH_2)_6NHCO-$	23 800	14	1700	265
$-(CH_2)_8CONH(CH_2)_6NHCO-$	26 520	18	1474	215
$-(CH_2)_n CONH-$	5800+680n	n+2	—	—
$-(CH_2)_4COO(CH_2)_2OCO-$	9880	10	988	52
$-(CH_2)_n COO-$	2900+680n	n+2	—	—
$-C_6H_4COO(CH_2)_2OCO-$	11 060	5	2212	264
$-C_6H_4COO(CH_2)_n OCO-$	9700+680n	n+3	—	—
$-C_6H_4-C_6H_4COO(CH_2)_2OCO-$	14 900	5	2980	346
$-C_6H_4-C_6H_4COO(CH_2)_8OCO-$	17 620	9	1958	214
$-CH_2C_6H_4CH_2COOCH_2C_6H_4CH_2OCO-$	16 320	10	1632	146
$-C_6H_4COO(CH_2)_2OCOC_6H_4O(CH_2)_2O-$	18 320	10	1832	240
$-O(CH_2)_2O-C_6H_4COO(CH_2)_nOCOC_6H_4-$	16 960+680n	n+8	—	—
$-(CH_2)_nOCONH-$	8740+680n	n+3	—	—
$-(CH_2)_nO-$	1000+680n	n+1	—	—
$-(CH_2)_nS-$	2200+680n	n+1	—	—
$-(CH_2)_nS_2-$	4400+680n	n+2	—	—
$-C(CH_3)=CH(CH_2)_2-$	3760	3	1250	*cis* 20 *trans* 6

TABLE 13. Molecular cohesion of groups.

Polymer	Groups responsible for attraction	Cohesion energy per 5 Å of chain, cal	Softening points of polymers, °C
Polymethylene $-CH_2-$	(CH_2)	1300	115—130
Polyisobutene $-CH_2-C(CH_3)_2-$	(CH_2); (CH_3)	1200	<0
Natural rubber $-CH_2-C(CH_3)=CH-CH_2-$	(CH_2); $(CH=CCH_3)$	1300	<0
Polybutadiene $-CH_2-CH=CH-CH_2-$	(CH_2); $(CH=CH)$	1100	—
Polychloroprene $-CH_2-CCl=CH-CH_2-$	(CH_2); $(CH=CCl)$	1600	—
Poly(vinyl chloride) $-CH_2-CHCl$	(CH_2); $(CHCl)$	2500	80—90
Poly(vinylidene chloride) $-CH_2CCl_2-$	(CH_2);(CCl_2)	3500	185—200
Poly(vinyl alcohol) $-CH_2-CH(OH)-$	(CH_2); $(CHOH)$	5100	~100
Poly(vinyl acetate) $-CH_2-CH(OOCH_3)-$	(CH_2); $(COOCH_3)$	3200	—
Poly(hexamethylene adipate) $-NH(CH_2)_6NHCO(CH_2)_4CO-$	(CH_2); $(CONH)$; H	3400	264
Poly(ethylene adipate) $-O(CH_2)_2OCO(CH_2)_4CO-$	(CH_2); (COO)	1800	50
Poly(ethylene terephthalate) $-O(CH_2)_2OCOC_6H_4CO-$	(CH_2); (COO)	1900	264
Polytetrafluoroethylene $-CF_2-CF_2-$	(CF_2)	1600	330
Polystyrene $-CH_2CH(C_6H_5)-$	(CH_2); (C_6H_5)	4000	80
Cellulose —C—O—C—	(OH); (—O—)	6200	—
Acetylcellulose —C—O—C—	$(OOCH_3)$; (—O—)	4800	—
Silk fibroin —C—N—C—	(CHP); (CONH); H	9800	—
Polyacrylonitrile $-CH_2-CH(CN)-$	(CH_2); $(CHCN)$	—	220

Korshak, Vinogradova, and Frunze[11,56,57] established several quantitative regularities linking the thermal stabilities of hetero-chain polyesters and polyamides with the structure of the polymer chain. They calculated mean values of the cohesion energy per monomer unit for polyesters of differing structure, and showed that, in homologous series of hetero-chain polyesters, the melting point depends on the mean cohesion energy of unit chain. Figs. 9 and 10[56,57] indicate that the melting points of polyesters obtained from polymethylenedicarboxylic acids and glycols lie on two curves when plotted against cohesion energy, passing through minima at 900–1200 cal.

The fact that the above relationship is not represented by a single curve, *i.e.* that the same cohesion energy corresponds to different melting points, indicates that interchain interaction is strongly dependent on the packing of the polymer chains. Less compact packing does not provide the conditions for complete development of interchain forces. There is no doubt that the polymer chains of aromatic polyesters are intrinsically less flexible than are aliphatic polyesters. However, interchain interaction is not always fully developed in the former. Good "packability" or, what is the same thing, a good "superposability factor" of the individual elements in the polymer molecules with respect to one another, is important for the occurrence of interchain interaction, since the energy of the molecular forces approach vary inversely as the sixth power of the distance between the molecules[57].

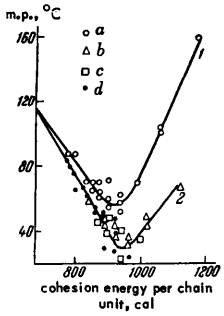


Fig. 9. Variation in melting point of polyesters of polymethylenedicarboxylic acids and glycols with mean cohesion energy per chain unit:
a) both dicarboxylic acids and glycols even; *b*) even acids and odd glycols; *c*) acids and glycols both odd; *d*) odd acids and even glycols.

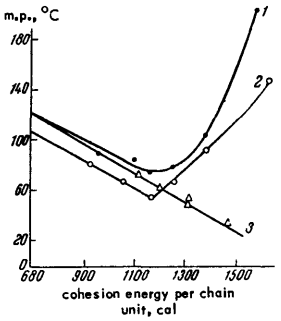


Fig. 10. Variation in melting point of polyesters with mean cohesion energy of chain unit:
1) *p*-xylylene glycol and even polymethylenedicarboxylic acids; 2) benzene-*p*-diacetic acid and even polymethylene glycols; 3) *p*-xylylene glycol and benzene-*p*-diacetic acid, polyesters containing an odd number of methylene groups in the repeating unit.

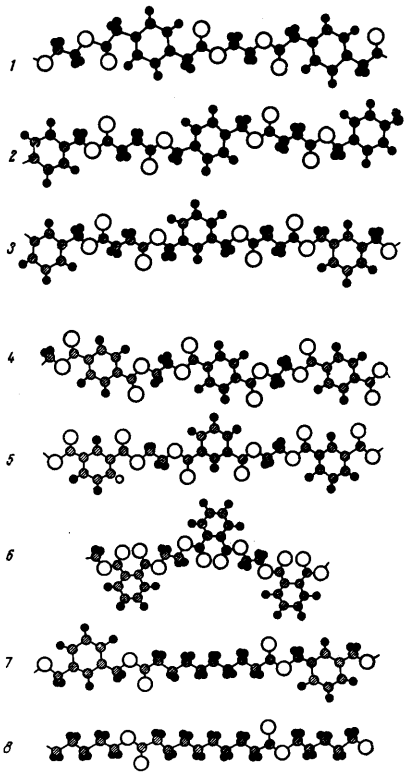


Fig. 11. Diagrammatic view of polymer chains in polyesters:
1) of benzene-*p*-diacetic acid with ethylene glycol; 2) of *p*-xylylene glycol with succinic acid; 3) of *m*-xylylene glycol with succinic acid; 4) poly(ethylene terephthalate); 5) poly(ethylene isophthalate); 6) poly(ethylene phthalate); 7) poly-(*m*-xylylene succinate); 8) poly(pentamethylene succinate).

The low superposability factor in some aromatic polyester molecules results in incomplete development of interchain interaction, in which π-electron interaction between benzene rings in neighbouring chains probably plays no minor role.

The superposability factor is closely linked with the structure of the initial aromatic component, with the relative arrangement of various structural groups in it, and with the degree of symmetry of the initial component[57]. The larger the value of this factor, the closer are the chains packed geometrically, the greater the possibility of more complete development of intermolecular interaction, and as a result the higher the softening temperature of the polymer.

The structures of the polyesters formed by ethylene glycol with terephthalic, isophthalic, and phthalic acids are shown diagrammatically in Fig. 11.[57] It is seen that the superposability factor should be highest with the terephthalic polyester (as a result of the greater symmetry of its molecule) and lowest with the phthalic polyester.

The aromatic rings in polyesters of isophthalic and especially phthalic acid act as a kind of wedge, separating the polymer chains and preventing them from being more closely packed. In such cases the additional rigidity of the polymer chain due to the aromatic rings is sometimes insufficient to compensate for the incomplete development of interchain interaction resulting from this separation.

Measurement of the activation energy of viscous flow for some polyesters containing aromatic units in their chain has shown that those of bicyclic dicarboxylic acids possess more rigid polymer chains than polyesters of monocyclic aromatic dicarboxylic acids, and the latter more rigid than polyesters of aliphatic dicarboxylic acids.

On passing from polyesters of *m*-dicarboxylic to those of *o*-dicarboxylic acids, as well as from polyesters of *p*-xylylene glycol to those of *m*-xylylene glycol, the density of packing of the polymer chains, *i.e.* the superposability factor, diminishes, an effect produced also by introducing a methyl side-chain into the glycol molecule.

The value of the superposability factor has a great effect also on the ability of polyesters to crystallise.

Aromatic polyesters comprising rigid macromolecules possessing high superposability factors are usually crystalline substances, while the ability to crystallise is greatly diminished in aromatic polyesters having low values of the factor. The greatest variation is found in the properties of polyesters obtained from "purely" aromatic components (polyarylates). The presence of aromatic rings joined together only by ester links in these polymer chains produces a very marked rise in the softening point [10,58].

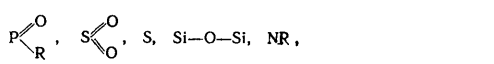
A similar effect of packing density and crystallinity on thermal stability can be traced in the polycarbonate series, where the general rule is that the tendency of the polymers to crystallise is weaker the more unsymmetrical and branched is the substituting group attached to the central carbon atom of the dihydric phenol [59].

Introduction of amide NHCO groups into the polymer chain has the opposite effect to that of ester groups, owing to formation in the first case of hydrogen bonds between the amide groups of separate macromolecules to produce a network. Their presence explains the higher melting points and mechanical strength which distinguish polyamides from polyesters and other polymers containing no hydrogen bonds.

