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Dependence of Thermal Stability of Polymers on Their Chemical Structure

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It is shown, on the basis of a large amount of experimental work, how the thermal stability of polymers depends on the strength of the bonds between the atoms forming the macromolecule, on the structure of the chain unit in the macromolecule, and also on the structure of the polymer molecule itself as a whole. Especially detailed attention is given to the effect on thermal stability of such structural features of the chain unit as the presence of side-chains, halogen atoms, and other elements (boron, silicon, phosphorus, various metals), the positions and number of these substituents, and also groups of aromatic character, including benzene rings and various heterocycles. Those structural features which tend to increase the thermal stability of polymers are elucidated.
An important place in the review is occupied by examining the dependence of thermal stability on such structural aspects of the macromolecule itself as the regularity in the arrangement of monomer units along its chain, the isomerism of substitution in the aromatic ring, the presence of branching and cross-linking, copolymerisation, and also the nature of end-groups, etc. A list of 100 references is given.

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I. INTRODUCTION

The most important problem of polymer chemistry is to establish the relation between the properties of polymers and their structure. Only when this is known is it possible to solve consciously and successfully the problems involved in preparing polymers having required properties which have been specified in advance.

Although relatively little experimental work has yet been done on the relations between the structure and the properties of polymers, it is already possible, on the basis of known data, to establish certain relations of this type. The main method for finding links between the structure and the properties of polymers is to study and compare the behaviour of series of polymers of analogous structure[1].

We shall not deal here with one extremely important aspect of this problem—the influence of the physical structure of polymers on their properties—which has been determined by the work of Kargin[2]. He has shown, on the basis of a large number of experimental results, that the physical structure of a polymer affects not only its strength but also several of its chemical reactions.

Without being concerned with the whole problem of the relation between structure and properties, we shall examine only its purely chemical aspect. The aim of the present review is to show quite clearly the relations which have now been elucidated between the chemical structure and the thermal stability of polymers, these being of interest in particular in connection with the problem of producing the heat-resistant materials which are so necessary for modern technology.

Let us first define the concepts of heat-resistance and thermal stability, with which we shall often be dealing. *Heat-resistance* we shall take to mean the limiting temperature at which a given polymer is able to maintain a particular mechanical strength. *Thermal stability* will imply the limiting temperature which a given polymer can withstand without chemical change. Above this temperature the polymer begins to undergo chemical breakdown, in most cases accompanied by loss of mechanical strength.

We shall not be concerned here with problems associated with the thermal breakdown of polymers under the simultaneous influence of high temperatures and chemical reagents such as oxygen, water, etc., i.e. the oxidative thermal degradation and the hydrolytic cleavage of polymers.

Various methods are used to assess the thermal stability of polymers. The most widely used are methods of *dynamic thermogravimetric analysis*, in which loss in weight is determined while the temperature is raised continuously and uniformly. *Isothermal thermogravimetric analysis* is often employed also, this being conducted at a constant temperature. These methods are of value only for the preliminary assessment of polymers under laboratory conditions. A more exact estimate of the thermal stability of polymers necessitates prolonged tests at the required temperatures. Methods of determining thermal stability from the loss in weight of polymers on heating has the disadvantage that they give no information on chemical changes unaccompanied by loss of volatile products. In many cases, however, comparative results of the thermogravimetric analysis of various polymers nevertheless give an idea of their thermal stability.

When discussing the dependence of the thermal stability of polymers on their chemical structure, we understand by the latter both the composition of the polymer and various structural features of its chain unit, the individual macromolecule, and the union of individual linear macromolecules joined by chemical bonds. Only a few experimental data have been published on this question, and attempts have been made at certain generalisations in individual reviews [3-8] and monographs [9,10].

The thermal stability of a polymer depends primarily on the strength of the bonds between the individual atoms and groups forming this macromolecule. The strength of these bonds determines the temperature at which they are ruptured as a result of dissociation or other chemical reactions caused by high temperature or various chemical agents. We shall therefore first examine the dependence of the strength of these bonds on the nature of the atoms constituting the polymer macromolecule, and then elucidate the effect on the thermal stability of the polymer of the chemical structure of the chain units and of the macromolecule as a whole.

II. STRENGTH OF BONDS BETWEEN ATOMS IN THE MACROMOLECULE

The strength of a chemical bond depends on the nature of the atoms between which it is formed, the sequence of bonded atoms, the nature of substituents, and other structural features. The strength of bonds can be characterised by the bond energy, which corresponds to the energy of their dissociation into free radicals (Table 1).

Table 1 shows that the most stable bonds are those between carbon atoms. The strength of a bond between atoms of other elements is considerably less. Therefore only those elements in which the energy of the bonds linking one atom to another is sufficiently large are able to form homochain polymers. If, however, the energies of bonds between atoms of elements are small, the polymers show poor stability; and at bond energies less than 37 kcal mole^{-1} elements are completely unable to form polymeric chains, since the latter would obviously break down as a result of thermal degradation even at ordinary temperatures.

The existence of a large number of carbon-chain polymers is due to the high bond energy between carbon atoms. Thus in this case the effect of strength of bonding on the properties of a polymer is shown quite clearly.

Heterochain polymers, whose macromolecules are formed from different elements, show considerably higher bond energies between the atoms (Table 2), so that a marked increase in their thermal stability is observed. Table 2 shows that the energies of bonds between atoms of different chain-forming elements, which are typical of heterochain polymers, are quite high, in many cases exceeding the bond energies encountered in homochain polymers. The highest energies are exhibited by boron–nitrogen and boron–oxygen bonds, and also by those between aromatic carbon and nitrogen or oxygen. The silicon–oxygen bond is also extremely stable. These are the bonds which occur in polymers having the greatest thermal stability.

Table 1. Energy of bonds (kcal mole^{-1}) between atoms of elements [11,12].

Bond	Energy	Bond	Energy
C_{arom}–C_{arom}	98.0	Te—Te	49.0
C_{aliph}–C_{aliph}	83.0	Sb—Sb	42.0
S—S	63.0	Ge—Ge	39.2
Si—Si	53.0	As—As	39.0
P—P	53.0	N—N	37.0
Se—Se	50.0	O—O	34.0

Table 2. Bond energies (kcal mole^{-1}) between atoms of different elements capable of forming heterochain polymers [11,13].

Bond	Energy	Bond	Energy
B_{arom}—N_{arom}	115.0	C_{aliph}—N^{III}	82.0
B—O	113.5	P^{III}—O	81.7
C_{arom}—N^{III}	110.0	C_{aliph}—Si	78.0
C_{arom}—O	107.0	As—O	64.5
Si—O	106.0	Al—C	61.6
B—N^{III}	105.0	C_{aliph}—S^{II}	61.5
B—C_{arom}	100.0	Si—S^{II}	60.9
C_{aliph}—O	93.0	C_{aliph}—As^{III}	54.6
B—C_{aliph}	89.0	N—O	37.0

Table 3. Bond energies (kcal mole^{-1}) of surrounding atoms [11].

Bond	Energy
Si—F	135
C—F	116
C_{aliph}—H	97
Si—Cl	91
C—Cl	80
Si—H	76

However, the strength of the bonds between atoms in the main chain of the macromolecule and atoms or groups attached to this chain is no less important. Table 3 shows that the fluorine–silicon and fluorine–carbon bonds possess the highest energy, which is the reason for the high thermal stability of organofluorine polymers. However, this is valid only when such bonds undergo cleavage by thermal dissociation. If the halogen can be removed in

other ways, e.g. by elimination as a hydrogen halide molecule containing a hydrogen atom from an adjacent carbon atom, the thermal stability of the polymer drops sharply. Thus poly(vinyl fluoride) and poly(vinyl chloride) show poor thermal stability owing to the ready elimination of the hydrogen halide. This applies also to poly(vinylidene chloride), poly(vinyl alcohol), and analogous compounds of general formula $[CH_2-CHX]_n$ as well as to polymers containing halogen in side-chains. Thus the higher thermal stability of pentone (the polymer of 3,3-bischloromethyloxacyclobutane) compared with poly(vinyl chloride) is due to the absence of hydrogen on the carbon atom adjacent to the chloromethyl group, which would be necessary for the formation of hydrogen chloride.

Table 4. Electronegativities of elements in different groups of Periodic System[14].

Group			
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
	Sr—1.5		W—2.0
	Pb—1.6		

The energies given in Tables 2 and 3 for bonds between atoms of different elements have been calculated for homolytic dissociation of the bonds. However, all these bonds are in some measure polar, and this must always be borne in mind. Application of Pauling's concept of the electronegativity of bonds[14] is especially convenient for this purpose. The electronegativities listed in Table 4 for the most important elements can be used to determine the ionic character of bonds. If the difference in electronegativity is 1.9, such bond is 50% ionic in character; if the difference is still larger, it is more correct to regard such a compound as having an ionic structure; and if the difference is less than 1.9, the bond is covalent.

The polarity of bonds has a fundamental effect on their stability at elevated temperatures, since the more polar a bond, the more marked the decrease in its strength with rise in temperature. Organic carbon-chain compounds of high molecular weight are built up solely by covalent bonds between carbon atoms, whose electronegativity is 2.5.

From a study of polymers containing inorganic chains Andrianov[15] concluded that the stability of a bond El–El′ will be greater the less ionogenic are the bonds forming the main chain, i.e. the closer the mean electronegativity of the two elements forming the bond to that of the carbon atom. As examples of the construction of organoelementary polymers on this principle, he mentions polyorganosiloxanes and polyalumino-organosiloxanes, the chains in which are made up of alternating atoms of electropositive silicon and aluminium and of electronegative oxygen, while the mean electronegativity of bonding of these two elements approaches the electronegativity of carbon. These chains reproduce the skeleton of naturally occurring inorganic polymers—quartz, aluminosilicates—and are thermally and hydrolytically stable.

III. DEPENDENCE OF THERMAL STABILITY ON STRUCTURE OF CHAIN UNIT

The thermal stability of polymers depends both on the structure of the monomeric chain unit and on that of the whole macromolecule, the presence and nature of all intermolecular bonds, and also the presence of various impurities.

Let us first examine how the structure of an individual chain unit affects thermal stability. For this purpose we regard all polymers as derivatives of two main types of macromolecular chains—polymethylene $[CH_2]_n$ and polyphenylene $[C_6H_4]_n$—as well as of various combinations thereof. These main units can also be separated by various heteroatoms or heterocycles.

Fig. 1 illustrates the results of a dynamic thermogravimetric analysis of the two extreme members—polyethylene and polyphenylene—of these classes of polymers. The thermogravimetric curves clearly show a fundamental difference in their thermal stability, which is characteristic of these two classes of substances.

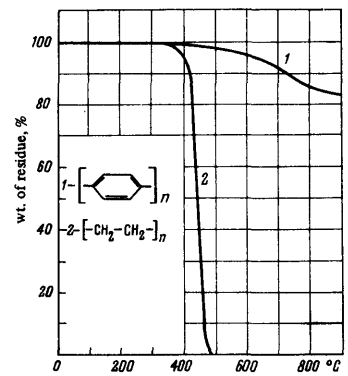
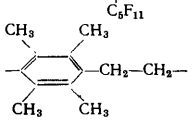
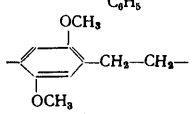
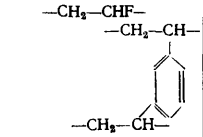


Figure 1. Dynamic thermogravimetric analysis (in vacuum, rate of heating 5 deg min^{-1}) of hydrocarbon polymers: *1*) polyphenylene; *2*) polyethylene.

The general dependence of the thermal stability of polymers on the structural unit can be illustrated by means of the relative thermal stabilities listed in Table 5. The values of the relative thermal stability of polymers (temperatures of half-decomposition T_h, at which 50% loss in weight occurs on heating for 40–45 min) are arranged in increasing order. Table 5 includes only those polymers which in a vacuum lose not less than 80–85% of their weight without the occurrence of stabilisation or cross-linking phenomena[16].

It must be remarked, however, that the half-decomposition temperature is an extremely rough indication of the thermal stability of polymers, since a far more important characteristic in this respect is the temperature of incipient decomposition of the polymer, determined as the point at which appreciable loss in weight of the heated polymer begins. The half-decomposition temperature is not characteristic of this point, but rather shows how rapidly thermal degradation of the polymer is taking place. Moreover,

Table 5. Relative thermal stability (temperature of half-decomposition) of polymers [16,17].

