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Chemical Defects in Macromolecules of Heterounit Polymers

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This review discusses reasons for the appearance of chemical faults in macromolecules during the preparation of polymers by addition polymerisation or polycondensation and as a result of substitution, oxidation, and other reactions of polymers. The presence of anomalous monomer units in chemically imperfect macromolecules leads to the formation of heterounit polymers, and their presence in the latter exerts a great influence on the chemical and physical properties of the polymers. A list of 198 references is included.

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I. CHEMICAL DEFECTIVENESS OF MACROMOLECULES

The dependence of the properties of polymers on their structure is one of the most important problems of polymer science, to whose solution a large number of investigators—both chemists and physicists—have directed their efforts. The Reviewer has adduced many examples of quite clear relations between structure and such properties of polymers as heat resistance and thermal stability[1]. It was found that, although the structure of a given polymer and its inherent combination of chemical and physical properties are determined by the fundamental structure of the monomer unit, a significant influence is exerted by the presence of anomalous units, which are responsible for the "chemical defectiveness of the macromolecular structure"[2-5]. This exhibits some analogy with the physics of solids, where the currently favoured theory is that the imperfection of the physical structure is the most important factor determining the real strength of any solid, including of course polymers[6,7].

The present Review aims to assess the significance of the chemical imperfection of macromolecules as a factor in determining the dependence of the properties of polymers on their structure. The Reviewer would also like to direct the attention of research workers to the finer details of the structure of macromolecules, and to show their value in establishing the dependence of the properties of polymers on structure.

The method generally adopted at present for representing polymer macromolecules indicate the structure only of the main component, whose repetition leads to formation of the macromolecular chain, as shown for instance by the formula of poly(vinyl chloride) $-[CH_2-CHCl]-$. All other structural features, usually designated the microstructure of the polymer—the nature of the end groups, the presence of branches and their number and size, the presence of abnormal monomer units differing in some way from the main units forming the polymer chain, the sequence of alternation of abnormal and normal polymer units, the spatial arrangement of the units and groups (the stereochemistry of the monomer unit and of the macromolecule), etc.—are incapable of representation by this method. This is probably one reason for the disregard of many important structural details of macromolecules, which are extremely significant for an understanding of the relation between the structure of polymers and their properties.

The importance of establishing the structure of the monomer unit and the relative arrangement of units in the macromolecule for an understanding of the properties of polymers was first appreciated by Harries[8] and Lebedev[9], and was systematically explored for a large number of polymers by Staudinger[10], Marvel[11], and other workers. Staudinger showed that the monomer units in the polystyrene macromolecule are linked in a uniform sequence[12]. Marvel[11] showed, with many different polymers as examples, that the same regular arrangement of monomer units is the fundamental law of the construction of macromolecules by polymerisation.

Further development of methods of investigation and a deepening knowledge of polymers led to our realisation that, together with the regular sequence of monomer units, there are several stereochemical and structural factors that are important for an understanding of the structure and the properties of polymers. Present-day methods of synthesising polymers are always accompanied by various types of side-reactions, leading to the formation in the polymer chain of a larger or smaller number of abnormal monomer units of various kinds, differing in some way from the main units. Cases have recently become more and more frequent in which certain apparently minor structural details of a polymer molecule actually have a very significant effect on the whole set of physical and chemical properties characterising the given polymer. Close study reveals that this is due to chemical defects in the macromolecules resulting from the presence of abnormal monomer units[2-5].

Abnormal monomer units influence the properties of the polymer as structural components of the macromolecule, their presence leading to a change in the polar effects between atoms both in this unit and in adjacent and sometimes even fairly remote neighbours, which influences the chemical properties of the polymer; they also make their contribution to the flexibility of and intermolecular interaction between the macromolecules, either weakening or strengthening it, but also influencing the character and degree of order of the macromolecules, which affects the physical properties of the polymer. Ideas based solely on the study of homopolymers are therefore no longer adequate for a proper understanding of the relations between the properties and the structure of polymers. A new approach is required, which would take into account all the aspects of the structure of polymeric molecules. In this connection with concept of "heterounit" polymers is of

fundamental significance, being the main type of polymeric structures which arises from the introduction of abnormal units into the macromolecule.

The chemical defectiveness of the macromolecular structure characteristic of heterounit polymers can be produced intentionally, as in all kinds of copolymerisation and polycondensation, as well as by substitution in a polymeric molecules, which are widely used for modifying the properties of polymers. In these cases, where we control the processes and can choose a desired extent of change in the polymer, the equivalent degree of chemical imperfection can vary within very wide limits.

Cases in which chemical imperfection arises spontaneously, contrary to our wishes, during the synthesis or the modification of a polymer, are far more important. Chemical defectiveness of a macromolecular structure usually results from the inclusion in the polymer chain of abnormal monomer units, having some kind of structural difference from the chief units. In several cases very reliable evidence has been obtained of the presence of abnormal units in polymer macromolecules. Still more cases are known in which there are weighty grounds for assuming their presence.