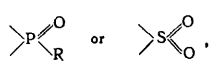
Substitution of alkyl groups on the nitrogen atom removes the possibility of hydrogen bonding, with the result that insoluble, hard, rigid, crystalline polyamides are transformed into soluble, soft, flexible products having considerably lower melting points and durability [60].

Complete manifestation of the second factor — interchain interaction — also requires maximum density of packing. The latter is associated with the structure of the initial aromatic component, with the presence and arrangement of substituents, and with the degree of symmetry of the macromolecule. An increase in density of packing of the chains improves the possibility of more complete development of intermolecular interaction, and hence is accompanied by a rise in the softening and melting points of the polymer. Thus it has been established, for example, that the introduction of rings (aromatic, hydroaromatic) into a polyamide macromolecule is in several cases accompanied by a rise in its melting point [11].

Introduction of groups containing hetero-atoms



into the macromolecule has a considerable effect on the properties of polyamides, the chief factor being the polarity of the group [56]. Thus replacement of a CH_2 group in a dicarboxylic acid by



results in a considerable rise in melting point and a decrease in solubility. Introduction of $-SiR_2.O.SiR_2-$ or $-S-$ makes the macromolecule more flexible, and, as a result of the presence of side-chains, diminishes the density of packing.

The breakdown in regularity in the macromolecules of mixed polyamides results in a weakening of intermolecular interaction owing to the diminished density of packing and the increased distances between the chains, as well as between corresponding amide groups involved in the formation of hydrogen bonds.

There is an important difference between the effects, on the properties of polymers of interchain forces of interaction (both dipole forces and hydrogen bonds) and valency cross-links: the former are strongly dependent on temperature, and rapidly become weaker as it rises, whereas the strength of cross-linking is independent of temperature over a wide range.

All the above facts provide evidence of the quite complicated character of the relation between the structure and the properties of polymers. This is not surprising when it is realised that the link between the macromolecular structure and the properties of the polymer in bulk is not direct but, as has recently been established, involves intermediate, so-called supermolecular structures. Research on the supermolecular structures of polymers has been widely developed during recent years, a leading position in this field being occupied by Soviet workers, mainly Kargin and his school.

Kargin *et al.* [61] suggested that polymers have a "bundle" structure, the formation of crystalline polymers being a very complicated process and involving a series of intermediate stages. Two types of aggregation of the macromolecules — into globules and bundles — are then possible. These are the primary structures, from which more complicated secondary structures are built up. In the former case further ordering involves the formation of macrocrystals from separate globules. In the latter case, completely crystallised bundles, tending to diminish their surface in virtue of thermodynamic considerations, join together to form strips. For the same reasons these latter join to form planar structures, sheets, from which crystals may ultimately be formed [62].

Little work has yet been done on the question of how the structure of the bundles and other intermediate formations affects the bulk properties of the polymer, or on how and to what extent the structure of the bundles is linked with that of the macromolecule itself and its monomer units. The general conclusion can obviously be drawn that a simple and fairly clear relation between the monomer structure and the bulk properties of the polymer is observed only when the intermediate steps in the packing of the macromolecules are governed by equally simple relationships. If however, the structure of the monomer units is such that this is impossible, the influence of these intermediate stages will so obscure the picture that it is now very difficult to establish simple relations between the monomer structure and the bulk properties of the polymer. In these cases we must confine ourselves to establishing most of the qualitative regularities, which make it possible to predict only the fundamental character of the variation in properties.

IV. DEPENDENCE OF THERMAL STABILITY ON REACTIVITY OF MACROMOLECULE

A very important factor in characterising the thermal stability of a polymer is its resistance to the action of atmospheric oxygen, water vapour, and other chemical reagents, as well as its tendency to degradation and cross-linking. All these changes take place rapidly at high temperatures, and therefore the liability of a polymer to undergo them is very important in assessing its possible practical uses.

Resistance to oxidation is a most important characteristic of a polymer. Reactions caused by the action of atmos-

pheric oxygen on polymers result in their degradation or cross-linking (or both simultaneously), which impairs their mechanical properties.

As Korshak *et al.*[63,64] have shown, polyamides on storage in air even at room temperature gradually oxidise and form peroxides; heating accelerates this process considerably, and results in oxidative degradation of the polyamides [12,65,66].

According to Harding and MacNulty[67] the main cause of the appearance of brittleness and loss in strength in a polyamide on being heated in air is oxidative degradation accompanied by hydrolysis.

Sharkey and Mochel[68] consider that in the oxidation of polyamides oxygen attacks the α-carbon atom of the amine residue according to the scheme

$$RCONHCH_2R' \xrightarrow{h\nu} R\dot{C}O + R'CH_2\dot{N}H,$$

$$R\dot{C}O + RCONHCH_2R' \rightarrow RCHO + RCONH\dot{C}HR',$$

$$R'CH_2\dot{N}H + RCONHCH_2R' \rightarrow R'CH_2NH_2 + RCONH\dot{C}HR,$$

$$RCONHCH(OH)R' \rightarrow RCONH_2 + R'CHO,$$

$$R'CHO + O_2 \rightarrow R'COOH.$$

Almost all polymers undergo oxidation by air, especially at high temperatures. Oxidation processes are accompanied by degradation of the polymer chains. Thus the degradation of polyesters on oxidation involves intermediate formation of free radicals, probably according to the general scheme for degradative reactions of this type[69]. The first stage is formation of a hydroperoxide, which then breaks down to form free radicals:

$$\ldots -O(CH_2)_4OCOR'CO- \ldots \xrightarrow{O} \ldots -O-\underset{OOH}{\overset{|}{C}}H(CH_2)_3OCOR'CO- \ldots \rightarrow$$

$$\rightarrow \ldots -O-\underset{O\cdot}{\overset{|}{C}}H(CH_2)_3OCOR'CO- \ldots + \ldots -OCH_2(CH_2)_3OCOR'CO- \ldots \rightarrow$$

$$\rightarrow \ldots -OCH(OH)(CH_2)_3OCOR'CO- \ldots + \ldots -O\dot{C}H(CH_2)_3OCOR'CO- \ldots$$

As a result of interchain interaction, free radicals can form a spatial network of a cross-linked three-dimensional polyester, and may also lead to further breakdown in the polyester chain:

$$-O\dot{C}H(-CH_2-)_3OCOR'CO- \ldots \rightarrow -OCH=CH_2 + CH_2-CH_2-OCOCO- \ldots$$

$$\ldots -O\dot{C}HROCOR'CO- \ldots \ldots -O-CH-ROCOR'CO- \ldots$$
$$\rightarrow$$
$$\ldots -O\dot{C}HROCOR'CO- \ldots \ldots -O-\underset{|}{C}H-ROCO-R'CO- \ldots$$

These reactions occur especially readily in the case of polymers containing double bonds and tertiary hydrogen atoms in the macromolecule. Thus polypropylene is more readily oxidised than is polyethylene.

Polymers containing benzene rings or heterocycles of aromatic character (benzimidazole, pyridine, thiazole, oxadiazole, etc.) are distinguished by their great resistance to oxidation. The hydrogen atoms in these systems are very firmly bound, and therefore the peroxy-radical is unable to abstract them, which results in chain termination in the oxidising process. Therefore such polymers begin to oxidise only at high temperatures (400–600°).

Polyorganosiloxanes are very resistant to thermal oxidation, which is explained by the inertness of the organic radicals attached to the silicon atom resulting from the polarity of the Si–C bonds. The siloxane Si–O bond in polyorganosiloxane molecules has a well-defined polar character, and it therefore increases the polarity of the Si–C bond and correspondingly lowers the force effect of the oxygen molecule acting on the organic radicals which are attached to the polymer chain[39]. However, linear polyorganosiloxanes, like linear organic polymers, undergo thermal degradation more readily than do three-dimensional cross-linked polymers, since in linear molecules not only Si–C but also Si–O bonds are broken by the action of high temperatures.

The resistance of polymers to hydrolysis is greatly diminished at high temperatures. Hetero-chain polymers are especially sensitive to hydrolysis. Thus in polyamides

$$-NH-\overset{\overset{O}{\|}}{C}-$$

the polar character of the amide link –NH–C(=O)– makes it more sensitive to the action of various polar reagents. It is ruptured under the influence of acids, alkalis, water, amines, etc. Reactions including hydrolysis, acidolysis, aminolysis, etc. in most cases involve degradation of the polyamide macromolecule.

Rate of hydrolysis depends on the nature of the hydrolysing agent, the conditions of hydrolysis, and the structure of the polyamide. In the cold, polyamides are fairly stable to the action of hydrolysing agents; water does not act at all on them without heating. They dissolve at room temperature in concentrated acids — sulphuric, hydrochloric, formic, nitric, etc. — without appreciable degradation[70,71]. The rate of hydrolysis is greatly increased at high temperatures[72,73].

The various types of polyamides can be arranged in the following sequence of increasing resistance to hydrolysis

$$[-NRCO-]_x < [-NHCH_2NHCO(CH_2)_4CO-]_x < [-NH(CH_2)_6NHCOO(CH_2)_4OCO-]_x <$$

$$< [-NH(CH_2)_5CO-]_x < [-NH(CH_2)_6NHCO(CH_2)_4CO-]_x <$$

$$< [-NH(CH_2)_6NHCO(CH_2)_8CO-]_x <$$

$$< [-NHCHRCO-]_x < \left[\begin{array}{c} N-N \\ \| \quad \| \\ C \quad C-(CH_2)_6- \\ \diagdown \diagup \\ N \\ \| \\ NH_2 \end{array}\right]_x.$$

The most stable to hydrolysis are the polyaminotriazoles, and also the polybenzimidazoles, which withstand prolonged heating with acids and alkalis[28,74].

Molecular chains built up from silicon, oxygen, and various elements — aluminium, titanium, boron, tin, etc. — whose bonds are appreciably ionic in character, exhibit considerable sensitivity to water. Andrianov and his collaborators have shown[39] that the hydrolytic stability of silicon–oxygen–element bonds is greatly affected by the bonding between various elements in the polymer chain and by their organic framework.

Investigation of the hydrolytic stability of compounds of general formula $[(C_2H_5)_3SiO]_nM$ (where M represents an atom of aluminium, titanium, or tin) has established the sequence Sn > Al > Ti in the rate of hydrolysis.