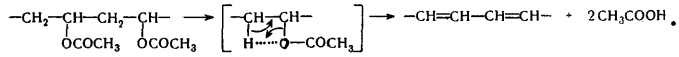
No.	Polymer	Chain unit	°C
1	Polyperfluoroheptene	$-CF_2-CF-$ C_6F_{11}	248
2	Polytetramethyl-*p*-phenylene-ethylene		265
3	Poly(methyl methacrylate) (M = 150000, obtained in the presence of benzoyl peroxide)	CH_3 $-CH_2-C-$ $COOCH_3$	283
4	Poly-α-methylstyrene	CH_3 $-CH_2-C-$ C_6H_5	287
5	Poly(propylene oxide) (atactic)	$-CH_2-CH-O-$ CH_3	295
6	Polyperfluoropropylene	$-CF_2-CF-$ CF_3	297
7	Poly(propylene oxide) (isotactic)	CH_3 $-CH_2-CH-O-$	312
8	Polyisoprene	$-CH_2-CH=C-CH_2-$ CH_3	323
9	Poly(methyl methacrylate) (M = 5100000, obtained by thermal polymerisation)	CH_3 $-CH_2-C-$ $COOCH_3$	327
10	Poly(methyl acrylate)	$-CH_2-CH-$ $COOCH_3$	328
11	Poly(ethylene oxide)	$-CH_2-CH_2-O-$	345
12	Polyisobutylene	CH_3 $-CH_2-C-$ CH_3	348
13	Polystyrene	$-CH_2-CH-$ C_6H_5	364
14	Poly-2,5-dimethoxy-*p*-phenylene-ethylene		375
15	Polychlorotrifluoroethylene	$-CF_2-CFCl-$	380
16	Polypropylene	$-CH_2-CH-$ CH_3	387
17	Poly(vinyl fluoride)	$-CH_2-CHF-$	389
18	Polydivinylbenzene		399
19	Polyethylene	$-CH_2-CH_2-$	406
20	Polybutadiene	$-CH_2-CH=CH-CH_2-$	407
21	Polytrifluoroethylene	$-CF_2-CHF-$	413
22	Polymethylene	$-CH_2-$	415
23	Polybenzyl	$-CH_2-C_6H_4-$	430
24	Poly-*p*-phenylene-ethylene	$-CH_2-C_6H_4-CH_2-$	432
25	Polytetrafluoroethylene	$-CF_2-CF_2-$	509

with aromatic and heterocyclic polymers, which are distinguished by great thermal stability, this constant is altogether unsuitable, since many polymers of this type lose less than 50% of their original weight when heated to high temperatures. Thus many polybenzimidazoles, polyquinoxalines, polyimidazopyrrolones, etc. lose only ~ 30% of their original weight at 900°C, polyphenylene only 18%, and carborane–polyamides only ~ 6%. At the present time we still have very little information on the thermal stability of polymers, so that half-decomposition temperatures, despite their inadequacy, nevertheless give some idea of the relative thermal stability of polymers.

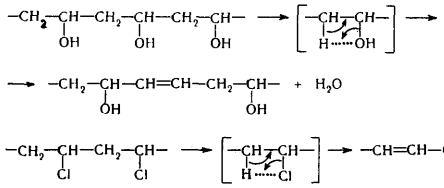
Let us examine the effect of the structure of the chain unit on thermal stability in various classes of polymers. Straight-chain polyalkenes have better thermal stability than have the branched polymers, as can be seen from a comparison of the half-decomposition temperatures of polymethylene (T_h = 415°C) and polyethylene (406°C) with those of polypropylene (387°C), polyisobutylene (348°C), and other polymers. (This question will be discussed in greater detail in Section IV, 3.)

The presence of a double bond in the chain hardly diminishes the thermal stability at all, as can be seen from a comparison of polyethylene with polybutadiene (T_h = 407°C). The thermal stability of *cis*- and *trans*-isomers shows no fundamental difference, as evidenced by natural rubber and gutta-percha, and also by synthetic polyisoprene[18].

Several polymers are characterised by low thermal stability owing to the presence in their chain units of such groups and atoms as OH, Cl, RCO, etc., which are readily eliminated as water, hydrogen chloride, alcohol, ammonia, etc. Examples of such compounds are poly(vinyl alcohol), poly(vinyl acetate), poly(vinyl chloride), etc. The breakdown of poly(vinyl acetate) yields polyvinylene via an intermediate activated complex:



Poly(vinyl alcohol) and poly(vinyl chloride) also decompose:



The formation of double bonds sharply diminishes the stability of adjacent hydroxy-groups, since the latter are in the β-position with respect to the double bond, and are especially easily split off. Therefore poly(vinyl chloride), poly(vinyl alcohol), and various derivatives easily eliminate almost 100% of halogen or hydroxyls, as the hydrogen halide or water, at relatively low temperatures[19,20]. Fig. 2 shows the loss in weight of poly(vinyl alcohol) and polyethoxyethylene compared with polyethylene, and Fig. 3 that of poly(vinyl chloride) and poly(vinylidene chloride), as a result of being heated at various temperatures.

In most cases replacement of hydrogen by fluorine atoms enhances the thermal stability of polymers, this being due to the higher energy of the carbon–fluorine bond compared with the carbon–hydrogen bond (see Table 3). Fig. 4 shows the quantity of volatile products lost by various fluorinated polymers when heated at various temperatures for 2 h.[21,22] The most stable proved to be polytetrafluoroethylene (T_h = 509°C). The other copolymers and polymers in Fig. 4 show lower thermal stability. Partial replacement of hydrogen by fluorine atoms, as e.g. in poly(vinylidene fluoride), or the presence of chlorine atoms in polychlorotrifluoroethylene lowers the thermal stability. Copolymers of trifluoronitrosomethane have the lowest thermal stability, since they contain –N–O– bonds, which are less stable than –C–C– bonds (Tables 1 and 2). On the other hand, –C–O– bonds are stable, and poly(hexafluoropentamethylene adipate) therefore possesses higher thermal stability. Polymers of fluorinated ethylenes and polyethylene are

arranged in the following sequence of diminishing thermal stability (T_h)

$$(-CF_2-CF_2-)_x > (-CH_2-CF_2-)_x > (-CF_2-CHF-)_x > (-CH_2-CH_2-)_x >$$
$$(T_h=509°) \qquad (T_h=445°) \qquad (T_h=412°) \qquad (T_h=406°)$$
$$> (-CH_2-CHF-)_x$$
$$(T_h=388°)$$

Only poly(vinyl fluoride) is inferior to polyethylene, while the other fluorinated polymers surpass it in thermal stability[22].

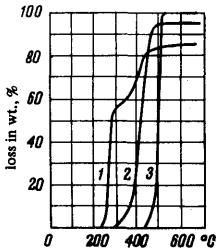


Figure 2. Dynamic thermogravimetric analysis (rate of heating 2 deg min^{-1}) of vinyl polymers[19]:
1) poly(vinyl alcohol); *2*) poly(ethyl vinyl ether); *3*) polyethylene.

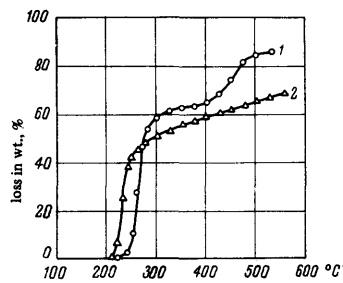


Figure 3. Isothermal thermogravimetric analysis (in atmosphere of nitrogen)[20] of:
1) poly(vinyl chloride); *2*) poly(vinylidene chloride).

A factor of fundamental importance in the relation between thermal stability and structure is the ability of a polymer to decompose on heating with formation of a volatile monomer. All polymers can be divided into two groups according to their behaviour on pyrolysis: polymers in the first group form monomers and other volatile products on thermal decomposition, and either volatilise completely or leave a small non-volatile residue when heated; polymers of the second group do not form volatile monomers, but are converted mainly into non-volatile products. The former group includes vinyl and diene polymers; the second group contains mainly polymers with benzene rings or heterocycles in the main chain.

The presence of benzene rings in the chain enhances the thermal stability of a polymer in comparison with polyethylene (T_h = 406°C), as is evident from the examples of polybenzyl (430°C) and poly-*p*-xylylene (432°C). The effect of position isomerism of the substituents in the aromatic ring must be noted here, as can be seen from Fig. 5, which gives thermogravimetric curves for polymeric *m*- and *p*-xylylenes and their copolymers.

Polymers containing aromatic rings linked together either directly or through various radicals are distinguished by great thermal stability. Table 6 gives values of the relative thermal stability of several polymers containing aromatic rings, determined at the temperature at which the weight of a specimen is halved in 2 h.[17]

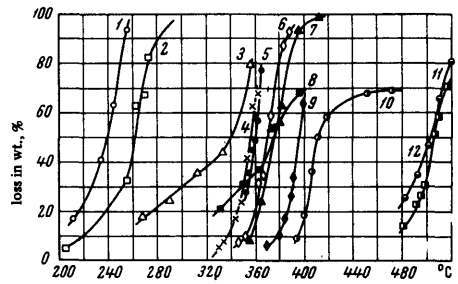


Figure 4. Isothermal thermogravimetric analysis (each point corresponds to a separate specimen heated in a vacuum for 2 h) of various fluorine-containing polymers[22]:
1) copolymer of trifluoronitrosomethane with trifluoroethylene;
2) copolymer of trifluoronitrosomethane with tetrafluoroethylene;
3) poly(hexafluoropentamethylene adipate);
4) polychlorotrifluoroethylene;
5) copolymer of vinylidene fluoride (36%) with chlorotrifluoroethylene (64%);
6) copolymer of vinylidene fluoride (55%) with chlorotrifluoroethylene (45%);
7) copolymer of vinylidene fluoride (77%) with chlorotrifluoroethylene (23%);
8) copolymer of octafluorocyclohexa-1,3-diene with butadiene;
9) copolymer of vinylidene fluoride with hexafluoropropylene;
10) poly(vinylidene fluoride);
11) copolymer of tetrafluoroethylene with hexafluoropropylene;
12) polytetrafluoroethylene.

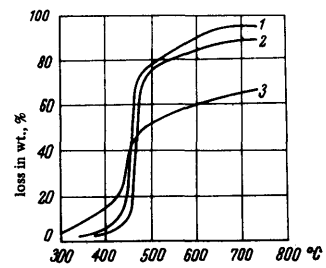
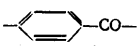
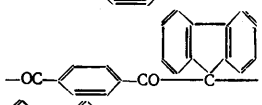
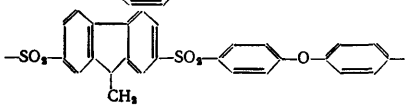
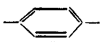
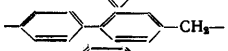
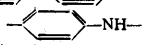
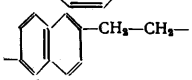
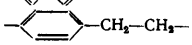
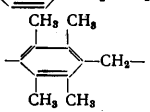
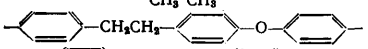
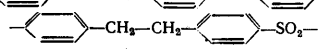
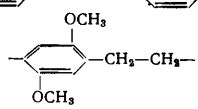
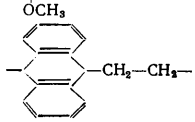
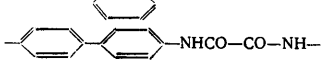
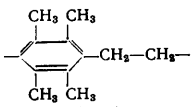
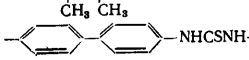
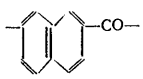


Figure 5. Thermal stability, determined by dynamic thermogravimetric analysis (rate of heating 2.5 deg min^{-1})[22], of polyphenylene-ethylenes:
1) *meta*-isomer; *2*) copolymer of *meta*- and *para*-isomers (1 : 1);
3) *para*-isomer.

The polymers listed in Table 6 can be divided into two types according to their behaviour on heating. The first type includes polymers whose chain unit is made up of such groups as *p*-phenylene (No. 4), *m*-phenylene (5), *pp'*-biphenylylenemethylene (6), tetramethyl-*p*-phenylenemethylene (10), tetramethyl-*p*-phenylene-ethylene (16), *p*-phenyleneimine (7), *pp'*-biphenylylenedi-imineoxalyl (15), naphthylenecarbonyl (18), *p*-phenylenecarbonyl (1), terephthaloylfluorenylidene (2), and also the condensation product of fluorene-2,7-disulphonyl chloride and diphenyl ether (3).

Table 6. Relative thermal stability of polymers (temperature at which the weight of the polymer is halved in 2 h).

No.	Chain unit	Stability, °C	Softening point, °C
1		700	>400
2		640	>400
3		>690	>400
4		<680	>400
5		540	400
6		525	>400
7		485	>400
8		450	>400
9		430	>400
10		430	225—230
11		425	150
12		415	225—230
13		375	215
14		360	>400
15		350	400
16		265	480
17		230	does not soften, but volatilises completely at 350°C
18		<250	>400

The second type includes 2,5-dimethyoxy-1,4-phenylene-ethylene (13), *p*-phenylene-ethylene (9), naphthylene-ethylene (8), anthrylene-ethylene (14), *pp'*-biphenylylenethioureylene (17), *pp'*-biphenylylene-ethylenephenoxy (11), and *p*-phenylene-ethylene-*p*-phenylenesulphonyl (12).

Compounds of the first type are characterised by a rapid loss of part of their weight during the initial stage of heating, after which the residue either undergoes no further change or decomposes slowly.

Polymers of the second type lose weight more slowly on being heated, but these losses are larger than in the first type. They all contain the ethylene group, which is probably readily eliminated. Polymers containing a carbonyl group as linking unit show the greatest thermal stability. An exception is the thermally least stable naphthylenecarbonyl, which already shows appreciable loss in weight at around 250°C, but on further heating to 500°C decomposes only slightly: this is, perhaps, due to contamination with products of low molecular weight.