In every chemical reaction the main product is accompanied by a larger or smaller quantity of secondary products. The yield of the main product usually shows the proportion of the main reaction. The secondary products are removed on purification, and thus do not affect the quality of the main product, merely diminishing its yield. In the formation of polymers, however, all secondary products remain as an integral part of the polymer in the form of abnormal units, and this is one reason for its chemical defectiveness. Therefore, although we write the general formula for a polymer as $[M]_X$, where M represents a monomer residue, this is an idealised formula. It would actually be more correct to represent the structure of a real polymer by a formula such as $[-[M]_m-[A]_n-]_X$, where A is an abnormal unit and M a normal unit [3,5].

The types of chemical defectiveness of macromolecules and the ways in which the corresponding abnormal monomer units arise can be indicated briefly.

1. Abnormal units resulting from cross-links, side-chains, branches, and other abnormal structures.
2. Differences during addition polymerisation or polycondensation in the coupling of units "head to head" or "head to tail".
3. Isomerisation of monomer units during addition polymerisation and polycondensation.
4. Appearance of abnormal units owing to differences in the configuration of asymmetric carbon atoms forming the macromolecular chain ("tacticity").
5. Formation of abnormal units resulting from differences in the configuration of groupings having central, axial, and planar asymmetry.
6. Differences in geometrical isomerism of units formed by the polymerisation of dienes, and also those containing disubstituted rings.
7. Differences in the structure of monomer units resulting from conformational asymmetry and hindered rotation of the units.
8. Abnormal units resulting from incomplete trimerisation in the polycyclotrimerisation of diynes.
9. Abnormal units as the residue of incomplete formation of a carbocyclic or a heterocyclic ring during polycyclisation or polycyclocondensation.
10. Appearance of abnormal units as a result of copolymerisation and copolycondensation.
11. Abnormal monomer units resulting from chemical reactions of units in the macromolecule (chlorination, oxidation, dehydration, etc.).

The abundance of published data more or less closely connected with the present problem does not permit a complete review of the whole literature on this question, and only individual researches can be mentioned below as examples illustrating the principles under discussion.

II. MODES OF APPEARANCE OF ANOMALOUS MONOMER UNITS IN MACROMOLECULES OF HETEROUNIT POLYMERS

All the known syntheses and transformations of polymers are accompanied by various side-processes leading to the appearance of abnormal monomer units and the formation of heterounit polymers. Among reactions leading to the appearance of abnormal units are the recombination of macroradicals, intra- and inter-molecular chain transfer, formation of an atactic chain structure, isomerisation of monomer units, various types of copolymerisation and copolycondensation, various substitutions in the chain, and also various secondary processes occurring during polymerisation and polycondensation [3,5]. We use individual examples to examine the ways in which chemical imperfection appears in macromolecules during the synthesis and the transformation of polymers.

1. Appearance of Abnormal Monomer Units during Polymerisation

The polymerisation of unsaturated compounds by a radical or other mechanism is accompanied by such reactions as the recombination of macroradicals and also intramolecular and intermolecular chain transfer, isomerisation of the monomer unit, etc., leading to the formation of abnormal units. In the first case the recombination

$$(-CH_2CHX)_m-CH_2CHX^{\cdot} + {}^{\cdot}CHXCH_2-(-CHXCH_2-)_n- \rightarrow (-CH_2CHX-)_m-CH_2CHX-CHXCH_2-(-CHXCH_2-)_n$$

results in the appearance of the anomalous group $-CHX-CHX-$ in the chain. In the second case branches and side-chains of various lengths appear as a result of chain transfer.

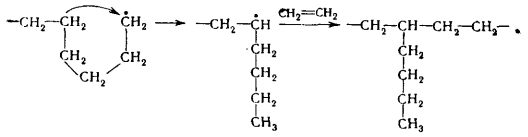
The simplest example of such a polymer containing abnormal monomer units formed during polymerisation is high-pressure (low-density) polyethylene, in which the presence of a considerable number of small, and a small quantity of large, side-chains has been reliably demonstrated. As a result, of course, the macromolecule of such a polymer contains a considerable quantity of units having the structure

$$\cdots-CH_2-\underset{\vdots}{CH}-\cdots \quad \text{or} \quad \cdots-CH_2-\underset{R}{CH}-\cdots .$$

Such units arise from chain transfer, and their presence must therefore be assumed in all polymers obtained by radical polymerisation. The presence of such units in some polymers of this type has been proved experimentally [13]. The formation of long side-chains is a result of intermolecular chain transfer:

$$-CH_2-CH_2-CH_2-CH_2- \xrightarrow{R^{\cdot}} -CH_2-CH_2-\dot{C}H-CH_2- \longrightarrow$$
$$\xrightarrow{CH_2=CH_2} -CH_2CH_2-\underset{\displaystyle CH_2-CH_2-}{\overset{\displaystyle |}{CH}}-CH_2- .$$

Short branches are formed by intramolecular chain transfer [14]:



Butyl side-chains are formed in this way. Ethyl groups, however, are produced by the reaction

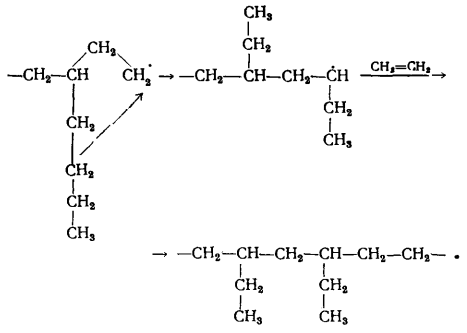
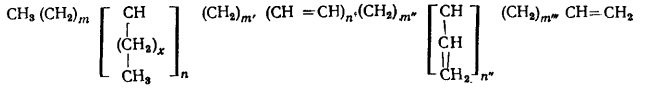


Table 1. Presence of abnormal groups in polyethylene [15].