The hydrolytic stability of polyaluminoorganosiloxanes was found to exceed that of various organosilicon compounds, which are cleaved by acid reagents. The great resistance to hydrolysis of $\gtrless$Si–O–Al$\lessgtr$ bonds compared with the $\gtrless$Si–O–Si$\lessgtr$ bond is explained by Andrianov[39] on the assumption that the action of an acid on polyalumino-siloxanes involves two reactions — rupture of the $\gtrless$Si–O–Al$\lessgtr$

bond and intermolecular condensation of the resulting hydroxy-groups on the silicon atom, with the formation of complicated polymeric molecules from chain fragments, which create steric hindrance to the development of acid hydrolysis of the $\rangle$Si–O–Al$\langle$ bonds.

Carbon-chain polymers are stable to hydrolysis.

Heating a polymer to high temperatures can cause the occurrence of two processes, degradation and cross-linking. Degradation is due to the rupture of chain molecules, with a progressive decrease in molecular weight of the polymer, and hence a deterioration in mechanical properties. Cross-linking involves the formation of bonds between the polymer chains, and is accompanied by an increase in molecular weight, which to some extent may tend to improve the physical and mechanical characteristics of the polymer as well as its thermal stability. The formation of a large number of bonds between separate macromolecules with the building up of a rigid network converts the polymer into a hard, brittle, infusible, and insoluble product. Most often both these processes take place in polymers at the same time, especially as the primary stages in both processes involve formation of free radicals, in the first case by the scission of carbon–carbon bonds, and in the second case by abstraction of hydrogen from CH_2 group.

For some time degradation and cross-linking in a polymer can in effect balance one another, so that it appears that no change has occurred in the polymer. As the processes continue, however, one of the two reactions begins to predominate, resulting in either rapid softening or a sudden breakdown in the material[75].

The resistance of a polymeric molecule to the action of high temperatures is governed by the strength not only of the bonds in the polymer chain itself but also of those linking atoms surrounding the main chain or forming side-chains, for example C–H bonds in hydrocarbons, C–F in fluorinated polymers, C–Cl in poly(vinyl chloride), etc., since their rupture is accompanied by degradative processes and results in a change in the structure and properties of the polymer.

This resistance is assessed quantitatively from the loss in weight of the polymer when it is heated at a specified temperature for a definite time.

Table 14 illustrates the thermal stability of polymers by the temperature at which they lose half their weight on being heated in a vacuum for 30 min[76,77]. On the basis of this work Madorsky[76,77] suggested the following sequence for the thermal stability of individual bonds and groups.

C–F > C–H > C–C > C–Cl

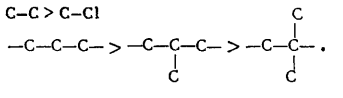
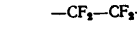
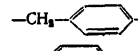
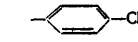
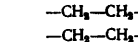
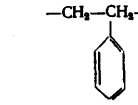
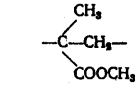
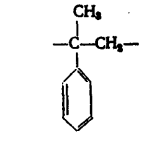


Table 15 gives the losses in weight of various polymers when heated at different temperatures for 24 h.

The thermogravimetric method has become widely used for determining the thermal stability of polymers. Figs. 12 and 13 give thermograms of polybenzimidazoles, from which it is clearly seen that appreciable loss in weight occurs only at 400–500° and above[28].

Sometimes a method based on measurement of the quantity of gaseous decomposition products evolved is used

TABLE 14. Thermal stability of polymers*.

Polymer	Structure	Softening temp., °C	T_η	$K_{350°}$, % min^{-1}	E, kcal mole^{-1}	Yield of monomer, %
Polytetrafluoroethylene		327	509	$2\cdot10^{-6}$	81	>95
Poly-p-xylylene		380—400	432	$2\cdot10^{-3}$	73	0
Polybenzyl		260—280	430	$6\cdot10^{-3}$	50	0
Polyethylene		135	404	$8\cdot10^{-3}$	63	<0.025
Polystyrene		145—160	364	$2.4\cdot10^{-1}$	55	40
Poly(methyl methacrylate)		155—180	327	5.2	52	>95
Poly-α-methylstyrene		160	286	226	55	>95

* T_η = decomposition temperature (loss of 50% of weight in 30 min);
$K_{350°}$ = rate of evolution of vapour;
E = activation energy of decomposition.

TABLE 15. Loss in weight of various polymers at different temperatures (in a vacuum).

Polymer	Loss in weight (%) after 24 h at			
	250°	350°	400°	450°
Polyphenylsiloxane	3.8	10.0	27.0	43.5
Polydimethylpolyphenylsiloxane	7.2	22.8	36.0	44.7
Polydiethylpolyphenylsiloxane	8.3	30.2	38.0	—
Polytetrafluoroethylene	1.3	2.1	2.5	—
Polychlorotrifluoroethylene	4.6	98.9	—	—
Poly(ethylene terephthalate)	5.3	68.0	—	—
Epoxide resin	22.7	93.1	—	—
Capron [poly-ε-caprolactam]	55.5	94.3	—	—

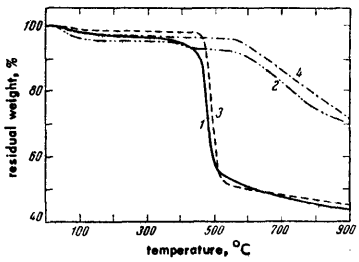


Fig. 12. Thermograms of polybenzimidazoles obtained from:
1) 1,2,4,5-tetraminobenzene and adipic acid;
2) 1,2,4,5-tetraminobenzene and isophthalic acid; 3) diaminobenzidine and adipic acid;
4) diaminobenzidine and isophthalic acid.

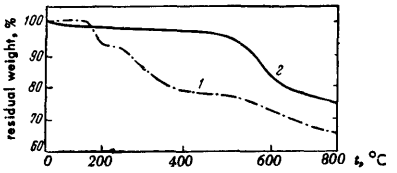


Fig. 13. Thermograms for polybenzimidazoles obtained from diaminobenzidine and:
1) ferrocene-1,1′-dicarboxylic acid; 2) imidazole-4,5-dicarboxylic acid.

to compare the thermal stabilities of polymers. Fig. 14 shows the relative rates of breakdown of three polymers, and it is evident that the polyarylate D-2 is extremely thermostable even at 400°.[35] Fig. 15 shows the extent of decomposition of the polyarylates D-1 and D-2 when heated at various temperatures for 1 h.[35] It is seen that appreciable breakdown of the polyarylates begins only above 400°.

According to Lee[78], the thermal degradation of polycarbonates is determined by the stability of the bonds linking atoms forming part of the macromolecule. Table 16 gives energy values for the various bonds in a polycarbonate, on the basis of which Lee suggests two possible

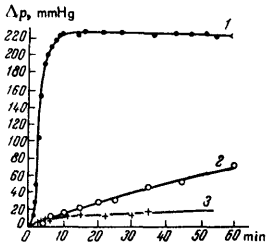


Fig. 14. Rate of thermal degradation at 400° of some polymers based on 2,2-diphenylpropane-*pp*′-diol determined from the pressure of the gases evolved:
1) epoxide resin (ED-6) hardened with 30% of maleic anhydride; 2) poly-(2,2-diphenylpropane-*pp*′-diol carbonate); 3) polyarylate D-2.

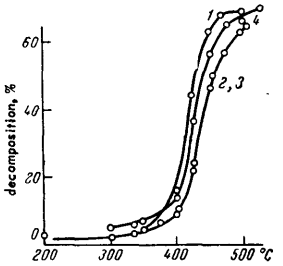
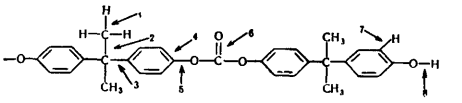


Fig. 15. Dependence of extent of decomposition of polyarylates D-1 and D-2 on temperature (maintained for 1 h):
1) D-1 obtained by equilibrium polycondensation; and D-2 obtained by: 2) equilibrium polycondensation; 3) interfacial polycondensation; 4) interfacial polycondensation.

TABLE 16. Energy of bonds in polycarbonate.

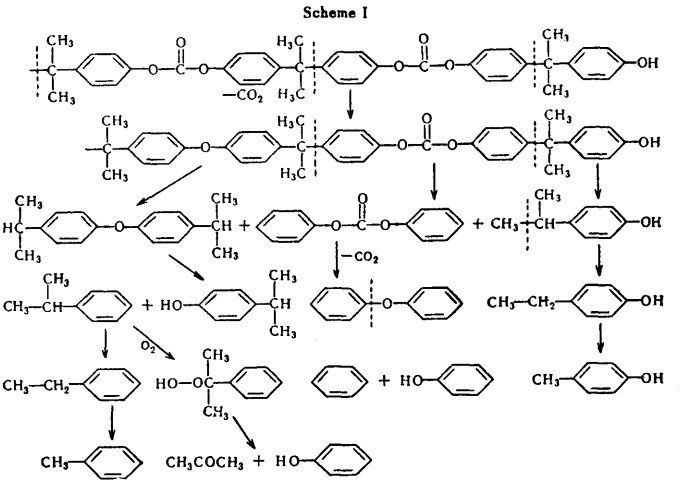


Serial No.	Bond	Bond energy, kcal mole^{-1}
1	C—H	98.7
2	C—CH_3	60.0
3	C—C	82.6
4	C=C	147.5
5	C—O	85.5
6	C=O	176.0—179.0
7	C≡C—H	102
8	O—H	101.5

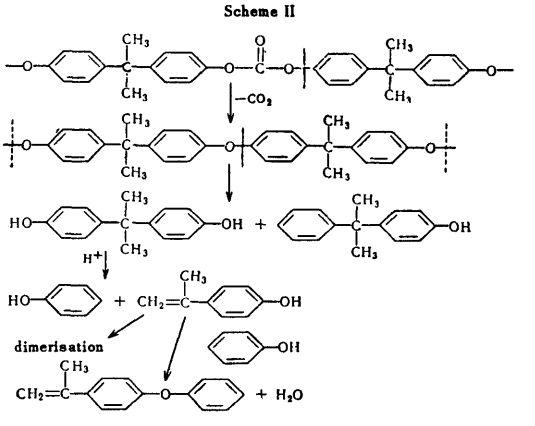
mechanisms of degradation. The accompanying Schemes I and II show that processes of thermal degradation are always accompanied by side-reactions, also resulting in cleavage of polymer chains, *e.g.* decarboxylation, hydrolysis, dehydration, etc.

Mechanism of degradation

Scheme I

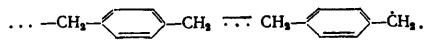


Scheme II

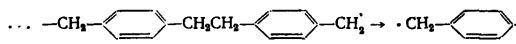


Regarding the degradation of polymers as a process involving the formation of free radicals, Grassie[79] explained the greater thermal stability of polymers containing aromatic rings in the chain, in comparison with vinyl polymers, by the ability of the unpaired electron in the former case to be delocalised along the whole polymer chain.