Fig. 6 shows the loss in weight of a series of polyalkylenephenylenes when heated in a vacuum for 2 h.[24] It includes for comparison the curve for polytetrafluoroethylene.

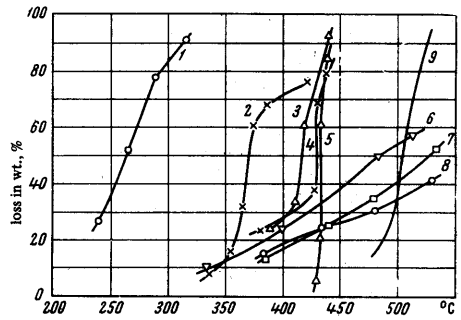


Figure 6. Isothermal thermogravimetric analysis (heating in a vacuum for 2 h) of various polyalkylenephenylenes[24]:
1) polytetramethyl-*p*-phenylene-ethylene; *2*) poly-2,5-dimethoxy-*p*-phenylene-ethylene; *3*) poly-2,5-dimethyl-*p*-phenylenemethylene; *4*) polytetramethyl-*p*-phenylenemethylene; *5*) poly-*p*-phenylene-ethylene; *6*) poly-*pp'*-biphenylylenemethylene; *7*) poly-*m*-phenylene; *8*) poly-*p*-phenylene; *9*) polytetrafluoroethylene.

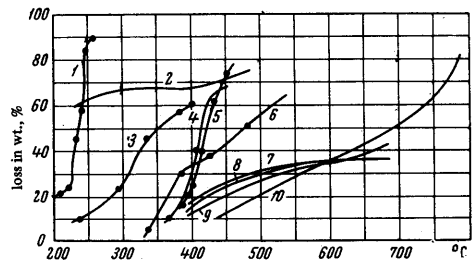
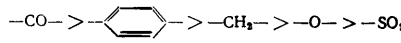


Figure 7. Thermal stability of aryl polymers containing various bridging groups, determined by isothermal thermogravimetric analysis[17] (heating in a vacuum for 2 h):
1) poly-*pp'*-biphenylylenethioureylene; *2*) polynaphthylenecarbonyl; *3*) poly-*pp'*-biphenylylenedi-imineoxalyl; *4*) poly-*p*-phenylene-ethylene-*p'*-phenylenesulphonyl; *5*) poly-*pp'*-biphenylylene-ethylenephenoxy; *6*) *p*-phenyleneimine; *7*) polymer of fluorene-2,7-disulphonyl chloride and diphenyl ether; *8*) polymer of terephthaloyl chloride and naphthalene; *9*) polyphenylenecarbonyl; *10*) polymer of terephthaloyl chloride and fluorene[17].

The nature of the bridging groups joining arylene units in polymers also has a substantial influence on thermal stability, as can be seen from Fig. 7, which gives curves showing the loss in weight of several polymers when heated at various temperatures for 2 h.[17] It can be concluded from these results that the thermal stability of polymers

containing aromatic rings in the chain diminishes according to the nature of the bridging groups in the sequence



The presence of hydroxyl and other substituents in the aromatic ring affects all the properties of the polymer, including its thermal stability. Thus phenol–formaldehyde polymers, which are fairly thermostable substances[25], clearly confirm this principle: the introduction of substituents into the benzene ring results in diminished thermal stability. The thermogravimetric curves for poly-*p*-phenylene and resite, reproduced in Fig. 8, show that the thermal stability of the latter is considerably lower than that of the former, which is explained by the presence of methylene and hydroxyl groups in the benzene rings of resite.

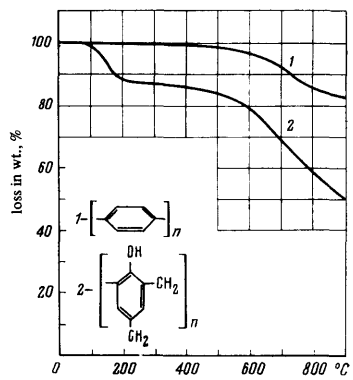


Figure 8. Dynamic thermogravimetric analysis (heating in argon at 15 deg min^{-1}) of:
1) poly-*p*-phenylene; *2*) resite.

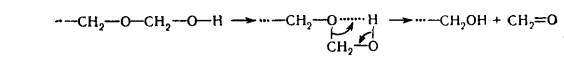
Table 7. Amine–formaldehyde polymers[27].

Amine	Loss in wt., %, at 330°C	Loss in wt., %, at 900°C	Temp. of max. gas evolution, °C
Fuchsine	19	35	700
p-Aminophenol	15	47	600
Melamine	36	56	450, 500
Dicyanodiamide	37	62	200, 700
2,6-Diaminopyridine	30	56	600
m-Phenylenediamine	20	57	600
Urea	36	70	300
Aniline	47	81	650

Phenoplasts can operate at 175°C for an indefinite period, but at 200°C for only a few hours; above 200°C their stability drops sharply. As a comparison it may be mentioned that the temperature at which thermal degradation of phenol–formaldehyde polymers begins in an atmosphere of hydrogen is 432°C, as determined by thermoparticulate analysis, whereas the corresponding temperatures for poly(methyl methacrylate) and polystyrene are 310° and 337°C respectively[26].

Many products of the polycondensation of formaldehyde with aromatic amines, which have been prepared by Sergeev et al.[27], are characterised by great thermal stability. When heated to 330°C they lose 15–30% of their weight, but when heated to 900°C they form a non-volatile residue constituting up to 65% of the weight of the original polymer (Table 7). The most thermostable are products of the polycondensation of formaldehyde with *p*-aminophenol.

The introduction of ethereal oxygen into the main chain of a polymer lowers its thermal stability. Thus the thermal stability T_h of polyformaldehyde, poly(ethylene oxide), and isotactic and atactic poly(propylene oxide) (170°, 345°, 312°, and 295°C respectively) is lower than for the corresponding hydrocarbon polymers—polymethylene, polyethylene, and polypropylene (415°, 406°, and 387°C).[16,21] Owing to the polarity of the C–O bond, polyethers show a great tendency to thermal degradation with liberation of the monomer or its conversion products:



As in the case of polyalkenes the presence of lateral substituents lowers the thermal stability. It is interesting that atactic poly(propylene oxide) is thermally less stable than the isotactic isomer. The irregular arrangement of substituents is obviously the cause of structural inhomogeneities facilitating breakdown of the polymer chain.

Aromatic polyethers, in contrast to the aliphatic polymers, are extremely thermostable[28]. Fig. 9 shows thermograms for poly-(2,6-dimethyl-1,4-phenylene oxide) in an atmosphere of nitrogen[29]. It is seen that the poly(phenylene oxide) begins to decompose at 350°C.

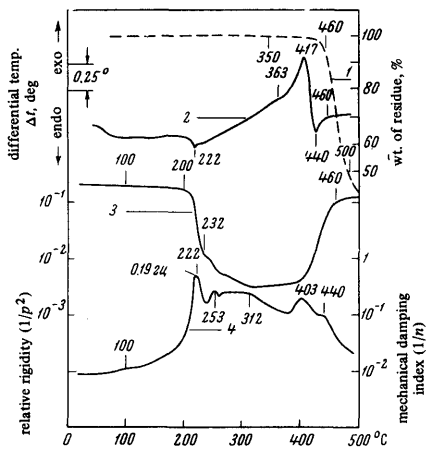


Figure 9. Thermograms of poly-(2,6-dimethyl-*p*-phenylene oxide) determined in an atmosphere of nitrogen[22]:
1) dynamic thermogravimetric analysis (rate of heating 5 deg min^{-1}); *2*) differential thermal analysis (5 deg min^{-1}); *3*) thermomechanical torsion method (2 deg min^{-1}); *4*) thermomechanical torsion method (2 deg min^{-1}).

The thermal stability of polyesters depends on their structure. Table 8 gives Ritchie's measurements[30] of the temperatures at which a series of unsaturated polyesters and their copolymers begin to decompose. It is seen from Table 8 that the temperature at which carbon dioxide is eliminated lies in the range 280–345°C depending on the structure of the polyester. Formation of unsaturated products and aldehydes takes place over practically the same

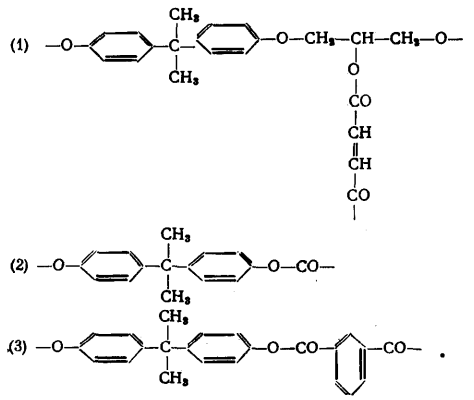
temperature range. It must be noted that a polyester of the saturated succinic acid begins to break down at a higher temperature than is found for polyesters of the unsaturated fumaric acid.

Table 8. Temperatures of start of thermal decomposition of various unsaturated polyesters* and their copolymers[30].

Polyester	Initial temperature, °C			
	evolution of CO_2	formation of unsaturateds	formation of aldehydes	formation of methyl methacrylate
Poly(ethylene fumarate)	295	305	305	—
Poly(neopentyl fumarate)	290	335	290	—
Poly-(*p*-phenylene fumarate)	280	+	+	—
Poly(ethylene succinate)	345	320	330	—
Ethylene fumarate + methacrylate copolymer	305	305	310	265
Neopentyl fumarate + methyl methacrylate copolymer	310	380	310	260
Methyl fumarate + methacrylate copolymer	—	—	—	250
Poly(methyl methacrylate)	—	—	—	240

* Up to 500°C neither ethylene, acetylene, nor aldehyde evolved.

It is seen from the above data that aliphatic polyesters and their copolymers have no great thermal stability. In contrast to them, polyesters of arenediols and aromatic dicarboxylic acids—"polyarylates"—are highly thermostable substances. The curves in Fig. 10 show the relative rates of decomposition of poly-(2,2-di-*p*-phenylenepropane isophthalate) (a polyarylate), a polycarbonate, and an epoxide resin at 400°C. It is seen that the polyarylate considerably surpasses the polycarbonate and the epoxide resin in thermal stability. These three polymers resemble one another in the structure of the principal chain unit, in which a 2,2-diphenylpropane-*pp'*-diol residue is present:



The differences in their thermal stability depend on the structure of the second component of the chain unit. Therefore the thermal stability of polyarylates should be improved by removing the aliphatic part of the chain unit, as also on replacing isophthalic by terephthalic acid. Fig. 11 illustrates the thermal stability of polyarylates of phenolphthalein with isophthalic and terephthalic acids: the extent of decomposition of the former considerably exceeds that of the latter at the same temperatures[32].

The thermal stability of polyarylates is greatly influenced by the nature of substituents in the central dihydric phenol. Polyarylates based on diphenylfluorene-*pp'*-diol are distinguished by especially high thermal stability, as can be seen from Fig. 12. These polyarylates have also a higher photostability[33].

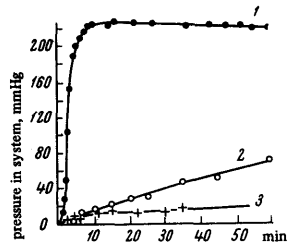


Figure 10. Rate of thermal degradation at 400°C of some polymers based on 2,2-diphenylpropane-*pp'*-diol (dian), determined from pressure of gases evolved[31]:
1) epoxide polymer obtained by hardening the epoxide oligomer ED-6 with maleic anhydride; *2*) poly(dian carbonate); *3*) poly(dian isophthalate) (polyarylate D-2).

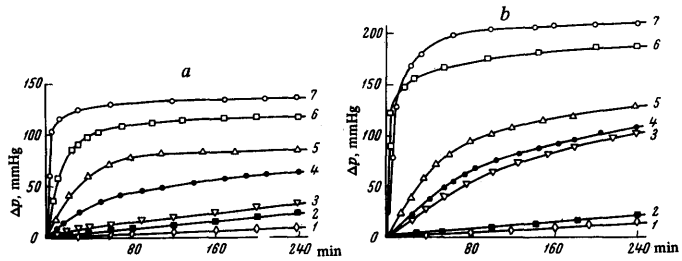
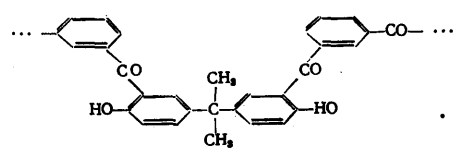


Figure 11. Kinetics of the degradation, determined from the increase in pressure in a closed system[32], of the polyarylates of phenolphthalein and: *a*) terephthalic acid; *b*) isophthalic acid. Temperature (°C): *1*) 350; *2*) 375; *3*) 400; *4*) 425; *5*) 450; *6*) 475; *7*) 500.