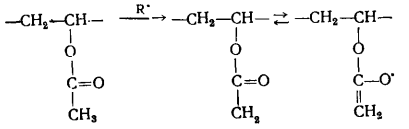
Abnormal group	Abnormal groups per 1000 carbon atoms in	
	low-density (high-pressure) polyethylene	high-density (low-pressure) polyethylene
Methyl (total content) including end-groups	21.5	3.0
Methyl (in side-chains)	4.6	~2.0
Ethyl (in side-chains)	2.5	—
Ethylenic bonds including (% of bonds)	14.4	1.0
$R-CH=CH_2$ type	0.6	0.7
$RR'C=CH_2$ type	15.0	43.0
$R-CH=CH-R'$ type	68.0	32.0
	17.0	25.0

As a result of this, polyethylene obtained by radical polymerisation (low-density polyethylene) contains such groups as ethyl and butyl, together with long side-chains [13]. Furthermore, its macromolecule contains double bonds both in the main chain and in side-chains. Table 1 gives the results of an investigation of the structure of polyethylene [15]. Consequently the actual structure can be represented by the formula



where in low-density polyethylene $n = 20-40$, $n' = 1$ or 2, $n'' = 1$ or 2, and $x = 0-1000$; and in high-density polyethylene $n = 1$ or 2, $n' = 1$ or 2, $n'' = 1$ or 2, and $x = 0-10$. Determination of the presence of side-chains in several samples of high-pressure polyethylene showed that the relative degree of branching decreased as the chain grew, although the content of methyl groups per macromolecule increased (Table 2) [16].

Investigation of the copolymerisation of ethylene with vinyl acetate [14] showed that the degree of branching of the copolymer increased with rise in temperature (Fig. 1). In the case of poly(vinyl acetate) branchings of the polyethylene type may be accompanied by branchings as a consequence of chain transfer via the acetyl group [17]:



which leads to the formation of readily hydrolysable units having the structure

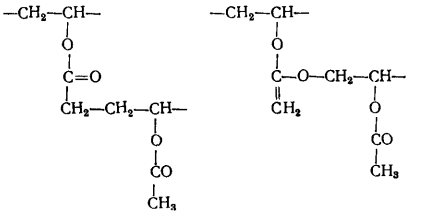


Table 2. Content of methyl groups in various specimens of high-pressure polyethylene.

Mol. wt.	No. of CH_3 per		Mol. wt.	No. of CH_3 per	
	1000 C	macromolecule		1000 C	macromolecule
1700	48	5.5	24000	31	52.0
2400	44	7.1	28000	28	54.0
4000	42	11.4	32000	23	52.0
5300	40	14.5	48000	20	67.2
6600	38	17.5	53000	18	67.5
19000	37	48.5	76000	18	93.5
21000	33	48.5			

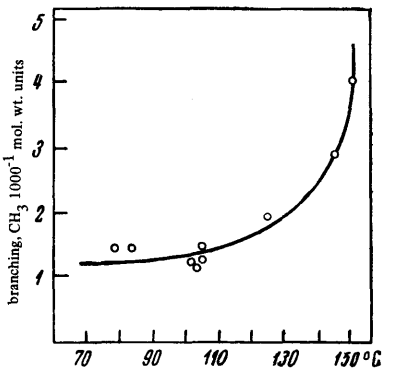
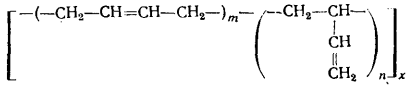


Figure 1. Effect of temperature of polymerisation on branching of a copolymer of ethylene with vinyl acetate.

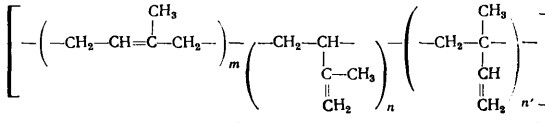
A similar branching reaction is possible also with other esters of poly(vinyl alcohol), as also with polyacrylic and polymethacrylic esters.

The polymerisation of dienes is extremely sensitive to conditions, so that polymers of varied structure can be obtained. Dolgoplosk and Tinyakova[18] examined the mechanism of the polymerisation of dienes and the microstructure of the resulting polymer chain, and showed that the polymerisation of butadiene may lead to the formation of polymers containing monomer units linked together at the 1,2- and 1,4-positions, of *cis*- and *trans*-configuration, and also cyclic units and other structures. With polymers of isoprene 3,4-units may also appear[19].