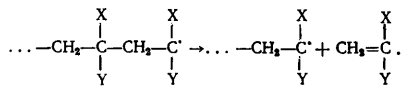
Therefore conditions are not created which would favour intramolecular disproportionation resulting in the splitting off of a terminal monomer unit (monomer), which can be represented in general by



In the degradation of poly-*p*-xylylene, for example, such units could be eliminated in the form of a diradical:



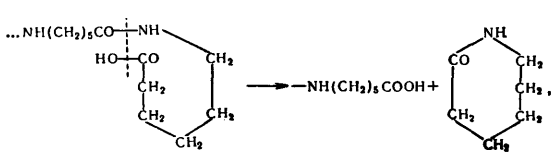
but, owing to its reactivity, the latter does not exist as such (in solution only at -78°), and will recombine again. Vinyl monomers other than polyethylene are degraded by high temperatures with the formation of monomers as final products:



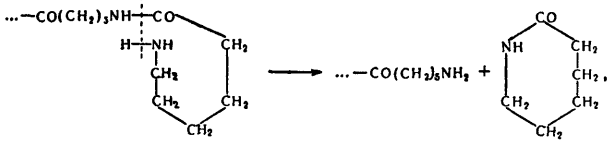
The role of the quaternary carbon atom involves the stabilising effect of the substituents X and Y on the resulting free radical, a decrease in reactivity of the macroradical, and hence the securing of intramolecular disproportionation with separation of the monomer. If one of the substituents X and Y is a phenyl group, its great resonance stabilisation effect makes the macroradical stable even in the presence of a quaternary carbon atom, and makes possible intramolecular disproportionation of the macroradical with separation of the monomer (*e.g.* the degradation of polystyrene).

We must also note the tendency shown by many polymers to form cyclic structures on degradation, especially if five–seven-membered rings can be obtained. Thus linear polyesters break down at high temperatures with the formation of cyclic esters[80]. According to Hill and Carothers[81], the ease with which this occurs depends on the structure of the monomer unit in the polyester and on the nature of the catalyst employed. Oxalic and carbonic esters undergo cleavage the most readily; when the monomer unit of the polyester contains 7–12 carbon atoms, the main decomposition products are dimeric esters; and with 13 or 14 carbon atoms a mixture of monomer and dimer is obtained. The presence of a larger number of atoms results in a monomeric ester. Various metal salts have been used as catalysts for the decomposition of polyesters[82].

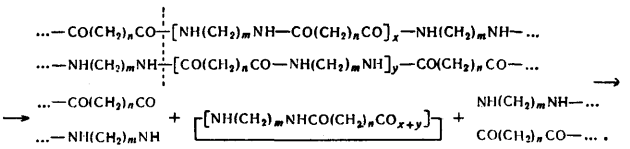
Cyclic as well as linear products have been detected in polyamides[9]. Ring formation is explained by the occurrence of exchange reactions between the macromolecules in the process of equilibrium polycondensation. These reactions also occur in the thermal degradation of polyamides. Rings can be obtained as a result of one of the reactions — (1) acidolysis



(2) aminolysis

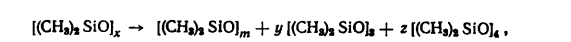


and (3) amidolysis



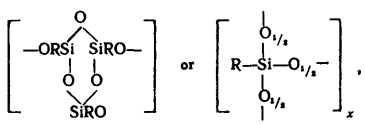
Small rings can be formed by reactions (1) and (2), whereas reaction (3) can give rings of any size.

Cyclic organosiloxanes have been observed as thermal degradation products of polyorganosiloxanes. Data have been published indicating that in polydimethylsiloxanes the molecular chains have a helical structure with 3–6 silicon atoms in a turn of the helix[39]. Under the influence of high temperatures such a structure provides conditions favouring the closure of six- and eight-membered rings with cleavage of the chains. Thus polydimethylsiloxanes, on being heated in a vacuum at around 300°, break down into cyclic oligomers of low molecular weight according to the scheme



where $m + 3y + 3z = x$.

In polyorganosiloxanes having a three-dimensional molecular structure



removal of a monomer unit or of a large segment from the polymer chain necessarily involves scission at three points, *i.e.* the rupture of two or three energetically stable Si–O bonds. In polyorganosiloxanes with bonds in three dimensions, therefore, no degradation of the molecular chains at Si–O bonds is observed even at 550°, independently of the nature of the organic radical[39].

The resistance of polymers to heat, light, and oxidising processes can be increased by the addition of stabilisers to the polymer. Since the primary act in the action of heat, oxygen, light, radiation, etc. on polymers is the formation of free radicals, the main role of stabilisers is to prevent such formation or inhibit the radical reactions.

Stabilisers have been selected for each class of polymers, their number being very large. Thus antioxidants are used to protect polyethylene from thermal oxidation, the best of them being mixtures of phenols and amines[83]. Antioxidants can also delay photochemical oxidation (aging under the influence of light) for some time. An effective remedy against photochemical oxidation and the action of radiation on polyethylene and rubber is gas black (2%),

whose stabilising effect is due to its ability to absorb free radicals.

Stabilisers for poly(vinyl chloride) slow down the elimination of hydrogen chloride, also preventing the formation of double bonds and being at the same time antioxidants and ultraviolet-absorbers. They include salts of carboxylic acids, thioplasts, the ammonium salt of the copolymer of styrene and maleic anhydride, carboxylic esters, organotin compounds, etc.[84]

Various substances have been suggested for the protection of polyamides from the action of oxygen, heat, and light, including copper compounds, alkaline phosphates and phosphites with alkali-metal halides, aluminium and manganese salts, finely divided powders of readily oxidisable metals — Mg, Al, Cr, Ca, Sr — and also several organic compounds, in particular those such as biphenyl and phenyl-1-naphthylamine, which have proved extremely effective for protecting polyamides from oxidative degradation [12].

The problem of producing stabilisers for highly thermostable polymers has not yet been solved. A possible method for its solution is the suggestion by Berlin *et al.*[85] that polymers having a system of conjugated multiple bonds should be employed as stabilisers.

The importance of the stabilisation of polymers in processing and service has attracted the close attention of research workers to this question, as has been reflected in numerous papers and monographs[84,86].

V. NEW THERMOSTABLE POLYMERS

Polymers employed at the present time can operate at temperatures up to 200°. Fig. 16 illustrates the working range for various polymers on the basis of Nowak's result[6]. It is seen that silicone and fluorine-containing polymers are the most thermostable, and can operate for a long time at temperatures reaching 200°. The use of polymers of other classes is confined to lower temperatures.

The novel thermostable polymers obtained by one of us together with Vinogradova[58], the polyarylates (see Table 17), have a higher range of working temperatures, as has been shown by the investigations of their properties by Slonimskii and Askadskii[87].

Fig. 17 compares polyarylates, based on terephthalic and isophthalic acids and phenolphthalein, with poly(methyl methacrylate) and a polycarbonate (makrolon)[87]. These polymers can function as structural materials up to the following temperature limits: (1) poly(methyl methacrylate) 70°, (2) polycarbonate 140°, (3) polyarylate F-1 200°, and (4) polyarylate F-2 260°. Several polyarylates are capable of operating at still higher temperatures. It is thus obvious that polyarylates considerably extend the range of thermostable polymers.

Fig. 18 shows the dependence of tensile strength on temperature for several rubbers[1]. Silicone rubber is seen to be the most thermostable, since it retains adequate strength even at 300°, when the other rubbers have already lost their strength.

Thermal stability can be characterised also by the temperature dependence of hardness. Fig. 19[1] illustrates data for nylon, Teflon, and reinforced Teflon. The relationship is seen to be in general similar to that in Fig. 18.

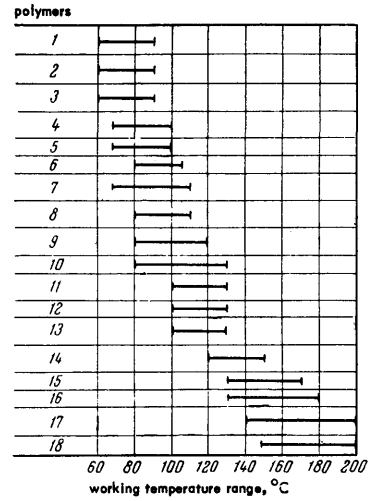


Fig. 16. Operating range for various polymers, bounded by limiting temperatures:
1) unmodified and modified poly(vinyl chloride); 2) ordinary and modified polystyrene; 3) rubbers based on purely organic latices; 4) polyacrylates and polymethacrylates; 5) polyolefins; 6) polyamides; 7) linear polyurethanes, unplasticised and plasticised; 8) unsaturated polyester resins; 9) modified polyester resins; 10) epoxide resins; 11) cross-linked polyurethanes; 12) polycarbonates; 13) linear terephthalates; 14) cross-linked terephthalate resins; 15) fluorinated elastomers; 16) siloxane elastomers; 17) ordinary and modified silicone resins; 18) rigid fluorinated polymers.