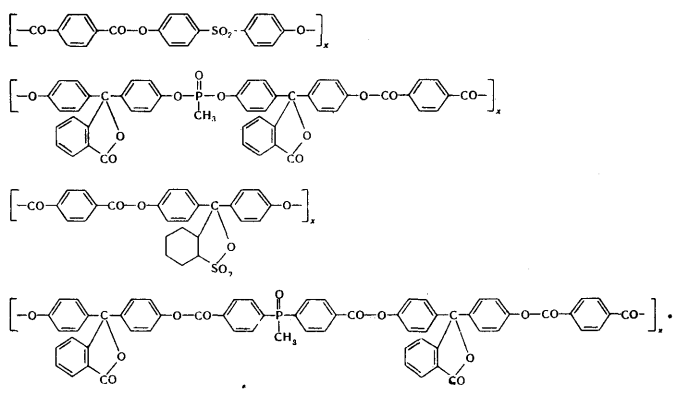
It has been shown with the polyarylates that the incorporation of certain groups may produce "self-protective polymers", which contain various groups and atoms enhancing their stability and protecting them from thermal and chemical breakdown. Self-protective polyarylates have been obtained in several ways[34,37]. Thus the Fries rearrangement or the use of trihydric phenols yields polyarylates containing free phenolic hydroxyls



Such polyarylates have improved thermal stability, and are also more resistant to the action of light and to hydrolysis[34,35].

An equally favourable effect is produced by introducing sulphonyl groups[36] or residues of phosphinic acids[37] into

the polyarylate molecule, as has been shown for the compounds



The introduction of residues of *p*-iodobenzoic acid as end-groups has also proved extremely effective[38]. Such self-protective polyarylates are considerably more resistant to the action of high temperatures.

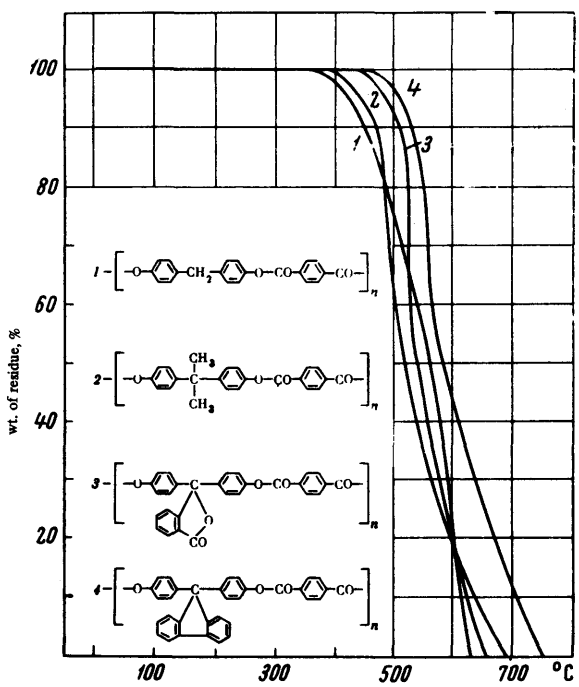


Figure 12. Dynamic thermogravimetric analysis (heating in nitrogen at 4 deg min^{-1})[40] of the polyterephthalates of:
1) diphenylmethane-*pp'*-diol; *2*) 2,2-diphenylpropane-*pp'*-diol; *3*) phenolphthalein; *4*) 9,9-diphenylfluorene-*pp'*-diol.

There are also several extremely thermostable compounds among heterochain polyamides. Aliphatic polyamides have a lower thermal stability than have aromatic polyamides. Thus polyhexano-amide fibre begins to decompose at 400°C, the maximum rate of decomposition occurring over the range 400–436°C.[29,39] Fig. 13 gives thermograms for polyhexano-amide characterising its thermal stability. In general the breakdown of polyamides begins with cleavage of the amide bond. Therefore they start to decompose at temperatures of around 350°C, independently of the structure of the rest of the chain unit, as can be seen from Fig. 14. Nevertheless, aromatic polyamides are more thermostable.

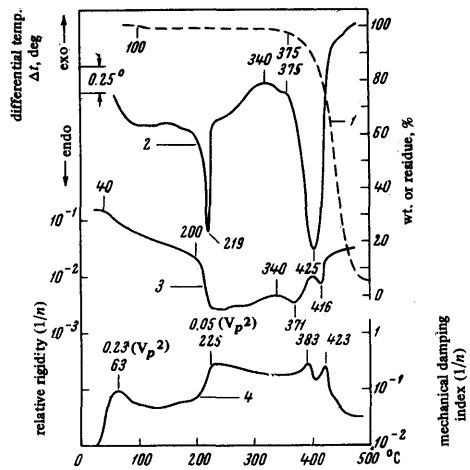


Figure 13. Thermograms of polyhexanoamide[29]:
1) dynamic thermogravimetric analysis (heated in nitrogen at 5 deg min^{-1}); *2*) differential thermal analysis; *3*) thermomechanical torsion method (rate of heating 2 deg min^{-1}); *4*) thermomechanical torsion method.

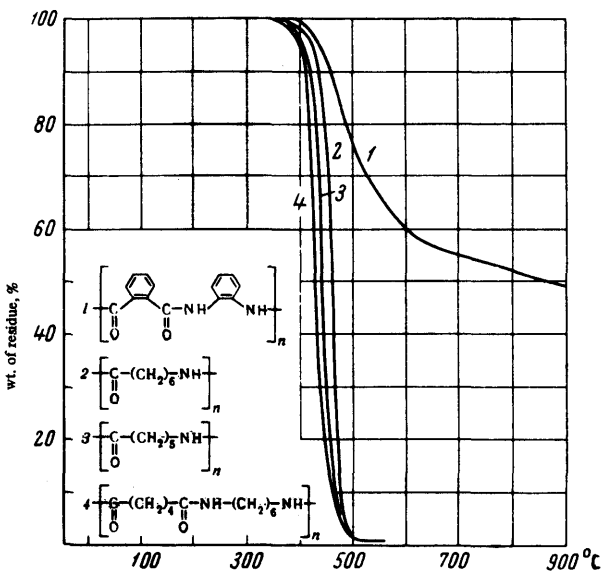
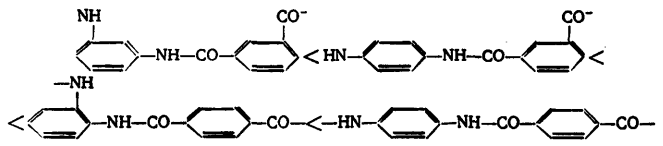


Figure 14. Dynamic thermogravimetric analysis (heated in helium at 5 deg min^{-1}) of polyamides:
1) poly-*m*-phenyleneisophthalamide; *2*) poly-ω-heptanoamide; *3*) polyhexanoamide; *4*) polyhexamethyleneadipamide.

Aromatic polyamides obtained from phenylenediamines and benzenedicarboxylic acids can be arranged according to increasing thermal stability, in the sequence



i.e. polyamides of isophthalic acid are inferior to those of terephthalic acid, just as polyamides from *p*-phenylenediamine are more stable than those from *m*-phenylenediamine (Fig. 15).[41] Thermogravimetric analysis of the polyamide obtained from anilinephthalein and terephthalic acid has shown that this polymer possesses high thermal stability (Fig. 16).[42]

Ordinary polyurethanes begin to decompose at a temperature above 220°C. The thermal stability of polyurethanes can be increased by replacing the hydrogen atoms of the carbamate group by an alkyl or an acyl group[43], and also by using di-isocyanates, in which the isocyanate groups are separated from an aromatic ring by methylene groups, which hinders intramolecular resonance[44-46].

As we have already seen, replacing aliphatic by aromatic groups in the chain unit produces a sharp increase in the thermal stability of polymers. The same result is achieved also by introducing heterocyclic groups of aromatic character into the chain unit, which yields such polymers as polybenzimidazoles, polybenzoxazoles, polyimides, polybenzothiazoles, pyrrones, polypyrazoles, polythiazoles, polyoxadiazoles, polytriazoles, etc. A large number of polymers of this type have now been prepared, and their properties investigated. The results have been summarised in reviews[3,4,8,48,49].

An important feature of these polymers—"polyheteroarylenes"—is their extremely high thermal stability (Table 9). The results of a thermogravimetric analysis of four polybenzimidazoles are plotted in Fig. 17. Polymers containing an aliphatic residue in the chain unit begin to decompose above 450°C, and those containing phenylene groups above 550°C. Even at 900°C the losses in weight of the last two polymers are only 30%.

Table 9. Thermal stability (temperature at which decomposition begins) of some polymers containing heterocycles in the chain.

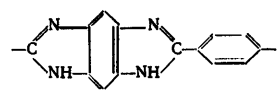
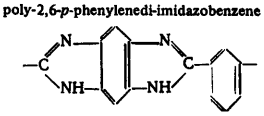
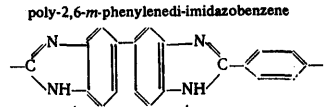
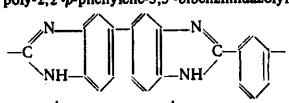
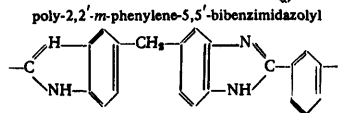
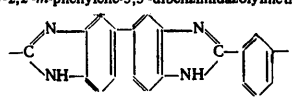
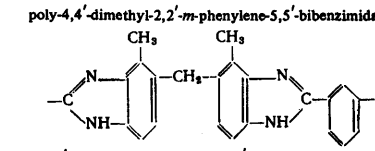
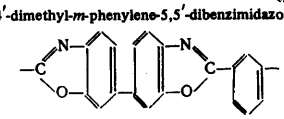
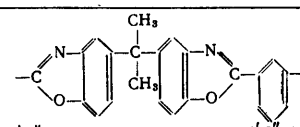
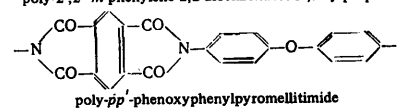
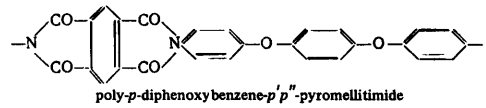
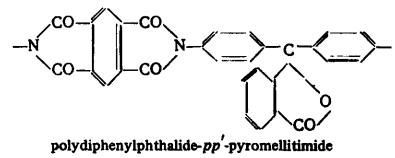
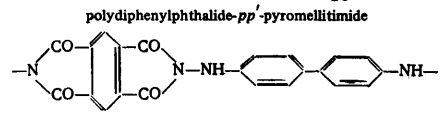
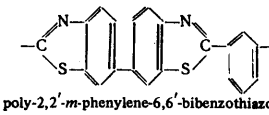
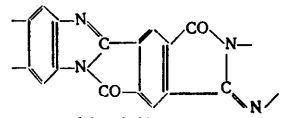
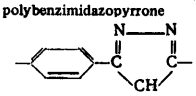
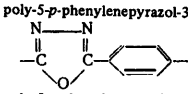
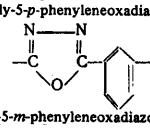
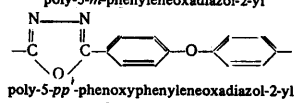
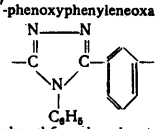
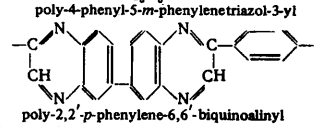
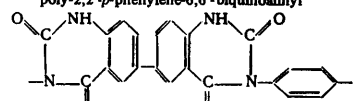
Starting materials		Chain unit and polymer	°C	Ref.
dicarboxylic acid or derivative	second component			
Diphenyl terephthalate	benzene-1,2,4,5-tetra-amine	 poly-2,6-*p*-phenylenedi-imidazobenzene	500	50
Diphenyl isophthalate	benzene-1,2,4,5-tetra-amine	 poly-2,6-*m*-phenylenedi-imidazobenzene	500	50
Diphenyl terephthalate	biphenyl-3,3′,4,4′-tetra-amine	 poly-2,2′-*p*-phenylene-5,5′-bibenzimidazolyl	550	50
Diphenyl isophthalate	biphenyl-3,3′,4,4′-tetra-amine	 poly-2,2′-*m*-phenylene-5,5′-bibenzimidazolyl	550	50
Diphenyl	diphenylmethane-3,3′,4,4′-tetra-amine	 poly-2,2′-*m*-phenylene-5,5′-dibenzimidazolylmethane	490	51
Diphenyl isophthalate	2,2′-dimethylbiphenyl-3,3′,4,4′-tetra-amine	 poly-4,4′-dimethyl-2,2′-*m*-phenylene-5,5′-bibenzimidazolyl	490	52
Diphenyl isophthalate	2,2′-dimethyldiphenyl-methane-3,3′,4,4′-tetra-amine	 poly-4,4′-dimethyl-*m*-phenylene-5,5′-dibenzimidazolylmethane	400	52
Diphenyl isophthalate	4,4′-diaminobiphenyl-3,3′-diol	 poly-2,2′-*m*-phenylene-6,6′-bibenzoxazolyl	500	53

Table 9. (cont'd).