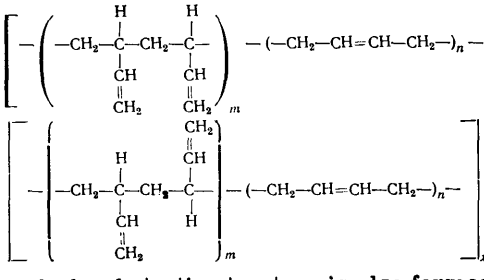
We thus meet a very large variety of abnormal units in the polymers of dienes. The first type of synthetic rubber, obtained by Lebedev's method[20] of polymerising butadiene by the action of metallic sodium, were polymers containing butadiene units linked together at the 1,2- and 1,4-positions in both *cis*- and *trans*-configurations[21]



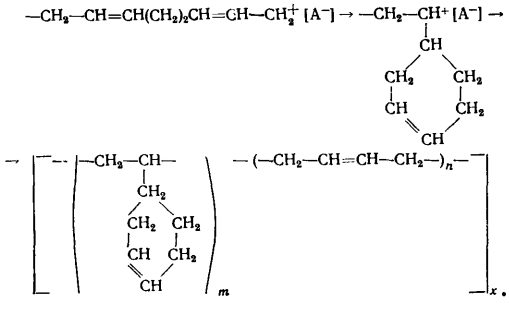
Polymers of butadiene and isoprene obtained in the presence of organometallic catalysts contain far fewer abnormal units. Thus polyisoprene contains 96% and 92% of *cis*-1,4-units when prepared in the presence of a complex of titanium(IV) chloride and triethylaluminium[22] and in the presence of alkyl-lithium catalysts[22,23] respectively. The isoprene polymer obtained in the presence of π-allylnickel iodide contains 95% of 1,4-*trans*-units, 1% of 1,2-units, and 4% of 3,4-units, and its structure can be represented by the formula[24]



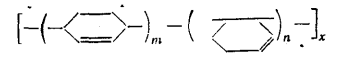
Butadiene and isoprene 1,2-polymers containing predominantly isotactic or syndiotactic units were obtained in the presence of a Ziegler–Natta catalyst[25]. The structure of these heterounit polymers can probably be represented



A branched and atactic structure is also formed, though to a less extent, in the case of ionic polymerisation, as we have already seen in the case of low-pressure (high-density) polyethylene. In the cationic polymerisation of butadiene Dolgoplosk et al.[18,26] observed the formation of six-membered rings by the reaction



The polymerisation of cyclohexa-1,3-diene yields polycyclohexene having different degrees of chemical imperfection depending on the nature of the catalyst: in the presence of organometallic and Ziegler catalysts a polymer containing 1,2- and 1,4-units and having the structure[27]

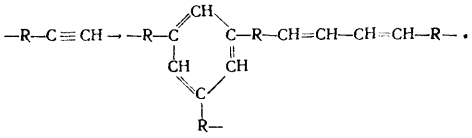


is formed; with π-allylnickel iodide as catalyst the resulting polymer contains 83% of 1,4-units[24].

Atactic polymers, which are formed both in radical and in ionic polymerisation, also represent a case of the presence of randomly arranged foreign *laevo*-units in a chain of *dextro*-units, which is in general characteristic of polymers obtained by radical polymerisation[28]. Natta showed[29] that in this case the difference in structure of the units is stereochemical. Atactic polymers are in general more correctly regarded as random copolymers of *dextro*- and *laevo*-forms, in contrast to a regular copolymer of these forms, represented by the corresponding syndiotactic polymer.

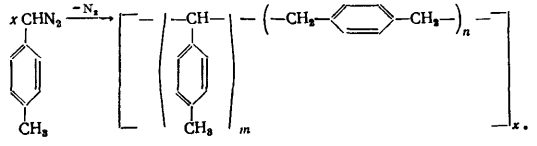
Polymerisation in the presence of oxygen leads to the formation of polymers containing anomalous peroxy-units[30] $CH_2.CHX.O.O$ or ether links $CH_2.CHX.O$ arising from the breakdown of these peroxides. Similar abnormal units appear when polymerisation is initiated by polymeric acyl peroxides, e.g. terephthaloyl peroxide[31]. The initiation of polymerisation by radiation leads to the formation of branched or cross-linked polymers containing abnormal units[32].

In the polycyclotrimerisation of diacetylenic derivatives with the formation of polyphenylenes defective units are produced as residues of incomplete cyclisation[33]:



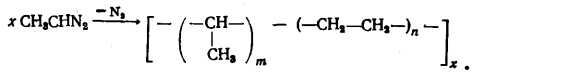
2. Abnormal Units Resulting from Isomerisation of Units During Polymerisation

In several cases of polymerisation the resulting units undergo isomerisation, so that heterounit polymers are formed containing two or more types of units. Isomerisation occurs mostly as a result of hydrogen migration, but cases are known of the migration of chlorine, e.g. in the polymerisation of 3,3,3-trichloropropene, or even rearrangement of the electronic structure of the monomer without the migration of hydrogen, as with acrylonitrile, dimethylketen, glutaraldehyde, and other dialdehydes. Thus Korshak et al. showed[34] that the polymerisation of *p*-tolyldiazomethane involved not only formation of the normal *p*-methylbenzylidene units but also isomerisation with the appearance of an appreciable quantity of *p*-ethylenephenylene units. As a consequence the structure of the resulting polymer corresponds to the formula