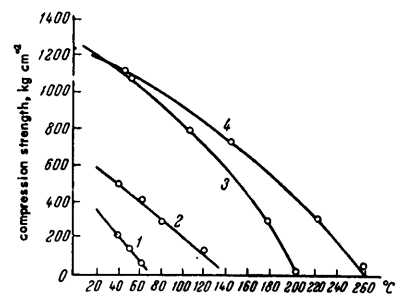
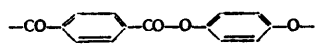
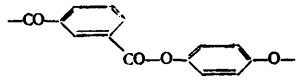
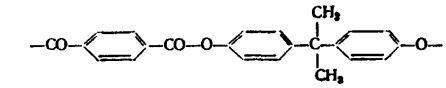
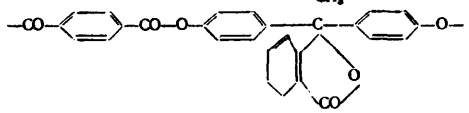
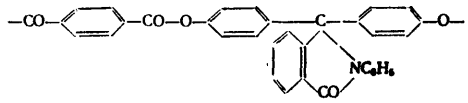
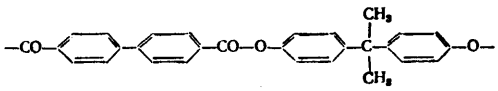
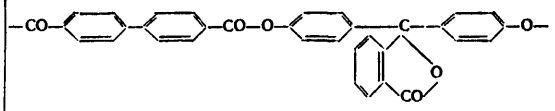
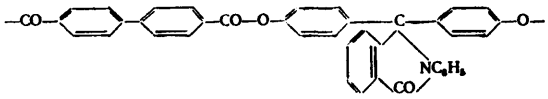
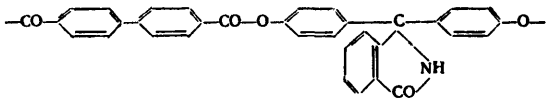
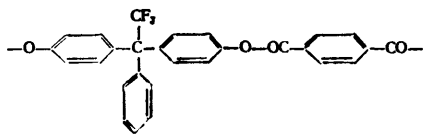
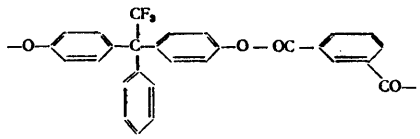
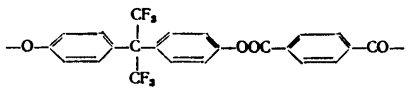
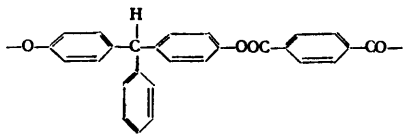
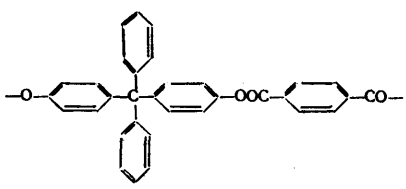


Fig. 17. Range of operating temperatures of polymers:
1) poly(methyl methacrylate); 2) poly-(2,2-diphenylpropane-*pp'*-diol carbonate); 3) polyarylate F-1; 4) polyarylate F-2.

We shall now examine individual classes of polymers and recently prepared thermostable compounds.

As already pointed out in Section II (Fig. 2), among the immense number of polymers only the following groups have members with a thermal stability above 300° — (1) stereoregular polyhydrocarbons, (2) unsaturated polyhydrocarbons, (3) perfluorohydrocarbons, (4) polyesters,

TABLE 17. The most important polyarylates[58].

Brand	Formula of monomer unit	Softening temp., °C
G-2		>500
I-1		>300
D-2		~350
F-2		~320
F-7		305
D-6		~410
F-4		~350
F-9		~350
F-12		~310
D-11		~310
D-12		~300
D-15		~350
D-17		~290
D-19		~300

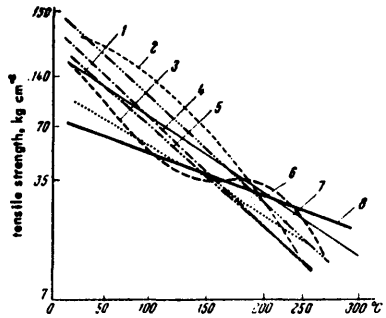


Fig. 18. Temperature dependence of tensile strength for various rubbers:
1) butyl rubber; 2) natural rubber; 3) Hypalon; 4) styrene–butadiene rubber; 5) nitrile rubber; 6) polyacrylate rubber; 7) neoprene; 8) silicone rubber.

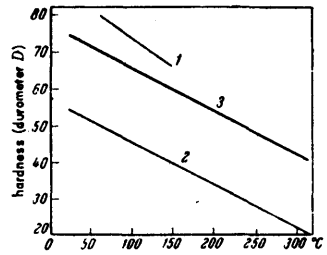


Fig. 19. Temperature variation of hardness for:
1) nylon; 2) polytetrafluoroethylene; 3) reinforced polytetrafluoroethylene.

(5) polyamides, (6) carbocyclic chain polymers, (7) heterocyclic chain polymers, (8) organoelementary polymers, and (9) inorganic polymers. Let us examine in this order recently published work on the synthesis and investigation of thermostable polymers.

Stereoregular Polymers

Stereoregular polymers include several compounds melting above 300°, which are listed in Table 9. The most thermostable are the polymers of *o*-methylstyrene (melting at 360°) and of 3,3-dimethylbut-1-ene (370°).

Nametkin *et al.*[42] have obtained isotactic polymers of allyldimethylphenylsilane (m.p. 300°) and of diallyldimethylsilane and diallylmethylphenylsilane, which are extremely high-melting substances (m.p. 400–410°).

Unsaturated Polyhydrocarbons

Among the numerous class of unsaturated polyhydrocarbons only those which have a continuous chain of conjugation in the macromolecule are of outstanding thermal stability[88,89]. The simplest representative of this type is "carbyne", obtained by Korshak *et al.*[90] It is formed by

the oxidative dehydropolycondensation of acetylene by the reaction

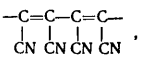
$$x\,HC{\equiv}CH \xrightarrow{\text{oxidation}} (-C{\equiv}C-)_x.$$

Carbyne is an insoluble, hard black powder. When heated in the absence of oxygen, it is converted into graphite at 2300°. It is semiconducting.

Polymethine $(CH=CH)_x$ was obtained by Kern[91] by the action of concentrated sulphuric acid on poly(vinyl alcohol). It withstands heating to 600°. It is a semiconductor above 150°, and is used for the manufacture of light-polarising materials. This same polymer has been obtained by Berlin[92] by the dehydrochlorination of poly(vinyl chloride) in the presence of sodium pentyloxide.

Polyvinylene hydrocarbons having the structure $[C(CH_3)=CH]_x$ have been obtained by Kargin *et al.*[93] from acetone by polycondensation in the presence of zinc chloride. Recently a large number of polyvinylene hydrocarbons have been prepared by the polymerisation of acetylene and its homologues[94]. They have the structure $[C(R)=CH]_x$, and are distinguished by high thermal stability and the presence of semiconductor properties.

Beneš *et al.*[95] prepared polymers of dicyanoacetylene by polymerisation in the presence of anionic catalysts. The polymer has the structure



and does not melt below a red heat.

Perfluorohydrocarbons

Apart from the members which have now been known for some time — polytetrafluoroethylene, polychlorotrifluoroethylene, and copolymers of hexafluoropropene with tetrafluoroethylene and vinylidene chloride (Viton A) — several new members of this extremely interesting group of thermostable polymers have been described. Investigation has shown that polymers containing the maximum quantity of fluorine are the most interesting.

Several defects of vinyl polymers can be eliminated by replacing hydrogen by fluorine, since the energy of the C–F bond is greater than that of the C–C and C–H bonds. Completely fluorinated polymers are known to possess higher thermal and chemical stability than their hydrocarbon analogues[96].

Polymers of styrenes containing less than three fluorine atoms in the aromatic ring do not possess interesting properties; the homopolymer of pentafluorostyrene $(C_6F_5CH=CH_2)_x$ and copolymers of *m*-trifluoromethylstyrene and butadiene exhibit better mechanical properties and greater thermal stability than do polymers obtained from styrene itself[97]. Polymers have been prepared of β-fluorostyrene $(C_6H_5CH=CHF)_x$ with softening points of 240–260°, ββ-difluorostyrene (~ 180°), αβ-difluorostyrene (about 220°, with decomposition), and αββ-trifluorostyrene (185–190°).[97,101]

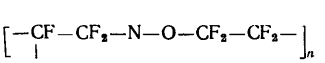
Fluorinated aromatic polymers of the type of perfluoropolyphenylenes



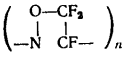
possess very high thermal stability. Perfluoropolyphenylene was obtained by the reaction of tetrafluoro-*p*-diiodobenzene with copper powder, and contained up to eleven phenylene residues. Perfluorophenylene oxide, obtained by heating sodium or other pentafluorophenoxide, was also of low molecular weight. No information is yet available on the thermal stability of these polymers[97,101].

Great interest attaches to tetrafluorophthalic acid, which can be used for the synthesis of polyesters and polyamides[98].

Recently a novel type of polymer has been prepared, containing perfluoroalkyl groups and the N–O bond in the macromolecule. These polymers are obtained by the copolymerisation of perfluoroalkylnitroso-compounds with fluorinated ethylenes. They have elastic properties and high chemical stability. Thus the copolymer of trifluoronitrosomethane and tetrafluoroethylene consists of repeating

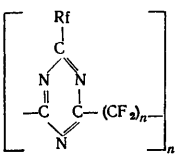


units. It is soluble only in chlorofluorohydrocarbons, retains its elasticity down to -30°, has a glass temperature of -51°, and decomposes on being heated to 210°; it can be vulcanised with benzoyl peroxide[99]. The homopolymer of trifluoronitrosoethylene



forms an elastomer which is stable up to 400°; it is very resistant to the action of nitric acid[100].

The perfluoropolytriazine elastomers described by Brown[102] are stable in air up to 350–410°, and retain their properties unchanged after being boiled with fuming nitric acid for 24 h. These polymers are obtained by the condensation of perfluorodiamidines with perfluoroamidines, which results in the formation of triazine rings



Rf = perfluoroalkyl.

Unfortunately, almost nothing is known of stereoregular perfluorohydrocarbon polymers, which should be of great interest. Only isotactic perfluoropropylene (m.p. 110–120°) is known[103].

Polyesters

From the number of known representatives, polyesters represent an immense group of polymers. All aliphatic polyesters have low melting points. Only polyesters of aromatic dicarboxylic acids and ethylene glycol have fairly high melting points[8] — poly(ethylene terephthalate) 265°, poly(ethylene biphenyl-*pp'*-dicarboxylate) 330°, poly(ethylene diphenylmethane-*pp'*-dicarboxylate) 320°, poly(ethylene azobenzene-*pp'*-dicarboxylate) 365°, and poly(ethylene dithioterephthalate) 335°. Polycarbonates — polyesters of dihydric phenols and carbonic acid — likewise are not characterised by high melting points[59]. Only the polycarbonate formed by diphenylmethane-*pp'*-diol

melts above 300°, and that from 1,2-diphenylethane-*pp'*-diol at 290–300°. The highest melting points are possessed by polyesters of aromatic dicarboxylic acids and dihydric phenols, which have the general name "polyarylates".[58] Table 17 lists the most thermostable representatives of this group.

The presence of good electrically insulating properties in polyarylates, and their ability to form films and fibres, make this class extremely promising for the manufacture of all kinds of thermostable goods.

In the absence of oxygen, polyarylates withstand prolonged heating at high temperatures (300–400°). Oxidising processes occur at an appreciable rate only above 250°. With all resins, appreciable gas evolution starts on heating in an atmosphere of nitrogen above 400°, and rapidly intensifies with rise in temperature, reaching 20% of the original quantity of polyarylate at 500° (see Figs. 14 and 15).