Starting materials: dicarboxylic acid or derivative	Starting materials: second component	Chain unit and polymer	°C	Ref.
Diphenyl isophthalate	3′,3″-diamino-2,2-diphenylpropane-4′,4″-diol	 poly-2′,2″-*m*-phenylene-2,2-dibenzoxazol-5′,5″-ylpropane	500	54
Pyromellitic anhydride	phenoxybenzene-*pp*′-diamine	 poly-*pp*′-phenoxyphenylpyromellitimide	450	55
Pyromellitic anhydride	*p*-diphenoxybenzene-*p*′*p*″-diamine	 poly-*p*-diphenoxybenzene-*p*′*p*″-pyromellitimide	—	56
Pyromellitic anhydride	anilinephthalein	 polydiphenylphthalide-*pp*′-pyromellitimide	450	57
Pyromellitic anhydride	biphenylylene-*pp*′-di hydrazine	 poly-*N*-*p*-benzidinopyromellitimide	400	58
Diphenyl isophthalate	4,4′-diaminobiphenyl-3,3′-dithiol	 poly-2,2′-*m*-phenylene-6,6′-bibenzothiazolyl	550	59—61
Pyromellitic anhydride	benzene-1,2,4,5-tetra-amine	 polybenzimidazopyrrone	450	62
p-Bisdiazoxylene	*p*-diethynylbenzene	 poly-5-*p*-phenylenepyrazol-3-yl	550	63
Terephthaloyl chloride	terephthalodihydrazide	 poly-5-*p*-phenyleneoxadiazol-2-yl	400	64
Isophthaloyl chloride	isophthalodihydrazide	 poly-5-*m*-phenyleneoxadiazol-2-yl	400	64
Phenoxybenzene-*pp*′-dicarbonyl chloride	phenoxybenzene-*pp*′-dicarbohydrazide	 poly-5-*pp*′-phenoxyphenyleneoxadiazol-2-yl	430	65
Polyisophthalohydrazide	aniline	 poly-4-phenyl-5-*m*-phenylenetriazol-3-yl	450	66
p-Diglyoxyloylbenzene	biphenyl-3,3′,4,4′-tetra-amine	 poly-2,2′-*p*-phenylene-6,6′-biquinoalinyl	470	67
Benzidine-3,3′-dicarboxylic acid	*p*-phenylene di-isocyanate	 poly-1,1′,2,2′,3,3′,4,4′-octahydro-2,2′,4,4′-tetraoxo-3,3′-*p*-phenylene-6,6′-biquinazolinyl	540	68

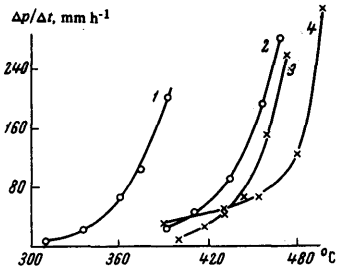


Figure 15. Temperature variation in rate of decomposition, determined from pressure of gases evolved[41], of aromatic polyamides: *1*) poly-*m*-phenyleneisophthalamide; *2*) poly-*m*-phenyleneterephthalamide; *3*) poly-*p*-phenyleneisophthalamide; *4*) poly-*p*-phenyleneterephthalamide.

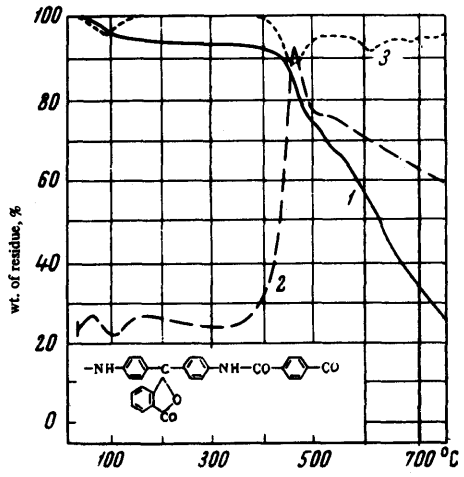


Figure 16. Thermal analysis (heated in nitrogen at 3.7 deg min^{-1})[47] of polyamide obtained from anilinephthalein and terephthalic acid: *1*) dynamic thermogravimetric analysis; *2*) differential thermal analysis; *3*) differential thermogravimetric analysis.

The products obtained by the polycondensation of tetraamines with anhydrides of tetracarboxylic acids are more thermostable. Fig. 18 illustrates the results of a thermogravimetric analysis of two polybenzimidazoimides (pyrrones) prepared from pyromellitic anhydride; they have a ladder structure and are distinguished by great thermal stability.

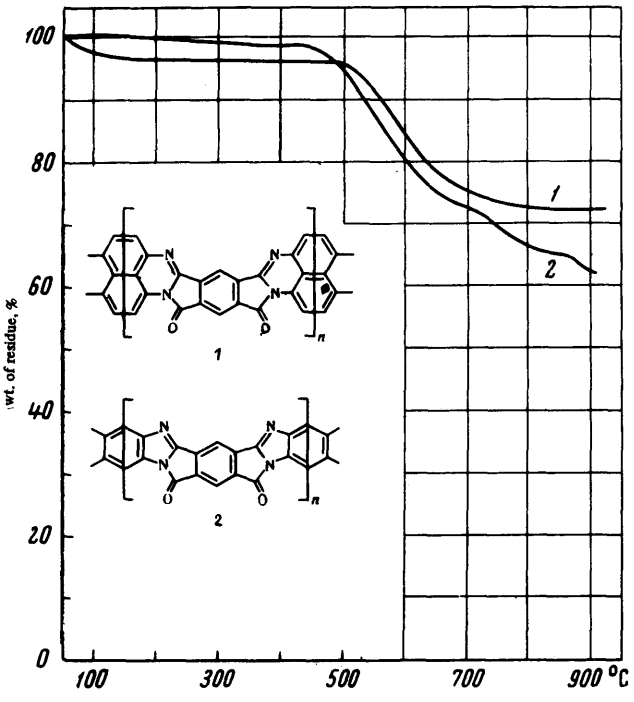


Figure 18. Dynamic thermogravimetric analysis of polybenzimidazoimides[62] (heated in nitrogen at 6 deg min^{-1}).

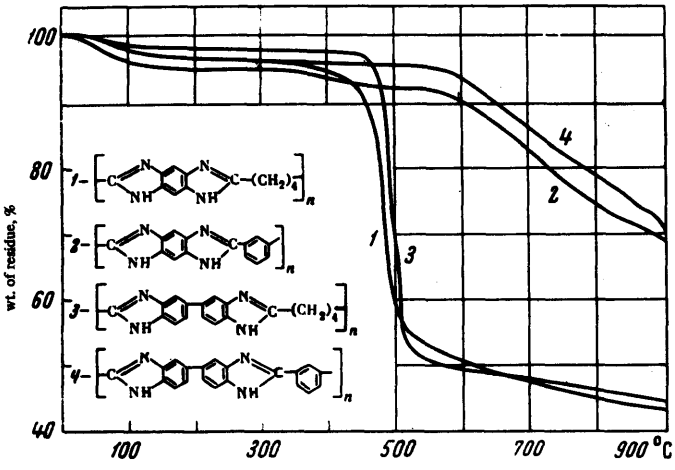


Figure 17. Dynamic thermogravimetric analysis of polybenzimidazoles[50] (heated in nitrogen at 2.5 deg min^{-1}).

Polyimides also constitute an extremely thermostable class of polymers. Thus thermogravimetric analysis of four polypyromellitimides shows (Fig. 19) that a polymer containing a biphenylylene group is the most thermostable, polymers containing a *m*-phenylene or a diphenylene oxide group are not quite so good, and the most unstable is the polymer containing a diphenylenemethane group. Soluble polypyromellitimides obtained from anilinephthalein and diaminodiphenylfluorene are extremely thermostable (Fig. 20). Results of a dynamic thermogravimetric analysis of a polyimide and of several vinyl polymers are illustrated in Fig. 21.

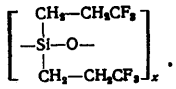
Fig. 22 gives for comparison results of a thermogravimetric analysis of polyquinoxaline, polybenzoxazole, and polyoxadiazole. Curves for polyquinazolinediones—representatives of a new class of thermostable polymers—are given in Fig. 23.

In a large group of thermostable polymers other elements accompany carbon in the chain of the macromolecule. The most interesting are polymers containing silicon, boron, phosphorus, and various metals. The chief factor determining the thermal stability of these polymers is the energy of the bond between atoms in the main chain

and those surrounding it. A characteristic feature of polydiphenylsilanes is their tendency to oxidise when heated in the air to 300°C. As a consequence, the weight of a specimen increases, as shown in Fig. 24.

Fig. 25 gives thermogravimetric curves for a series of organosilicon polymers. The thermal stability of polysiloxanes containing aromatic radicals is higher than that of those containing aliphatic radicals. The introduction of phenylene groups into the main chain produces an especially marked increase in thermal stability, as occurs with silaphenylene polymers.

Polyfluoroalkylsiloxanes are also characterised by enhanced thermal stability, but both this and their hydrolytic stability depend on the position of the fluorine relative to the silicon, as is evident from Table 10.[71] The most thermostable were polyfluoroalkylsiloxanes containing fluorine atoms in the γ-position relative to the C–Si bond, and having the structure



A large number of organoboron polymers are known, containing B–C, B–N, and other bonds[73]. However, very few data are at present available on their thermal stability. Thermogravimetric analysis of a polybenzoborimidazoline and of a polybenzimidazole containing phosphorus shows

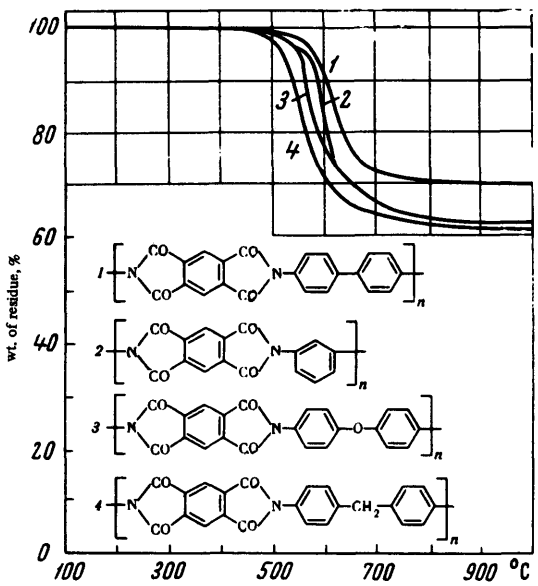


Figure 19. Dynamic thermogravimetric analysis of polypyromellitimides[70] (heated in dry helium at 3 deg min^{-1}).

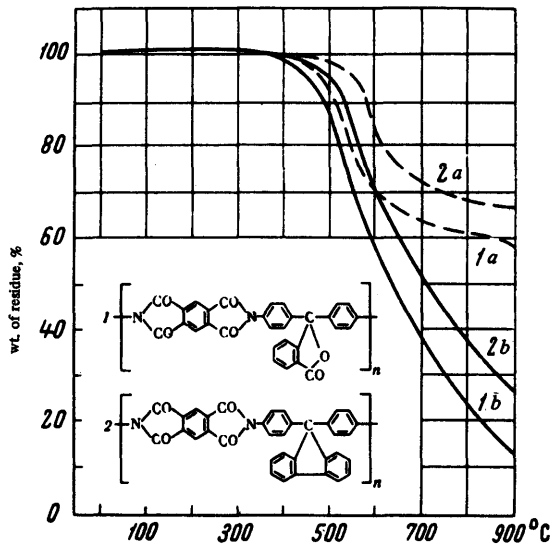


Figure 20. Dynamic thermogravimetric analysis of polypyromellitimides prepared from:
1) anilinephthalein; *2*) 9,9-diphenylfluorene-*pp'*-diamine[57]. Heated at 5 deg min^{-1}: *a*) helium; *b*) air.

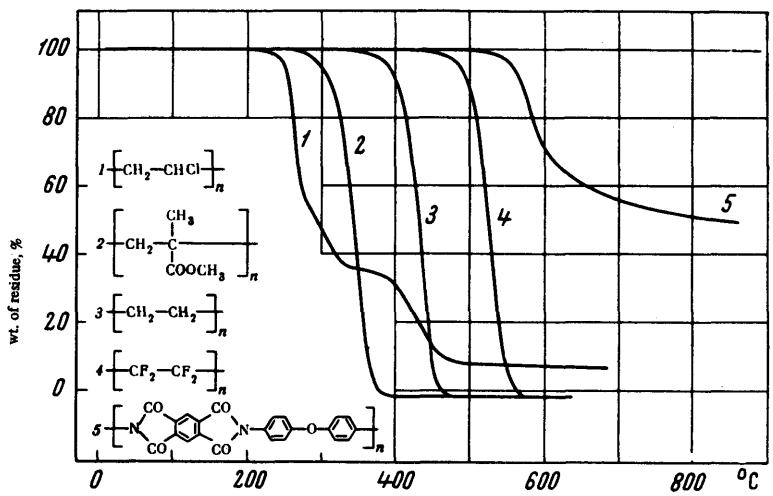


Figure 21. Dynamic thermogravimetric analysis of polymers in nitrogen (rate of heating 5 deg min^{-1})[69].