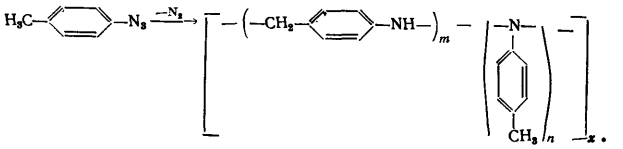


Similar isomerisation was observed in the polymerisation of diazoethane, with the formation of a heterounit polymer

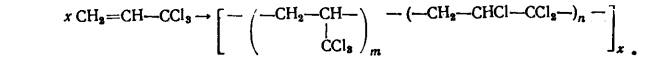
containing ethylene units [35]:



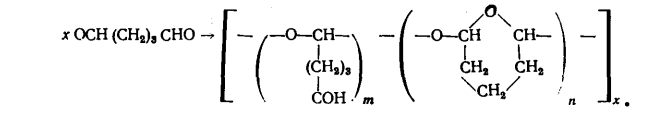
A heterounit polymer with isomerised units probably having the following structure was formed [36] in the catalytic decomposition of *p*-tolyl azide in the presence of sulphuric acid:



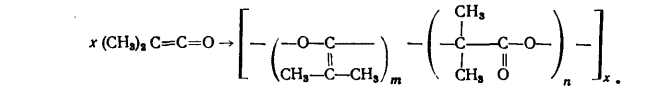
Suprun et al. found [37] that the polymerisation of 3,3,3-trichloropropene, owing to isomerisation involving migration of a chlorine atom, yields a heterounit polymer:



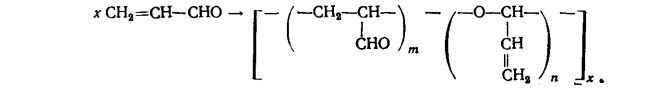
The polymerisation of glutaraldehyde occurs in two ways, with formation of a heterounit polymer [38]:



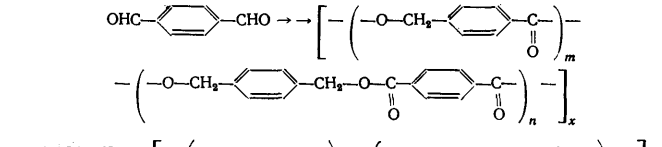
According to Natta et al. [39] dimethylketen polymerises in the presence of triethylaluminium to a polyketone–polyacetal, which is a heterounit polymer:



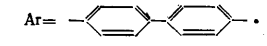
The polymerisation of acrylaldehyde in the presence of weak ionic catalysts lead to the formation of a heterounit polymer containing both ether and carbon–carbon links [40]:



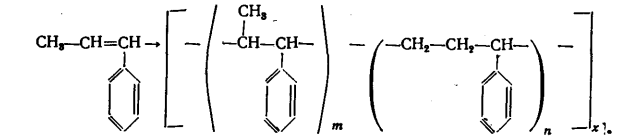
The polymerisation of terephthalaldehyde and of biphenyl-*pp'*-dialdehyde in the presence of organoaluminium or organozinc compounds also shows an unusual course, leading to the formation of heterounit polymers [41,42]:



where

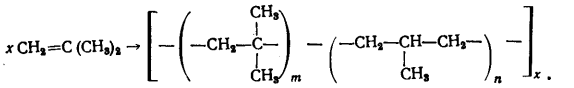


The ionic polymerisation of certain vinyl compounds, substituted styrenes, and vinylpyridines often occurs as migration polymerisation with hydrogen transfer and the formation of heterounit polymers containing in the main chain carbocyclic and heterocyclic rings together with other abnormal units [43,44]. The first case of this type of isomerisation polymerisation with migration of hydrogen [45,46] was probably the polymerisation of anethole [46] and β-methylstyrene [45] studied by Staudinger, which in the latter case gave a heterounit polymer of probable structure

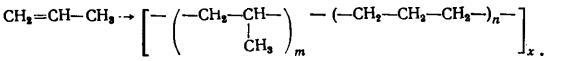


Kennedy showed [48] that an analogous polymer is obtained by the cationic polymerisation of allylbenzene.

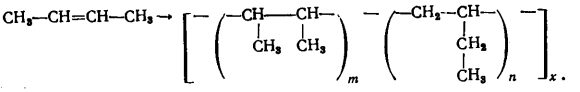
Topchiev et al. [47] showed that in the case of isobutene isomerisation polymerisation led to the formation of a heterounit polymer:



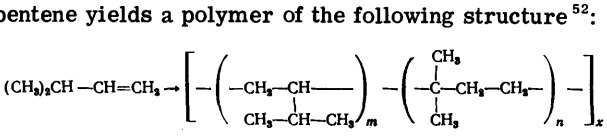
Isomerisation polymerisation with hydrogen transfer has been observed also with many other alkenes [43]. Thus propene gives a heterounit polymer corresponding to a copolymer with ethylene [49,50]:



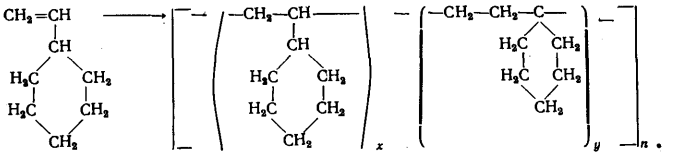
But-2-ene also forms a heterounit polymer [51]:



Isopentene yields a polymer of the following structure [52]:

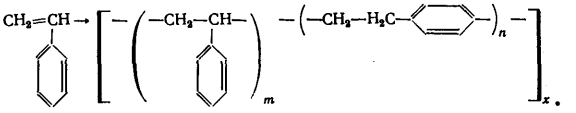


The ionic polymerisation of vinylcyclohexane produces a heterounit polymer containing, together with normal units, abnormal units in which the cyclohexane ring enters the polymer chain [53]:

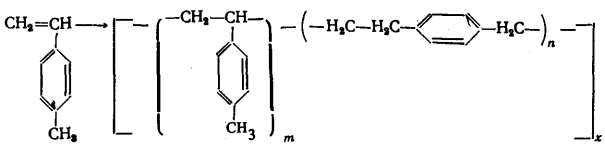


Abnormal monomer units of this type are characteristic of "card" polymers.

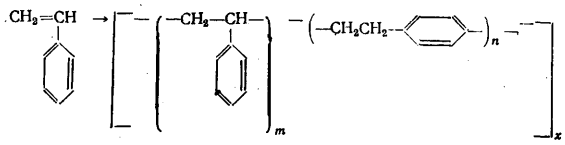
Styrene as a result of isomerisation polymerisation forms a polymer containing not only styrene but also *p*-ethylenephenylene units [54]:



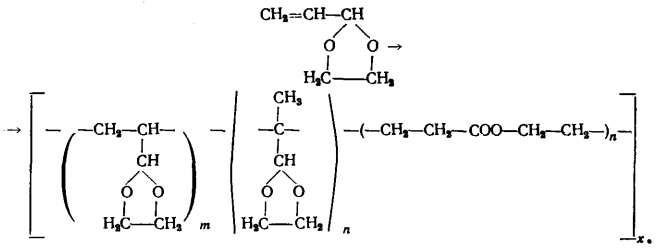
An analogous result was obtained also by the polymerisation of *p*-methylstyrene [55]:



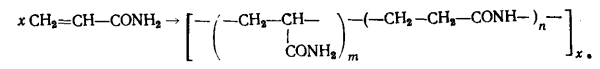
In the case of allylbenzene the resulting polymer has the following structure[56]:



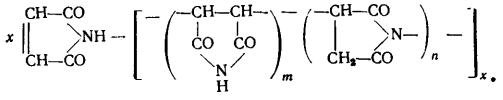
In the case of 2-vinyl-1,3-dioxolan the polymer may have a still more complicated structure[57]:



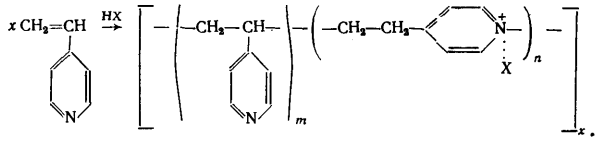
Acrylamide in the presence of basic catalysts undergoes isomerisation to form a heterounit polymer[44,58]:



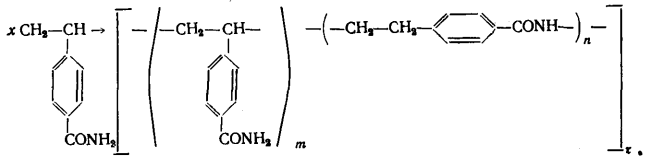
The anionic polymerisation of maleimide in dimethylacetamide similarly yields a heterounit polymer containing not only normal units but also abnormal units formed by the migration of hydrogen[44,59]:



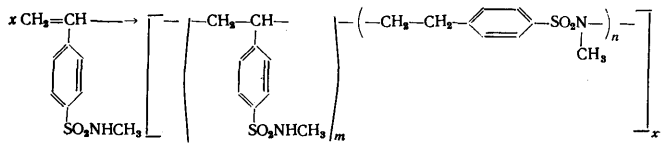
Migration of hydrogen takes place in the polymerisation of 4-vinylpyridine in the presence of acids with the formation of ethylenepyridinium units[60]:



Under conditions of anionic polymerisation *p*-vinylbenzamide forms a heterounit polymer containing different proportions of normal and abnormal units[44,58,59,61-63]:

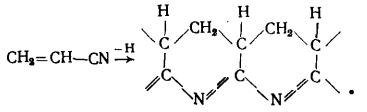


N-Substituted *p*-vinylbenzenesulphonamides behave similarly, forming heterounit polymers by the reaction[44,64,65]



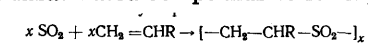
The polymerisation of acrylonitrile under the influence of X-rays[66], γ-rays[67], or fast electrons[68] produces a heterounit polymer containing up to 10% of ketenimine structures:

Nevertheless, the radiation polymerisation of acrylonitrile in the solid phase at low temperatures leads to formation of a syndiotactic polymer, wnereas at high temperatures fused nitrogen-containing rings are obtained[68,69]:

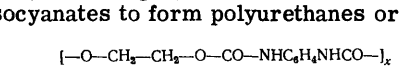


3. Appearance of Abnormal Units during Copolymerisation

Copolymerisation leads to the formation of copolymers containing various quantities and proportions of foreign units, which are therefore heterounit polymers. In this case not only the quantity but also the arrangement of foreign units is especially important. Thus with a regular alternation of the different units we no longer have a copolymer but a true homopolymer having a long repeating unit, as occurs e.g. in the copolymerisation of sulphur dioxide with unsaturated compounds to form polysulphones



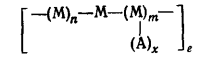
or in the migration copolymerisation of diols or diamines with di-isocyanates to form polyurethanes or polyureas



The concept of the defectiveness of macromolecules is of practical value, of course, only when one type of unit predominates. When the two types of units are present in equal quantities, the concept obviously loses the meaning in which it is used in the present paper.

Simultaneous polymerisation may lead to the formation of different types of copolymers, which may even have the same elementary composition. Thus at present we are acquainted with such different types as block copolymers (in particular polyallomers), graft copolymers, random copolymers, and also diagonal or insymmetrical copolymers and copolymers with a regular alternation of different units[70-72]. The introduction of one or more other types of copolymers into a particular type will undoubtedly yield a "copolymer of copolymers", which may be a polymer with chemically defective macromolecules.

Among the above types of copolymers those with a regular alternation of units must be regarded as homopolymers. Their structure can be represented by the general formula $[M.A]_X$, whereas in the case of statistical copolymers, which are heterounit polymers, the general formula expressing their structure will be $[[M]_n.[A]_m]_x$, where $n = 1, 2, 3, \ldots$, $m = 1, 2, 3, \ldots$, and $n \neq m$. Hence we should again have a regular copolymer when $n = m$. A block copolymer will be represented by the same general formula but with $n \neq m$, $n > 10$, and $m > 10$. In the case of a graft copolymer the general formula will be



in which $n + m > 1000$, $x > 10$, and $e = 1-10$ and above.

The copolymerisation of styrene with divinylbenzene by Staudinger [73] was the first case in which a branched and cross-linked polymer was obtained. This type of imperfection is met widely in ion-exchange resins, since in this way insoluble granules of limited swelling can be obtained. The "copolymerisation" of styrene with ϵ-caprolactam also yields a graft copolymer with a chemically imperfect macromolecular structure [74].

The peculiar polymers known as "diagonal" or "unsymmetrical", obtained by the copolymerisation of a mixture of two monomers of variable composition, should also be regarded as heterounit polymers. They differ from the other examples in the variation in structure of the units along the length of the macromolecule [71].

A more detailed description of copolymerisation and the properties of copolymers lies outside the scope of the present paper. The account will therefore be confined to the above examples, illustrating the fact that most copolymers are heterounit polymers.

4. Formation of Abnormal Units during Polycondensation

Two groups of polycondensation processes, differing significantly in reaction mechanism and termed respectively "equilibrium" and "non-equilibrium" polycondensation, have been distinguished. We must therefore take into account their differences in considering individual examples of reactions of each type [75-83]. Heterounit polymers can also be formed in various ways during polycondensation.

As in the various cases of polymerisation discussed earlier, polycondensation may also involve reactions leading to the formation of various abnormal units—containing side-chains and branches, cross-links, anomalous groups in the main chain—as well as all kinds of stereochemically distinguishable units yielding macromolecules having structures similar to those in atactic, isotactic, and syndiotactic polymers obtained by stereospecific polymerisation. The concept of "tacticity" has a specific sense when applied to polycondensates [84]: it covers units containing carbon atoms with two different substituents, *cis*- and *trans*-isomers with multiple bonds and with a disubstituted ring, and also groups with central, axial, and planar asymmetry. In complicated polymers stereoregular structures may be formed also as a result of the appearance of stable conformations [85]. Another important source of abnormal units is the residue of incompletely cyclised units remaining during polycyclisation or polycyclocondensation.

Let us cite a few examples of the formation of heterounit polymers during equilibrium polycondensation. Thus the polycondensation of dicarboxylic acids with glycols in the presence of mineral acids is accompanied by the formation of ethers:

$$HOR—OH+HO—R—OH \xrightarrow{-H_2O} HO—R—O—R—OH.$$

As a consequence, abnormal units containing an ether bond

$$—O—R—O—R—O—CO—R'—CO—$$

appear in the polyester macromolecule [86]. In the polycondensation of glycerol this reaction leads to the formation of units containing biglycerol

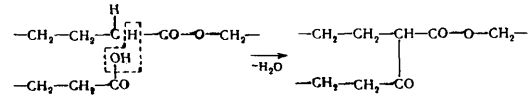
$$—O—CH_2—\underset{\displaystyle OH}{CH}—CH_2—O—CH_2—\underset{\displaystyle OH}{CH}—CH_2—O—$$

and polyglycerols [87,88].