Polyamides

Several polyamides also have high melting points[9]. In most cases they contain residues of aromatic diamines or aromatic dicarboxylic acids in the macromolecule, as is evident from Table 18.

Aliphatic polyamides oxidise comparatively easily at high temperatures. Aromatic and hydroaromatic polyamides are considerably more resistant to oxidation.

Cyclo-Chain Polymers

This class of polymers, which has recently attracted great attention from research workers, contains benzene, naphthalene, cyclohexane, and other carbocyclic rings, as well as various heterocyclic rings, in the main chain. We shall term the first group "carbocyclochain", and the second group "heterocyclochain", polymers. Koton[120] has given a detailed account of progress in the field of carboheterocyclochain polymers. The same questions have been considered in other reviews[121,122].

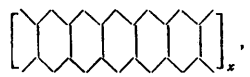
TABLE 18. Polyamides having high melting points.

Starting materials		Melting or softening point, °C	Ref.
diamine	dicarboxylic acid		
Hexamethylenediamine	terephthalic	350 (decomp.)	104
»	biphenyl-*pp'*-dicarboxylic	360 (decomp.)	105
»	2,5-dihydroxyterephthalic	334 (decomp.)	105
»	benzene-*p*-diacetic	320	106
»	di-*p*-carboxyphenyl ketone	350	107
»	*trans*-hexahydroisophthalic	310	108
»	*trans*-hexahydroterephthalic	360 (decomp.)	108
Piperazine	adipic	330	109
»	suberic	300	110
»	4-oxosebacic	350	110
»	terephthalic	400 (decomp.)	111
Cyclohexane-*trans*-1,3-diamine	adipic	300	112
Ditto	azelaic	300	112
Cyclohexane-1,4-diamine	adipic	400	105
Ditto	biphenyl-*mm'*-dicarboxylic	390	105
Bis-(4-amino-3-methylcyclohexyl)methane	terephthalic	300	113
Bis-*trans*-4-aminocyclohexylmethane	adipic	310	114
m-Phenylenediamine	*pp'*-dicarboxytriphenylphosphine oxide	340	107
p-Phenylenediamine	ditto	340	107
p-Xylylenediamine	succinic	360	115
Ditto	adipic	340	115
»	terephthalic	350	115
m-Xylylenediamine	terephthalic	300	116
Benzidine	adipic	400	117
»	sebacic	375	117
»	terephthalic	500 (decomp.)	118
Diphenylmethane-*pp'*-diamine	adipic	350	105
Ditto	terephthalic	420	117
mm'-Dimethyldiphenylmethane-*pp'*-diamine	adipic	324	119
Diphenylethane-*pp'*-diamine	adipic	400	105

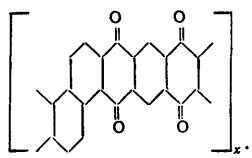
Carbocyclochain Polymers

There are many thermostable carbocyclochain polymers. Poly-*p*-phenylene

is an insoluble powder which does not melt below 530°, and withstands unchanged prolonged heating at 230–240°.[123] Extremely thermostable products were obtained by Pohl and Engelhardt[124] by condensing 1,2,4,5-tetrabromobenzene in the presence of a potassium–sodium alloy, these being cyclic "strip" polymers and having the structure



as well as by the condensation of pyromellitic acid with aromatic compounds (biphenyl, terphenyl, naphthalene, anthracene), yielding polymers of the type



The same type of polymer structure occurs in carbonised or graphitised fibres[125]. They are obtained from viscose rayon which has been heat-treated, first at 800–900° and then at 2700–2900°:

$$(C_6H_{10}O_5)_n \xrightarrow{800-900^\circ} (C_{24}H_5O)_n \xrightarrow{2700-2900^\circ} (C_{24}H)_n.$$

viscose rayon — carbonised (carbon fibre) — graphite fibre

These fibres and fabrics are distinguished by high thermal stability. They are employed fpr the manufacture of rocket nozzles, filters for hot gases, high-temperature thermal insulation, etc.

Insertion of methylene groups between aromatic rings makes macromolecules more flexible, often with preservation of the thermal stability. Thus polyarylenemethyls, obtained by Vansheidt *et al.*[126] by the polycondensation of formaldehyde with aromatic hydrocarbons, have high melting points — 350° with 1,2,4,5-tetramethylbenzene, 408° with 1,2,3,5-tetramethylbenzene, and 295° with anthracene.

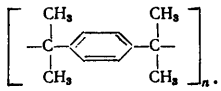
This group includes the phenol–formaldehyde resins, which are distinguished by appreciable thermal stability, especially in the series of modifications which have been described recently. Table 19 gives data on the thermal stabilities of phenol–formaldehyde resins as a function of the time of exposure. Furfuraldehyde–acetone and other resins based on furfuraldehyde are also characterised by high thermal stability[128].

We may also note poly-*p*-xylylene

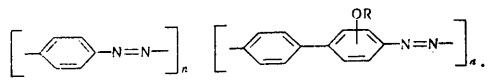
TABLE 19. Thermal stability of phenol–formaldehyde resin[127].

Temperature, °C	Duration
1000–1500	seconds
500–1000	minutes
250–500	hours
200–250	days
Below 200	indefinitely long

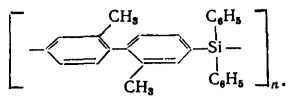
which was obtained by Szwarc [19] by the pyrolysis of *p*-xylene. In a vacuum it melts at 400°, but in air it decomposes at 225°. [129] Its homologue poly-*p*-diisopropylbenzene (polytetramethylquinodimethide) was obtained by Korshak and Sosin [130] by a reaction of polyrecombination (m.p. 300°).



Polyazobenzenes, obtained by polyrecombination, also contain a system of conjugated bonds and possess thermal stability up to 600° [131]



An extremely interesting silicon-containing polymer has been obtained by polyrecombination from diphenylsilane

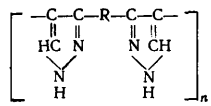


It is very thermostable, and does not char on prolonged heating up to 900°, when its loss in weight is only 5%. [132]

Heterocyclochain Polymers

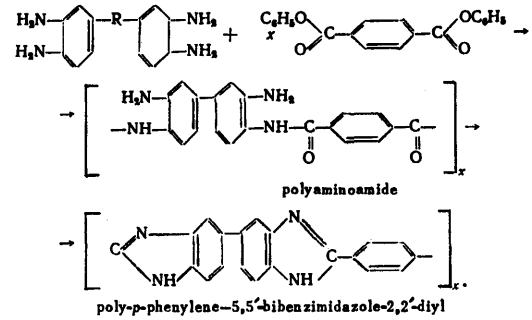
Heterocyclochain polymers form a very promising group of thermostable compounds, characterised also by great chemical stability. At the present time polymers have been described containing in the chain pyrazole, imidazole, triazole, quinoline, pyridine, oxadiazole, thiazole, pyromellitimide, and triazine rings.

Polymers containing pyrazole rings in the chain, especially when an unsubstituted NH group is present in the ring, have thermal stabilities reaching 400–500°. Polypyrazoles of this type were first obtained by the polycyclisation of bisdiazoalkanes with butadiynes, and have the structure



Their improved thermal stability compared with polypyrazoles in which the nitrogen atom is substituted is explained by the formation of hydrogen bonds [29,133].

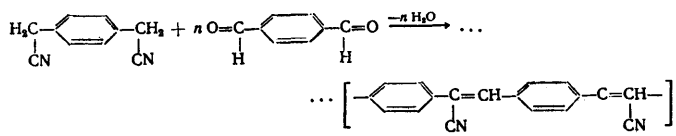
Polybenzimidazoles form a group of exceptionally thermostable polymers. Especially high thermal stability is characteristic of those obtained from aromatic tetramines and aromatic dicarboxylic acids by the reaction



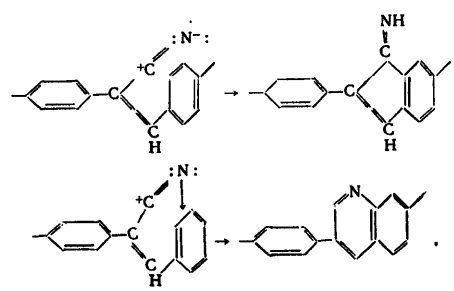
Several of these compounds have been obtained by Marvel and his coworkers [28,134], Korshak *et al.* [135], and other investigators [136]. The most interesting members of this group are listed in Table 20.

Polybenzimidazoles obtained from aliphatic acids begins to decompose at 450–500°, whereas their aromatic analogues break down appreciably only at 500–600°, and in an atmosphere of nitrogen a loss in weight exceeding 30% occurs only at 900°. Decomposition is more vigorous in air. Figs. 12 and 13 give thermograms illustrating the high thermal stability of aromatic and organoelementary polybenzimidazoles [28,134].

Reaction of $\alpha\alpha'$-dicyano-*p*-xylene with terephthalaldehyde



gives a polymer which after heat-treatment at 550° is thermostable [137]. The absence of the characteristic absorption of nitrile groups and double bonds from the infrared spectra indicates that the heat-treatment is accompanied by cyclisation with formation of a quinoline group in the chain or of an iminoindene structure



Polydicyanoterephthalidene does not lose more than 2% of its weight after heat-treatment at 550° followed by further heating at 550° for 30 min. [137]

TABLE 20. Properties of polybenzimidazoles[28,134,135].