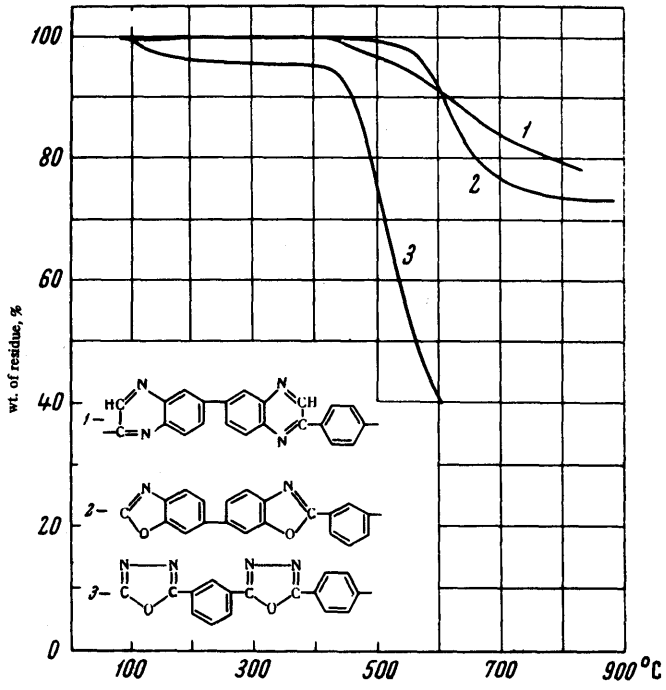


Figure 22. Dynamic thermogravimetric analysis (in nitrogen) of the polymers:
1) poly-2,2′-*p*-phenylene-6,6′-biquinoxalinyl; *2*) poly-2,2′-*m*-phenylene-6,6′-bibenzoxazolyl; *3*) poly-5-*m*-phenyleneoxadiazol-2-yl-5′-*p*-phenyleneoxadiazol-2′-yl.

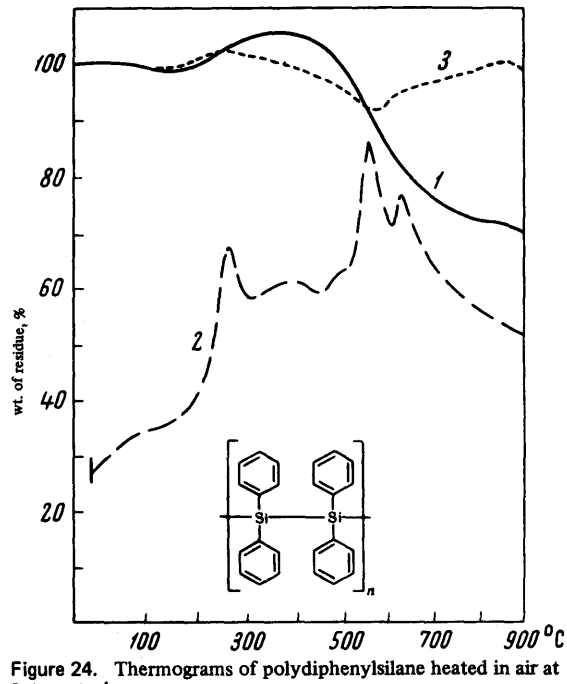


Figure 24. Thermograms of polydiphenylsilane heated in air at 9 deg min^{-1}:
1) dynamic thermogravimetric analysis; *2*) differential thermal analysis; *3*) differential thermogravimetric analysis.

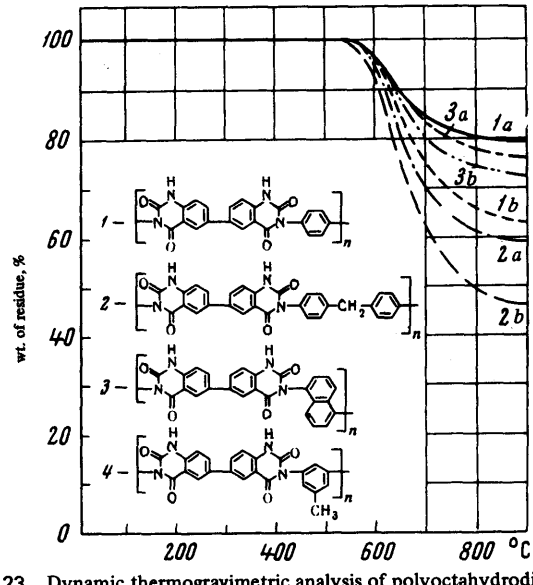


Figure 23. Dynamic thermogravimetric analysis of polyoctahydrodioxobiquinazolinyls[68] heated at 6 deg min^{-1} in:
a) nitrogen; *b*) air.

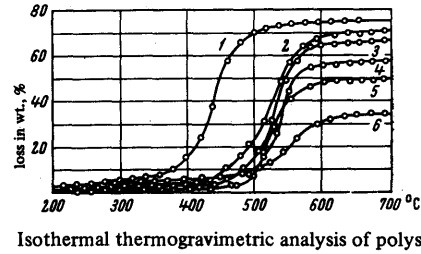
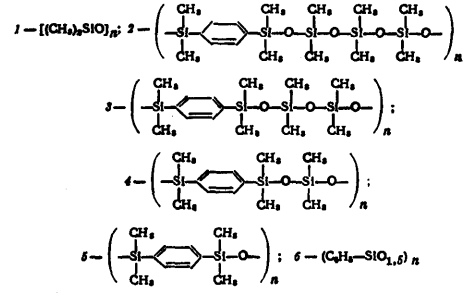


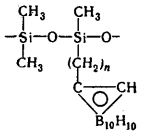
Figure 25. Isothermal thermogravimetric analysis of polysiloxanes[72]:



(Fig. 26) that the thermal stability of the benzoborimidazoline ring is lower than that of the imidazole ring.

Polymers containing carborane (barene) residues in the chain unit are extremely interesting[74]. Introduction of a carborane residue into a polymer molecule produces a considerable increase in thermal stability. Thus polyesters, polyamides, and other polymers obtained from dicarboxylic acids containing carborane ring systems are distinguished by exceptionally high thermal stability. The introduction of a carborane system into polysiloxanes produces

polycarboranesiloxanes having the structure



which show considerably better thermal stability than does polydimethylsiloxane[75]. Equally high thermal stability is characteristic of the polycarboranebenzimidazole

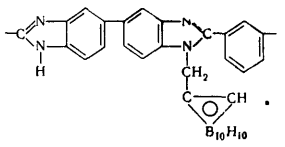


Table 10. Thermochemical and chemical stability of polyfluoroalkylsiloxanes[71].

Chain unit	Thermal stability on heating in sealed tube for 6 h: temp., °C	Thermal stability on heating in sealed tube for 6 h: polymer decomposed, %	Resistance to hydrolysis by 10% aq. NaOH 20°C
[—Si(CF$_2$CHF$_2$)—O$_{1,5}$]$_n$	172	8	Si–C bond ruptured
	240	67	
[—Si(CH$_2$CHF$_2$)—O$_{1,5}$]$_n$	170	14	ditto
	220	75	
[—Si(CH$_2$CH$_2$CF$_3$)—O$_{1,5}$]$_n$	450	4	stable
	500	80	

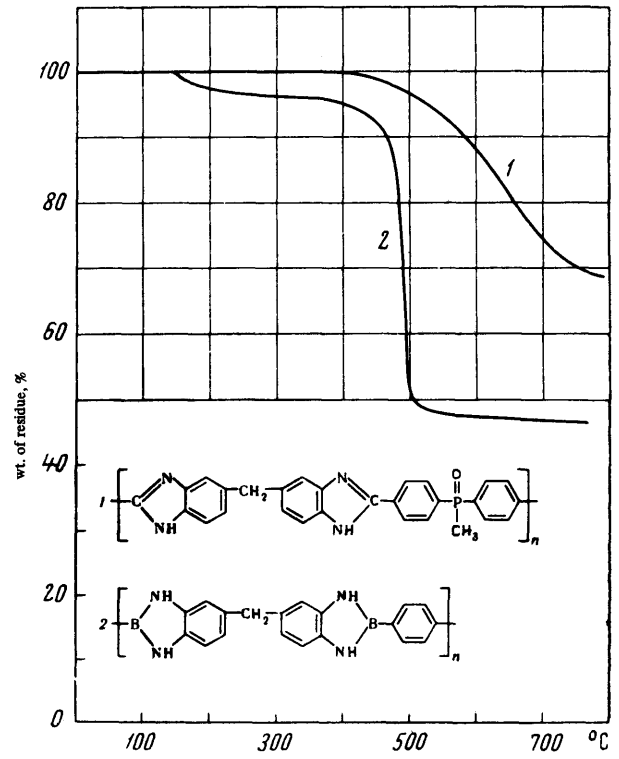


Figure 26. Dynamic thermogravimetric analysis (in nitrogen) of organoelementary polymers containing boron and phosphorus[77].

It surpasses the analogous unsubstituted polybenzimidazole in thermal stability, and when heated in the air to 900°C it loses only 25% of its original weight[76].

Very few phosphorus-containing polymers are characterised by high thermal stability. Among them are poly(phosphonitrile chloride) [PCl$_2$=N]$_n$ and PON polymers.

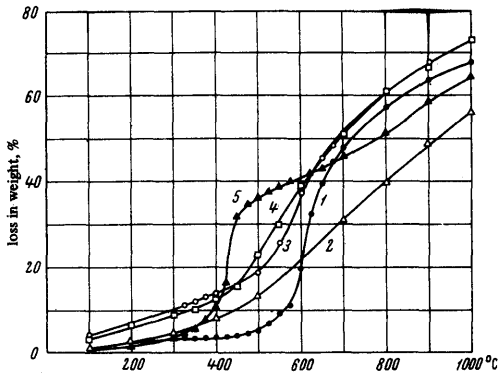


Figure 27. Relative thermal stability (determined by isothermal thermogravimetric analysis) of coordination polymers of bis-8-hydroxyquinol-6-ylmethane with the metals:
1) zinc; *2*) manganese; *3*) cobalt; *4*) nickel; *5*) copper.

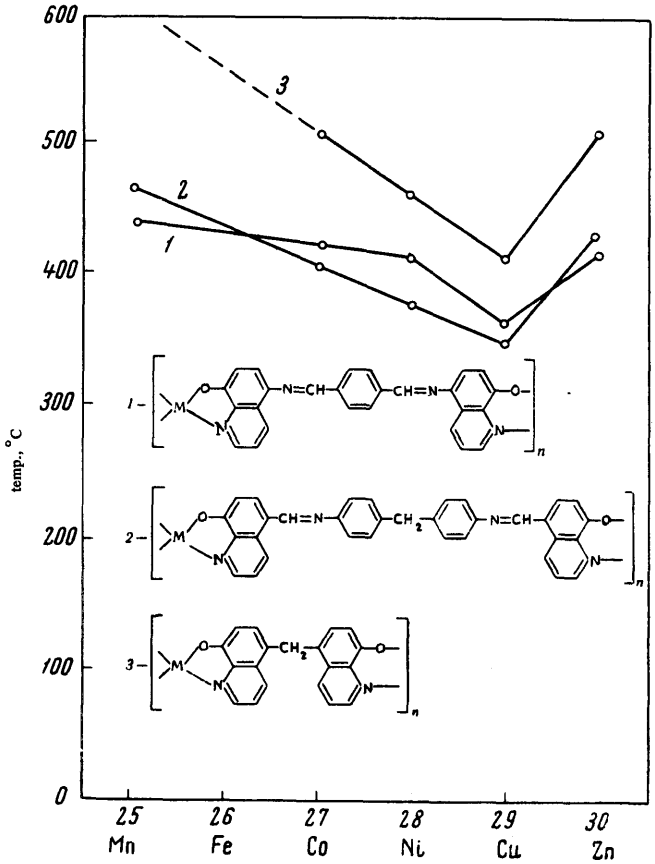
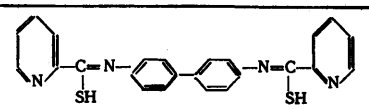
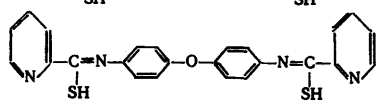
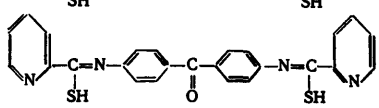
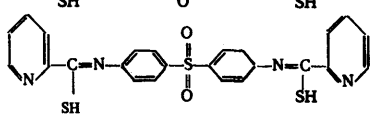


Figure 28. Dependence of decomposition temperature (thermal stability) of coordination polymers on atomic number of metal[79].

Table 11. Thermal stability of some coordination polymers[80].

Ligand	Metal	Loss in weight, %, at the temperatures (°C)								
		220	250	270	290	310	340	370	390	420
	Cu^{II}	2	1	1	decomp.	—	—	—	—	—
	Ni^{II}	0.3	0,1	0	0	0,2	6	decomp.	—	—
	Zn^{II}	0	0	0	0	0	0	0.5	0.2	decomp.
	Cu^{II}	0	0	2	2	3	decomp.	—	—	—
	Ni^{II}	0	0	0	0	0	0.5	3	decomp.	—
	Zn^{II}	0	0	0	0	0	0	0.5	3	decomp.
	Cu^{II}	0	0	0	0	2	decomp.	—	—	—
	Ni^{II}	0	0	0	0	2	decomp.	—	—	—
	Zn^{II}	0	0	0	0	0	0	0	0	decomp.
	Cu^{II}	0	0	0	1	3	decomp.	—	—	—
	Ni^{II}	0	0	0	3	0	decomp.	—	—	—
	Zn^{II}	0	0	0	0	0	0.2	0.3	0	decomp.

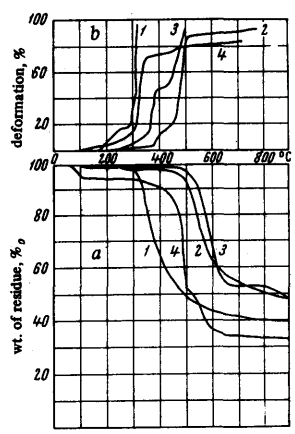


Figure 29. Thermal analysis[82]:
a) dynamic thermogravimetric analysis (heated in nitrogen at 4 deg min^{-1});
b) thermomechanical analysis of polydiphenylphosphinates of:
1) copper; *2*) zinc; *3*) cobalt; *4*) nickel.

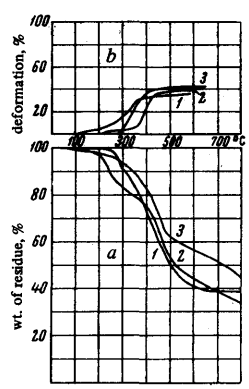


Figure 30. Thermal analysis of chromium polyphosphinates[83]:
a) dynamic thermogravimetric analysis (heated in air at 20 deg min^{-1});
b) thermomechanical analysis (with load of 100 g on tool of diameter 4 mm, heated in air at 70 deg h^{-1}):
1) polydiphenylphosphinate; *2*) poly-2,8-dimethylphenoxaphosphinate;
3) copolymer of equimolecular quantities of the two phosphinates.

Metal-containing polymers, especially inner-complex (chelate) polymers, are distinguished by high thermal stability. Inoy[78] determined the thermal stability of a series of coordination polymers of zinc, copper, nickel, cobalt, and manganese with bis-8-hydroxyquinol-5-ylmethane (Fig. 27). The dependence of the decomposition temperature (thermal stability) of several coordination polymers on the atomic number of the metal is shown in Fig. 28: the thermal stability of these polymers falls in the sequence Mn > Fe > Co > Zn > Ni > Cu. As is evident from Table 11, zinc gives the most thermostable coordination polymers, and copper the least stable[80].

The zinc complexes of salicylideneimines have also been shown to be the most stable[81]. This can be explained by the electronic structure of the bivalent ion of zinc, which possesses only one state of oxidation. Other transition metals can be oxidised to higher valencies, and this may catalyse processes of thermal decomposition.

The replacement of organic ligands by phosphinic acids enables coordination polymers to be obtained having an inorganic main chain. Such polymers are also characterised by high thermal stability, as is shown (Fig. 29) by thermomechanical and thermogravimetric analyses of copper, zinc, cobalt, and nickel polydiphenylphosphinates[82]. The nature of the metal ion plays an important part here. Cobalt polyphosphinate proved to be the most thermostable. The nature of the ligands is also significant, as is seen from Fig. 30, which illustrates the results of a dynamic thermogravimetric analysis of three chromium polyphosphinates[83]. The polydiphenylphosphinates proved to be more thermostable than the poly-2,8-dimethylphenoxaphosphinates.

IV. DEPENDENCE OF THERMAL STABILITY ON STRUCTURE OF MACROMOLECULE

As we have seen from many examples, the structure of the chain unit in the macromolecule plays an immense part in determining the thermal stability of the polymer. However, besides the structure of the monomer unit, various structural features of the macromolecule itself often play a no less fundamental part in determining the thermal stability. Among such factors are regularity of structure of the macromolecule, isomerism of substitution in the ring, the presence of cross-links between macromolecules, and also the molecular weight. Below we shall examine one by one the effect of these structural features on the thermal stability of polymers.

1. Dependence of Thermal Stability on Regularity of Structure of Macromolecule

The chain units in a macromolecule can be arranged in two ways—"head to tail" $-CH_2.CHX.CH_2.CHX-$ or "head to head" $-CH_2.CHX.CHX.CH_2-$.

Vinyl polymers are usually built up in the first way, "head to tail". The content of units arranged in the second way is minute (1–2%). However, even a small number of units joined "head to head" may substantially affect the properties of the polymer, in particular its thermal stability.

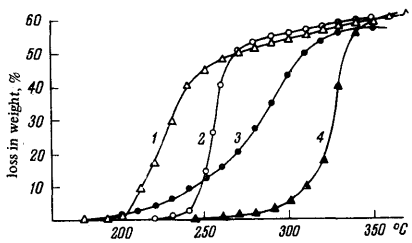
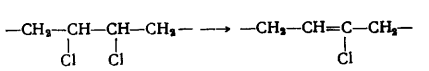


Figure 31. Isothermal thermogravimetric analysis of poly(vinyl chlorides) and poly(vinylidene chlorides) of various types[84].
1) poly(vinylidene chloride) of "head to tail" structure; *2*) poly(vinyl chloride) of "head to tail" structure; *3*) poly(vinyl chloride) of "head to head" structure; *4*) poly(vinylidene chloride) of "head to head" structure.

Murayama and Amagi[84] investigated the thermal breakdown of poly(vinyl chloride) and poly(vinylidene chloride) having head-to-head and head-to-tail structures. Fig. 31 shows that polymers having the latter type of arrangement begin to decompose at a great rate, and their decomposition extends as far as complete elimination of hydrogen chloride. In contrast to this, polymers with the head-to-head construction break down at a lower rate. The explanation is that, although the first stage occurs more easily owing to the lower stability of the head-to-head structure, the second stage occurs more slowly owing to formation of a chloroprene-like structure containing halogen attached to double-bonded carbon:



In this case there is no opportunity for a chain dehydrochlorination reaction to develop along the macromolecule.

2. Effect of Isomerism of Substitution in the Aromatic Ring

Polymers containing aromatic or heterocyclic rings in the chain differ substantially in thermal stability according to the relative arrangement of substituents in the ring.

Table 12 shows that polymers containing *para*-substituted rings are the most thermostable. Polymers containing the *meta*-isomers are less stable, as has been established with polyphenylenes, polyamides, and polybenzoxazoles. Derivatives of terephthalic acid surpass the corresponding derivatives of isophthalic acid in thermal stability.

In the case of aromatic heterocycles the relative arrangement of the heteroatoms also plays a significant part. Thus poly-1,2,4-oxadiazoles are less thermostable than are poly-1,3,4-oxadiazoles.

3. Effect of Lateral Groups and Branching

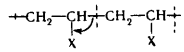
The presence of lateral groups and of branching in a macromolecule always leads to diminished thermal stability of the polymers. This principle is confirmed by comparing the relative thermal stabilities (T_h) of a series of polymers containing these structural features (Table 5).

The thermal stability of polyethylene (19)†, which is a branched-chain variety of polymethylene, is lower than that of the straight-chain polymer (22). The introduction of side-groups into every chain unit in the polymer lowers the thermal stability still more, as can be seen from the examples of polypropylene (16) and polyisobutylene (12). The same situation is observed on comparing poly(methyl acrylate) (10) with poly(methyl methacrylate) (3): the latter is inferior to the former in thermal stability.

A similar variation occurs in the perfluorocarbons, as is seen from the examples of polytetrafluoroethylene (25), polyperfluoropropylene (6), and polyperfluoroheptene (1). In this case the thermal stability also falls in the presence of side-groups, not only their presence but also their nature being significant: the larger the lateral group, the lower the thermal stability. Thus polyperfluoroheptene (T_h = 248°C) is less thermostable than is polyperfluoropropylene (297°C).

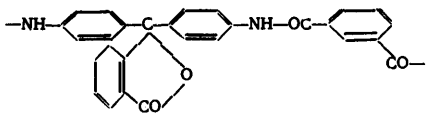
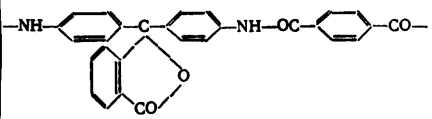
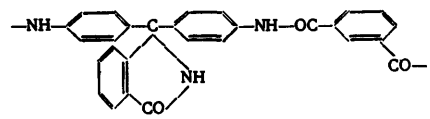
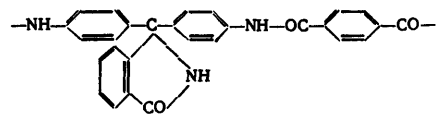
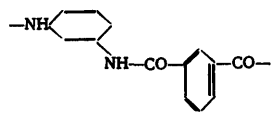
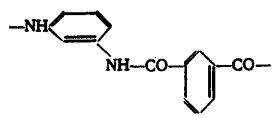
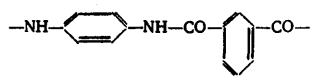
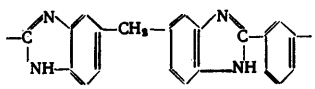
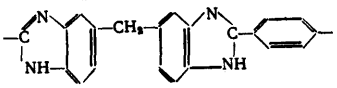
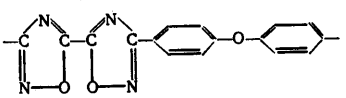
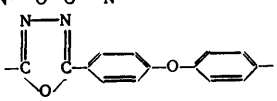
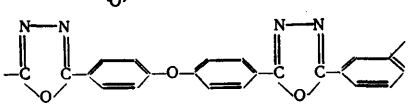
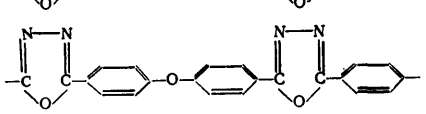
Substituents in the macromolecules of polyethers have an analogous effect: poly(propylene oxide) is less thermostable than is poly(ethylene oxide) (295° and 345°C respectively).

The presence of substituents in phenylene groups also lowers the thermal stability of polymers, as has been shown in the case of substituted poly-*p*-phenylene-ethylenes[17]. Thus polytetramethyl-*p*-phenylene-ethylene and poly-2,5-dimethoxy-*p*-phenylene-ethylene (265° and 375°C) are inferior in thermal stability to poly-*p*-phenylene-ethylene (430°C). In this case the number of substituents is also important. Thus the general rule can be formulated that the more substituents are present in a chain unit the lower is the thermal stability of the polymer. In the case of vinyl polymers this is because side-groups weaken the bonds between the chain units in the macromolecule, which facilitates their breakdown with the formation of monomer:



† The parentheses indicate the numbering of the polymers in Table 5.

Table 12. Thermal stability of isomeric polymers containing rings in the chain.

Polymer	Chain unit	Temp., °C	Ref.
Poly-*p*-phenylene		650*	17
Poly-*m*-phenylene		540*	17
Polyaniline-phthaleiniso-phthalamide		420**	85
Polyaniline-phthaleintere-phthalamide		450**	85
Polyaniline-imidophthalein-isophthalamide		420**	85
Polyanilineimido-phthaleintere-phthalamide		440**	85
Poly-*m*-phenyl-eneisophthal-amide***		330**	41
Poly-*m*-phenyl-eneisophthal-amide***		390**	41
Poly-*p*-phenyl-eneterephthal--amide***		410**	41
Poly-2,2′-*m*-phenylene-5,5′--dibenzimida-zolylmethane		490**	86
Poly-2,2′-*p*-phenylene-5,5′-dibenzimida-zolylmethane		500**	86
Poly-3,3′-*pp*′-phenoxyphenyl-ene-5,5′-bi-1,2,4,--oxadiazolyl		300**	87
Poly-2,5-*pp*′-phenoxyphenyl-ene-1,3,4-oxa-diazole		430**	65
Poly-5-*m*-phenyl-ene-1,3,4-oxa-diazol-2-yl-5′--*pp*′-phenoxy-phenylene-1′,3′,,4′-oxadiazol-2′-yl		380**	88
Poly-5-*m*-phenyl-ene-1,3,4-oxa-diazol-2-yl-5′--*p*′*p*″-phenoxy-phenylene-1,′3′,4′-oxadia-zol-2′-yl		430**	88

* Temperature at which a specimen loses half its weight during 2 h.
** Temperature of start of loss in weight on thermogravimetric curve.
*** Some of this information is obviously incorrect (Ed. of Translation).

4. Dependence of Thermal Stability on Degree of Cross-linking of Polymer

All the relations which we have considered hitherto have applied to linear macromolecules. However, there are also other structures, as is evident from Fig. 32. Linear chains may consist of (*a*) rings of spiran structure, or two linear polymer chains may be joined by cross-links, as in the case of (*b*) ladder polymers. Polymer chains joined to two adjacent chains in the same plane form (*c*) parquet structures, and finally chains joined to a large number of macromolecules arranged in all three directions form (*d*) spatially cross-linked three-dimensional structures. For the most part, bond formation between macromolecules leads in all the above cases to an increase in their thermal stability compared with that of the corresponding linear structure. Tessler[89] made a theoretical calculation showing that ladderlike structures form smaller quantities of volatile products during a given time than do analogous simple polymers.