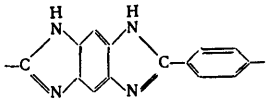
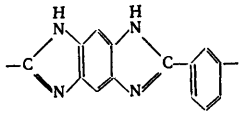
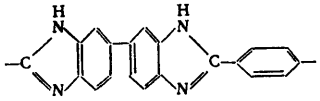
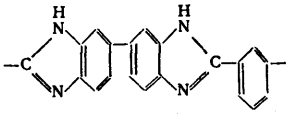
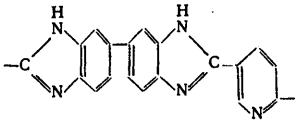
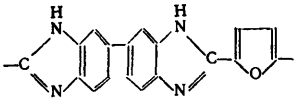
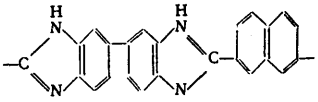
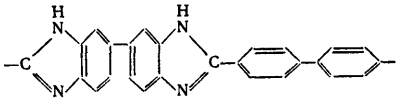
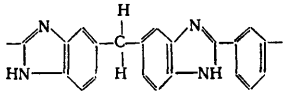
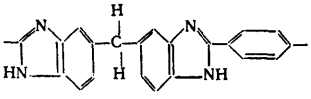
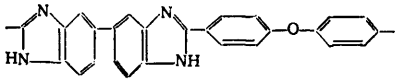
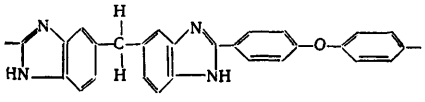
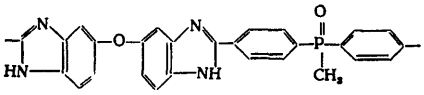
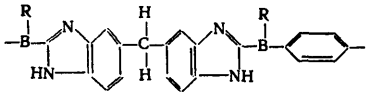
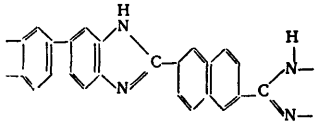
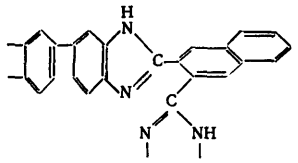
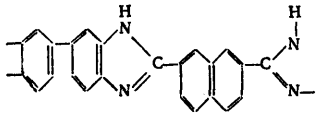
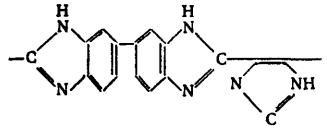
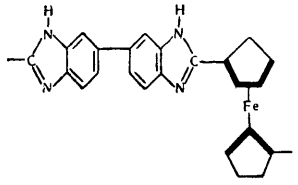
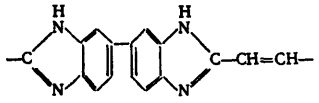
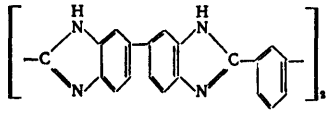
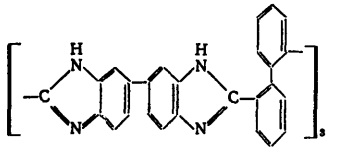
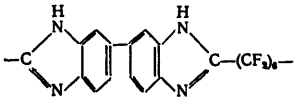
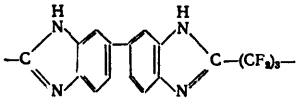
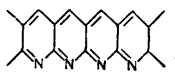
Monomer unit	Softening temp., °C	Loss in weight on heating in current of nitrogen, wt. %			
		400°	500°	550°	600°
	—	2.8	1.0	1.9	4.0
	—	0.7	0.3	1.4	1.4
	—	1.0	0	1.7	1.0
	—	0.6	0.4	1.3	2.2
	—	0.2	0.5	1.4	2.7
	480 (decomposition)	1.4	2.6	2.3	2.0
	—	0.4	0.8	1.2	3.7
	—	0.3	0.8	0.3	2.1
	380—390	—	5.16	15.45	31.30
	400—410	—	3.44	7.95	15.35
	460—470	—	5.44	7.48	10.20
	350—370	—	3.40	7.24	16.20
	380—400	—	27.50	39.80	47.85
	500	—	2.64	7.16	12.80
	—	—	5.0	10	15

TABLE 20 (contd.)

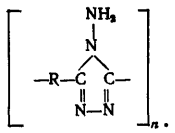
Monomer unit	Softening temp., °C	Loss in weight on heating in current of nitrogen, wt. %			
		400°	500°	550°	600°
	—	—	25	20	35 (700°)
	—	—	25	30	40 (700°)
	—	5	5	7—10	
	—	—	25	25	30
	—	—	20	—	25
	—	—	—	—	—
	—	—	20	—	25
	—	—	30	—	35
	—	—	40	—	50

By heat-treating polyacrylonitrile, Topchiev *et al.*[138] obtained a cyclic polymer to which they ascribed the structure



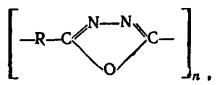
Polymers of this type are characterised by exceptional thermal stability, do not burn when introduced into a flame, and possess valuable semiconductor properties.

Polyaminotriazoles obtained by the polycondensation of hydrazine with aliphatic dicarboxylic acids have melting points of around 200–340°



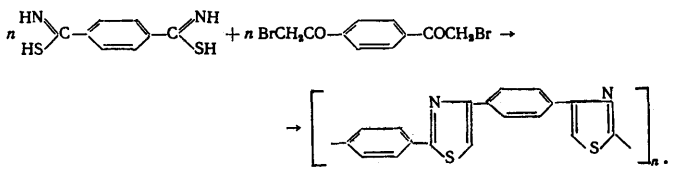
They are not decomposed on being boiled with concentrated acids and alkalis [139,140].

By the reaction of bistetrazoles with chlorides of dicarboxylic acids Abshore and Marvel [141] obtained polyoxadiazoles of general formula

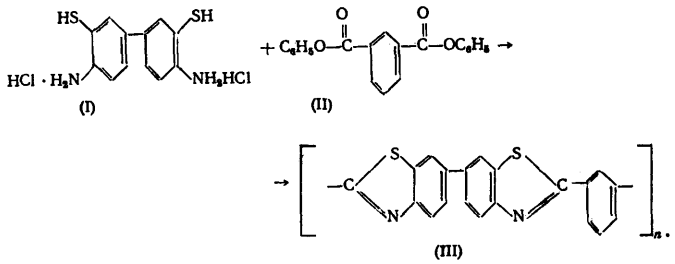


which were also stable up to 500°. When the polyoxadiazole obtained from *p*-phenylene–bistetrazole and terephthaloyl chloride was heated in air at 350° for 12 h, the loss in weight was 9.4%. Simpler methods have now been developed for preparing polyoxadiazoles, by the dehydration of polyhydrazides [142].

Polycondensation of *p*-bisbromoacetylbenzene with various dithioamides yields polymers containing repeating thiazole rings in their chain, characterised by stability up to 350°: [143]



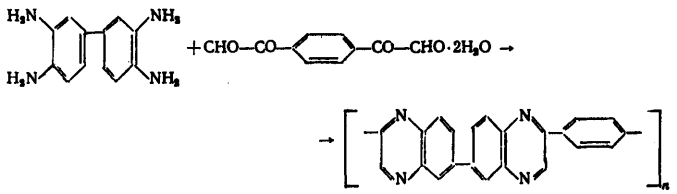
Polybenzothiazoles are formed also by the condensation of 3,3′-dimercaptobenzidine with aromatic dicarboxylic acids or their derivatives (dinitriles, diamides), in *NN*-diethylaniline or polyphosphoric acid solution, by the reaction



(I) (II) (III)

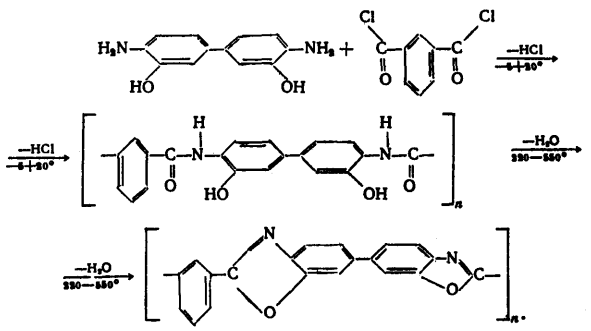
The resulting "precondensate" is precipitated with petroleum ether; on further heating at 400° for 1 h it is converted into polybenzothiazole. Poly-6,6′-bibenzothiazole-2,2′-diyl–*m*-phenylene (III) loses no weight at 538°, and at 593° its loss in weight is only 6%. [144]

Novel thermostable heterocyclochain polymers, the polyquinoxalines, have been described, which are stable in air at 500°, and in nitrogen lose 20% of their weight at 800°. They are obtained by the condensation of aromatic tetramines with tetracarbonyl compounds (the carbonyl groups should be located in the α position with respect to one another) [144–146]:

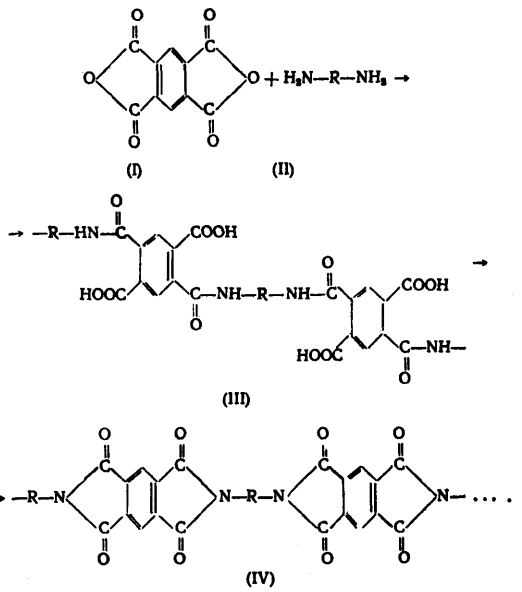


poly-6,6′-biquinoxaline-2,2′-diyl–*p*-phenylene

Polybenzoxazoles, synthesised by Takashi and his coworkers [147], have also proved to be extremely thermostable, withstanding 600° without change, and still retaining 80% of their weight at 900°. They are obtained in two stages:



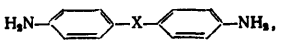
Pyromellitimide polymers are of particular interest [30,31]. They are obtained by the condensation of pyromellitic anhydride with diamines:



(I) (II) (III) (IV)

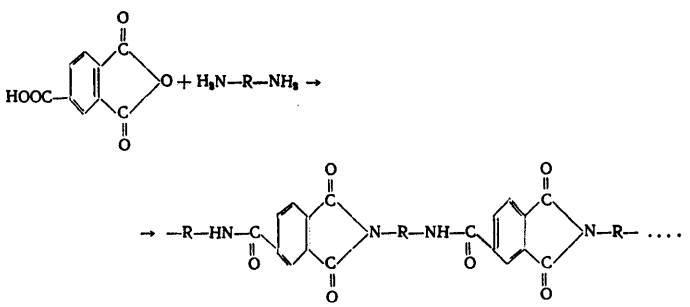
As a consequence of intramolecular ring-closure in the pyromellitimide system, the compound (III) becomes a bifunctional reagent, capable of forming linear polymers (IV). A disadvantage of these polymers is their infusibility and insolubility, which make the manufacture of articles difficult, while the liberation of water at the final stage limits their application. However, by using the soluble intermediate product (III), polypyromellitamide, formed in the first stage of the reaction, films can be obtained which can then be converted by cyclisation into the final polypyromellitimide[31].