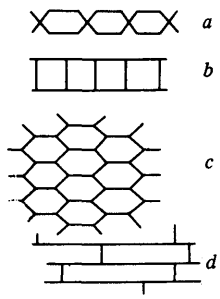


Figure 32. Various forms of macromolecules:
a) spiran; *b*) ladderlike; *c*) parquet; *d*) three-dimensional cross-linked.

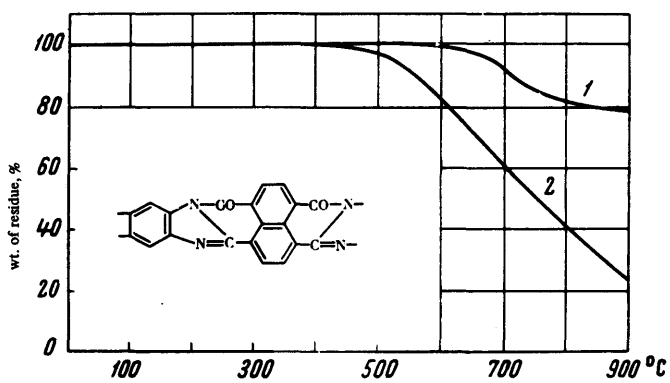


Figure 33. Dynamic thermogravimetric analysis (rate of heating 2.5 deg min^{-1}) of pyrrones[90] in:
1) nitrogen; *2*) air.

A dynamic thermogravimetric analysis of pyrrones shows (Fig. 33) that these ladderlike polymers have extremely high thermal stability. Such parquet structures as graphite, as well as porphyrin polymers, are characterised by exceptionally high thermal stability.

Cross-linked polymers have higher thermal stability because the introduction of cross-links increases the chemical stability of the polymers. A fundamental difference exists between the effect, on the properties of polymers, of interchain forces of interaction (both dipole forces and hydrogen bonds) and valency bridges: the former are strongly dependent on temperature, rapidly becoming weaker as the temperature rises, whereas the latter are independent of variation in temperature over a wide range.

Table 13. Temperature of half-decomposition T_h of styrene copolymers.

Content in copolymer, %			T_h, °C
styrene	divinylbenzene	trivinylbenzene	
100	0	0	364
98	2	0	365
75	25	0	373
75	0	25	393
0	100	0	399
44.2	55.8	0	401
0	0	100	462

Table 13 gives values of the thermal stability (T_h) for cross-linked copolymers of styrene with divinylbenzene and trivinylbenzene as a function of the frequency of cross-linking. Thus the cross-linking of chains has a considerable effect in raising the thermal stability, as is evident from the examples of polystyrene, polydivinylbenzene, and polytrivinylbenzene (364°, 399°, and 462°C respectively)[91-93].

This fact is illustrated by the thermogravimetric curves (Fig. 34) for polymers of divinylbenzene and trivinylbenzene and their copolymers with styrene. It is seen that the losses in weight of the trivinylbenzene polymers are smaller than those of the divinylbenzene polymers. The latter losses are in turn smaller than those of polystyrene. Fig. 35 shows comparative curves for the thermal stability of cross-linked polytrivinylbenzene and for several other polymers[92].

The strongly cross-linked polymer of 1,3,5-triacryloylhexahydro-1,3,5-triazine is a thermostable substance, decomposing at ~ 400°C.[94]

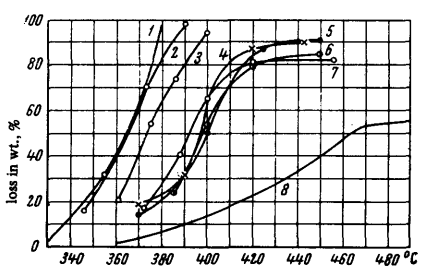


Figure 34. Relative thermal stability of polymers and their copolymers with styrene determined by isothermal thermogravimetric analysis[92,93]:
1) polystyrene; *2*) copolymer of styrene with 2% of divinylbenzene; *3*) copolymer of styrene with 25% of divinylbenzene; *4*) copolymer of styrene with 48% of divinylbenzene; *5*) copolymer of styrene with 55% of divinylbenzene; *6*) polydivinylbenzene; *7*) copolymer of styrene with 25% of trivinylbenzene; *8*) polytrivinylbenzene.

A marked improvement in thermal stability results from the formation of cross-links in polyarylates containing free hydroxyls in their macromolecule. Fig. 36 shows that a more thermostable polymer is formed by cross-linking such a polyarylate by means of maleic anhydride[95].

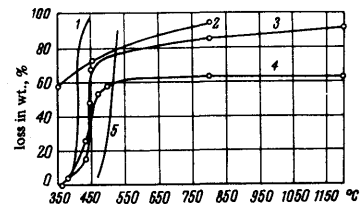


Figure 35. Relative thermal stability of polymers determined by isothermal thermogravimetric analysis[92]:
1) polymethylene; *2*) polyacrylonitrile; *3*) poly(vinylidene fluoride); *4*) polytrivinylbenzene; *5*) polytetrafluoroethylene.

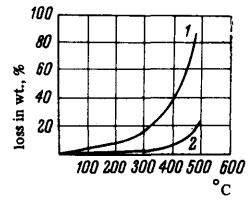


Figure 36. Thermogravimetric curves of polyarylates[95]:
1) original polyarylate D-5; *2*) polyarylate D-5 cross-linked with 15% of maleic anhydride.

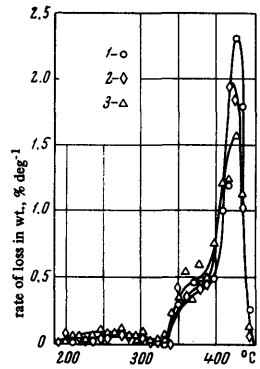
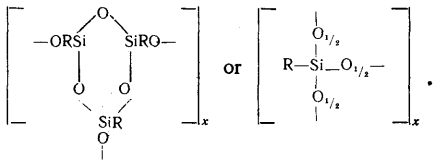


Figure 37. Differential thermogravimetric analysis of polyethylene exposed in air to different doses (Mrad) of radiation[96]:
1) 0; *2*) 5.2; *3*) 55.

The irradiation of polymers is a general method for cross-linking them and improving their thermal stability. Fig. 37 shows curves for the differential thermogravimetric analysis of polyethylene exposed in air to different doses of radiation[96]. It is seen that the thermal stability of the polymer increases with increase in the dose.

Andrianov[15] observed a marked increase in thermal stability as a result of the cross-linking of polyorganosiloxanes containing rings or irregular cross-links of the type

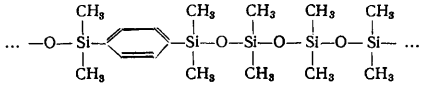


In this case the detachment of a chain unit or a large portion of the polymer molecule involves breaking the latter at three points, since the polymer contains cross-linked molecules. This is associated with the destruction of two or three energetically stable Si–O bonds. In polyorganosiloxanes containing three-dimensional bonds, therefore, no degradation of the molecular chains at a silicon–oxygen bond is observed even at 550°C, independently of the nature of the organic radical.

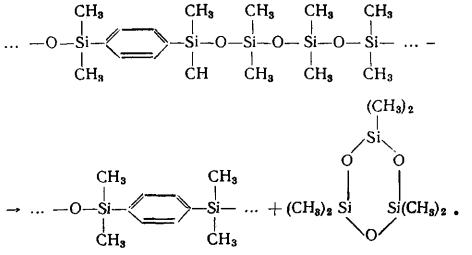
5. Effect of Copolymerisation

Copolymerisation or copolycondensation results in the formation of copolymers containing different types of unit in a chain. The presence of units differing in structure often presents difficulties in the detachment of molecules during thermal degradation.

A clear example of such improvement in thermal stability resulting from copolymerisation is provided by silaphenylene–siloxane copolymers having the structure



When such a polymer undergoes thermal breakdown, six-membered rings are split off:



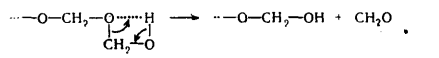
This process extends along that part of the chain which consists of dimethylsiloxane units. When a silaphenylene group is reached, however, ring formation becomes impossible, and degradation ceases. Therefore the thermal stability of such copolymers is considerably higher than that of polydimethylsiloxanes (temperatures at which breakdown begins 450° and 350°C respectively).

An analogous improvement in thermal stability is observed in copolymers of formaldehyde with cyclic oxides or acetals[97]. Polyformaldehyde itself already decomposes at 170°C, whereas its copolymers are stable up to 200°C.

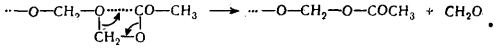
6. Effect of Other Structural Features on Thermal Stability

Several structural features of polymers, other than those which we have discussed, affect their thermal stability. We must first note the part played by end-groups.

It has been shown in the case of polyformaldehyde that its thermal stability depends on the nature of the terminal groups. Thus ordinary polyformaldehyde, having hydroxyls at the ends of the macromolecules, begins to decompose at about 170°C.[98] Acetylation yields a stabilised polyformaldehyde containing acetyl groups at the ends of the chain. The breakdown of polyformaldehyde takes place by a chain mechanism, beginning at the end-groups:



Acetylation changes the nature of the terminal group, and depolymerisation proceeds according to the equation



The acetyl group, being heavier and less mobile, requires more energy for its transfer, and therefore such acetylated polyformaldehyde decomposes at a higher temperature (200°C). Fig. 38 illustrates the results of a thermogravimetric analysis of polyformaldehyde in a vacuum, showing the higher thermal stability of acetylated polyformaldehyde[99].

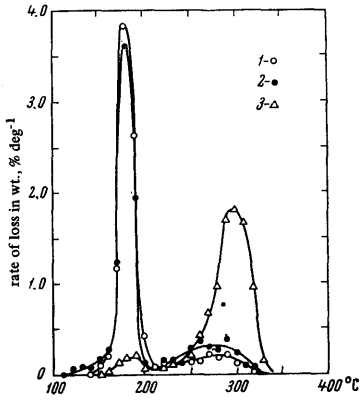


Figure 38. Differential thermogravimetric analysis of polyformaldehyde heated in a vacuum at different rates (deg min^{-1})[99]: *1*) polyformaldehyde (1); *2*) polyformaldehyde (0.5); *3*) acetylated polyformaldehyde (1).

In some cases the glass point and the thermal stability of polymers are also interrelated. If the glass point lies far below the temperature of decomposition, no relationship between them is observed, and the thermal stability is determined by the energies of the interatomic bonds. If, however, the glass point lies above or near the decomposition point, there is a clear relation between them: in these cases thermal breakdown is usually considerably accelerated after transition through the glass point.

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The data given above show that we are now aware of several relations linking the thermal stability of polymers with their chemical structure. Among a number of structural features having general significance and producing high thermal stability in polymers the most important are

high interatomic bond energies, the presence of stable aromatic and other groupings in the chain unit, the presence of intermolecular bonds, ladderlike, and other cross-linked structures.

High energy of the bonds between chain units, as also within a unit and with surrounding groups, constitutes an important factor determining the thermal stability of a polymer. It makes difficult the formation of free radicals, by either thermal or thermo-oxidative mechanisms, and prevents the occurrence of chain reactions of thermal and oxidative degradation. An effective way of producing thermostable structures is to introduce aromatic carbocycles and heterocycles, as well as carborane, ferrocene, and other stable groups. Improvement in the thermal stability parallels the increased content of aromatic rings in the chain. Decreasing the content of aliphatic groups, both in the chain and in side-groups, and increasing the content of aromatic rings in the polymer are of fundamental value. The thermal stability is improved in all cases on passing to ladderlike, parquet, and three-dimensional cross-linked structures, this being due to the diminished opportunities for the formation of volatile pyrolysis fragments. One way of improving the thermal stability of vinyl, oxide, and other linear polymers is to diminish their capacity for depolymerisation, this being accomplished by introducing large end-groups and by copolymerisation with monomers giving stable chain units, incapable of easy detachment as monomeric molecules.

An important way of improving thermal stability is to introduce, into the composition of the polymer, groups which are able to increase its resistance to oxidation or pyrolysis, as occurs in the case of "self-protective" polymers. The incorporation of groups which prevent oxidation or pyrolysis by combining with the free radicals formed and thus terminating the chain processes of decomposition considerably enhances the thermal stability of polymers. Such protective groups are sometimes formed in the course of chemical rearrangement of the polymer, but far more often they are introduced as "external" additives (stabilisers, antioxidants, etc.), which is a very widely used technical procedure for improving stability during the processing of polymers.

As is evident from the data which have been discussed, several relations have already been established linking the structure of polymers with their thermal stability. The task for future research is to refine these relations, so that they can be used still more widely for the consciously controlled synthesis of thermostable polymers.

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