Jones *et al.*[30] investigated the behaviour in this reaction of various diamines — *p*- and *m*-phenylenediamines, naphthalene-1,5(1,8 and 2,7)-diamines, 2,6-diaminopyridine, benzidine, and diamines of the type



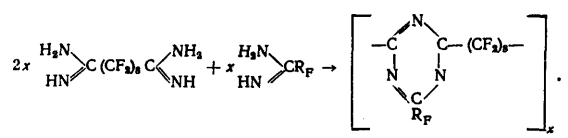
where X = O, SO_2, CH_2, CO. Polymers obtained from *m*-phenylenediamine, benzidine, and di-*p*-aminophenyl ether resist the action of solvents, possess high dielectric constants, and do not melt. The best mechanical properties and thermal characteristics are shown by films based on di-*p*-aminophenyl ether, the properties of the film being preserved after thermal treatment at 275° for 12 months.

Polycondensation of trimellitic anhydride with diamines yields imido-amide polymers:



They are somewhat inferior to pyromellitimide polymers in resistance to heat and oxidation[30].

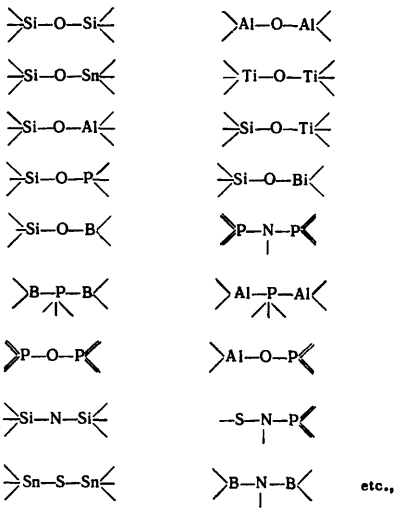
Brown[102] obtained a fluorinated polymer containing triazine rings in the chain by the pyrolysis of a perfluorodiamidine with a perfluoromonoamidine:



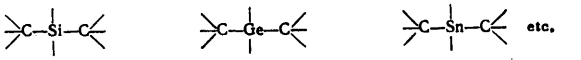
This polymer is thermostable up to 450°, and also possesses exceptional resistance to the action of fuming nitric acid (its properties remaining unchanged after 24 h). Losses in weight after heating in air at 470° and 475° for 30 min are 31% and 51% respectively.

Organoelementary Polymers

Polymers in this group are often extremely thermostable. Those containing the following types of bonds in their chain



are attracting great attention and are being intensively investigated. These elements can also be linked with carbon and with one another, for example

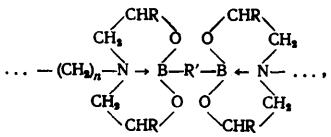


Polymers which do not contain carbon in the main chain of the macromolecule have been termed by Andrianov polymers with inorganic main chains. From a study of them he concluded[39] that the stability of the E–E bond is greater the less ionic in character are such bonds forming the main chain, *i.e.* the closer to the electronegativity of the carbon atom is the mean electronegativity of the two elements forming the bond.

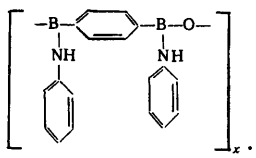
Among organoelementary polymers, the most detailed study has been made of polyorganosiloxanes and polymetalloorganosiloxanes, whose chains are built up from alternating atoms of electropositive silicon and another element (Al, Sn, Ti) and electronegative oxygen. Siloxanes, based on –Si–O– bonds, exist in the form of oils, elastomers, and plastics. The stability of the material depends on the organic substituent attached to the silicon atom, diminishing in the sequence methyl > phenyl > ethyl. Polymers resistant to heat and hydrolysis are also formed when the oxygen bridge is replaced by phenylene residues. The Si–O–Si and Al–O–Al chains reproduce the skeleton of naturally occurring inorganic polymers — quartz and aluminosilicates — and are thermally and hydrolytically stable. The metalloorganosiloxanes synthesised by Andrianov[39] have high thermal stability (up to 600°) and good solubility. Since polyorganosiloxanes have been described in detail in reviews and monographs, we shall not discuss them here[39].

The considerable development which has occurred recently in organoboron polymers is reflected in the review by Zamyatina and Bekasova[148]. Several thermostable polymers have been found among these compounds.

Bamford and Fordham [149] obtained polyesters of diboronic acids with tetrakishydroxyalkylated polymethylenediamines

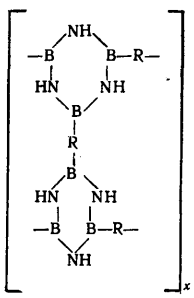


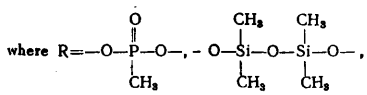
which were stable up to 300° and resistant to hydrolysis. The zinc and diethyltin salts of benzenediboronic acid are polymeric in character, and melt above 500°, as Korshak *et al.* [150] discovered. These workers also obtained polyaminoanhydrides of benzene-*p*-diboronic acid, which melt above 300° and have the structure



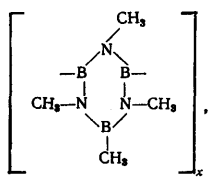
Polyesters of pentaerythritol and boric acid melt above 300°. [151]

Thermostable polymers containing borazole rings linked with residues of methylphosphonic acid or tetramethyldisiloxane

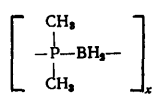




melting above 300°, were obtained by Korshak and his coworkers [150,152]. Eilar and Wagner [153] obtained a polymer comprising borazole rings

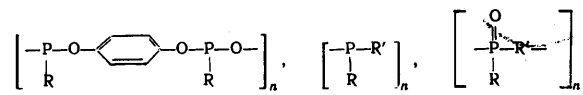


which is stable at 350–500°. Burg [154] prepared a phosphine–borane polymer of structure

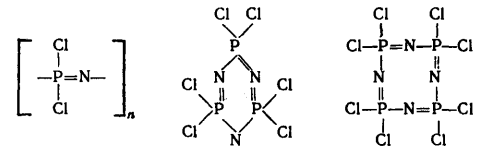


which was stable up to 400°.

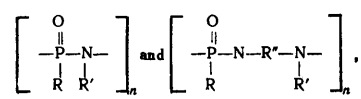
Let us discuss briefly polymers containing P–O and P–C bonds, for example [7]



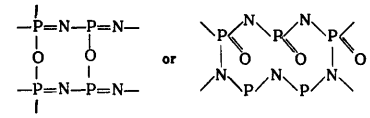
When R = R′ = phenyl, the polymers are stable in air at 300°. Their low molecular weight constitutes a disadvantage. When P is replaced by As, the stability of the polymers at 300° is preserved in a vacuum. Polymers containing P–N bonds exist in linear, trimeric, and tetrameric forms



On being heated to 300° the cyclic trimers are converted into a rubberlike mass having a linear structure. These polymers are unstable to hydrolysis. Polymers containing P–N bonds, obtained by the condensation of phosphorus chlorides with amino-compounds, of the type



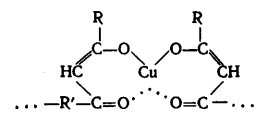
are stable up to 300°. Phosphoroxynitrides resemble ceramic materials [7]: they are stable over a wide range of temperatures, and above 1000° are converted into a glass. The disadvantage is that they are hydrolysed by water when heated above 200°. [7] They have the structure



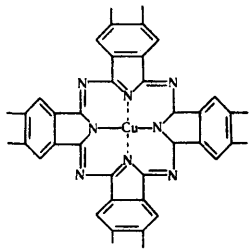
During recent years research has been carried on actively into the production of polymers containing boron–nitrogen bonds. A large number of such polymers have been obtained, their main defect being the comparative ease with which the B–N bonds are hydrolysed [147]. Polymers of this type containing borazole rings in the macromolecule are most interesting, as are also polymeric phosphine–boranes [7].

Coordinate bonds and bonds linking a metal with carbon in metallocene compounds can also be involved [155,156] in the formation of macromolecular organoelementary compounds containing various elements in the polymer chain.

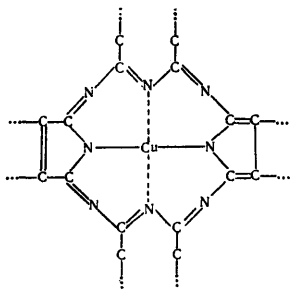
Many inner complex (chelate) polymers have been obtained of such metals as Cu, Be, Zn, Cd, Zr, Cr, Co, Ni, Fe, etc. [157-159]. As ligands linked with these metals various tetraketones have been widely used, yielding coordination polymers of the structure



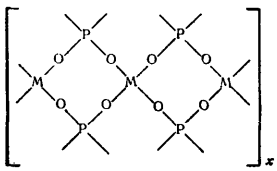
These are powders of various colours, decomposing at 250–400°; with the exception of the beryllium and zinc compounds [159], they are all insoluble. Phthalocyanine polymers of copper [160]



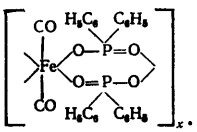
are very thermostable. Very interesting coordination polymers of copper and tetracyanoethylene, obtained by Berlin *et al.* [161], are infusible black powders of parquet structure



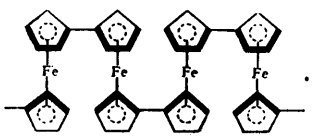
Interesting polymers of beryllium, zinc, copper, and chromium have been prepared by Block *et al.* [162] by the action of diphenylphosphinic acid on the metal salts. They have the structure



The beryllium, zinc, copper, chromium, and cobalt polymers decompose at 530°, 495°, 293°, 296°, and 400° respectively. Novel polymers have been obtained by Podall and Lapalucci [163] by the action of diphenylphosphinic acid on the carbonyls of chromium (decomp. temp. 360°) and iron (305°), which have the structure



Polyferrocenylene, which was prepared by Korshak *et al.* [151] by the polyrecombination of ferrocene, is a brown product melting at about 300° and having the structure



A large number of coordination polymers have been described in reviews by Berlin and Matveeva [157], Rode *et al.* [158], and other writers [38,122,159].

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The compounds discussed above by no means exhaust the possible types of thermostable polymers. Here we have given only a few examples illustrating the main routes used for the formation of thermostable polymers.

Immense opportunities for the synthesis of thermostable compounds, as yet undiscovered, are to be expected among inorganic polymers, which we have not discussed at all in this review, although several promising prospects in this interesting field are already beginning to appear [38].

By means of this review we have aimed to draw attention to this rapidly developing field, and to show that definite theoretical concepts have already been established to enable synthesis to be consciously directed towards the production of thermostable polymers.

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