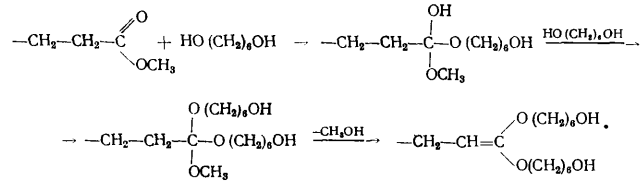
The equilibrium polycondensation of ethylene glycol with terephthalic acid or its dimethyl ester in the presence of most catalysts leads to the formation of poly(ethylene terephthalate) melting at 256°C. [89] However, the use of sulphuric acid as catalyst yields a polyester of lower melting point, owing to the formation of a heterounit polymer containing ether bonds

$$[—(—OCH_2CH_2OCOC_6H_4CO—)_m—(—OCH_2CH_2OCH_2CH_2OCOC_6H_4CO—)_n—]_x.$$

The formation of branched polyesters on prolonged heating of the reaction mass was observed by Staudinger and Schmidt [90], who explained this result by dehydration



or by formation of a keten acetal



When unsaturated monomers such as maleic and fumaric acids are used in polycondensation, polyesterification is accompanied by secondary addition of the glycol to the double bond with the formation of hydroxyethoxysuccinic esters [91,92]:

$$—CO—CH=CH—CO—O—CH_2CH_2—O— \xrightarrow{HOCH_2CH_2OH} \rightarrow —CO—CH_2—\underset{\displaystyle O—CH_2—CH_2—OH}{CH}—CO—O—CH_2CH_2—O—.$$

At the later stages of conversion this reaction leads to branching and cross-linking of the polymer. During polycondensation with the glycols investigated in detail by Petrov [93] and by others [94] maleic acid isomerises into fumaric acid, to yield polyesters which are heterounit polymers, and can be regarded also as copolymers of the two acids. The degree of conversion may reach 70–90% depending both on the nature of the glycol and on the conditions of polycondensation.

Polyamides prepared by prolonged heating in the molten state form branched products having the structure

$$\begin{matrix}—NH(CH_2)_6NH—CO(CH_2)_8CO \\ —NH(CH_2)_6NH—CO(CH_2)_8CO\end{matrix}\!\!>\!N(CH_2)_6NH—CO(CH_2)_8CO—.$$

Such observations were made by Champetier [95,96] and by other workers [97-99] on both aliphatic and aromatic polyamides. According to Meacock [100] as well as Kamerbeek et al. [101] heterounit polyamides result from the formation of secondary amino-groups by the reaction

$$—CO(CH_2)_4CO—NH(CH_2)_6NH_2 + H_2N(CH_2)_6NH—CO(CH_2)_4CO— \xrightarrow{-NH_3} \rightarrow —CO(CH_2)_4CO—NH(CH_2)_6NH(CH_2)_6NH—CO(CH_2)_8CO—.$$

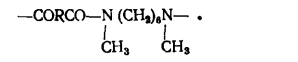
These groups react with terminal carboxy-groups of other macromolecules to produce branched polyamides

$$—CO(CH_2)_4CO—NH(CH_2)_6N(CH_2)_6NH—CO(CH_2)_4CO—$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad CO(CH_2)_4CO—NH(CH_2)_6NH—.$$

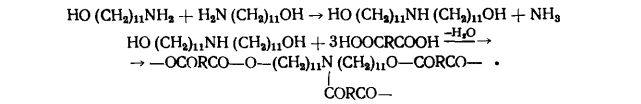
Thomas showed [102] that, when polyamides are prepared from diamines and dicarboxylic esters at high temperatures, the diamine may undergo alkylation

$$H_2NRNH_2 + 2R'COOCH_3 \rightarrow CH_3NHRNHCH_3 + 2R'CO[illegible]$$

with the formation of methyl side-groups in the polyamide

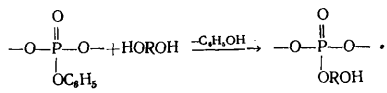


The formation of branched and three-dimensional poly(amide–esters) by the polycondensation of ω-amino-alcohols with dicarboxylic acids results from the elimination of ammonia and the formation of amino-glycols [103]:



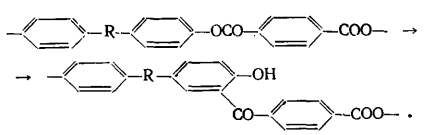
The presence of different functional groups in the initial monomers, and subsequently in the polymer macromolecule, may lead to branching and ultimately to the formation of three-dimensional polymers, as has been shown with *N*-cyanoethylated polyamides [104].

The synthesis of poly(ethyl ethylene orthophosphates) is accompanied by transesterification with the formation of branches [105]:

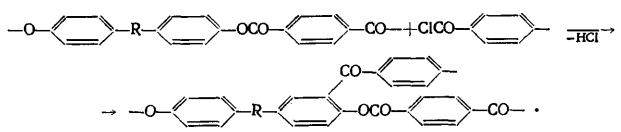


Formation of branched polyesters in the polycondensation of a glycol with an unsaturated acid, e.g. fumaric or maleic, may result also from the dimerisation or the polymerisation of the acid during the reaction [106]. Lavalou [107] observed cross-linking also in the polycondensation of ω-aminoundecanoic acids containing such *N*-substituents as allyl, undec-10′-enyl, and 2′-hydroxyethyl. Cross-linking of polyesters may result also from their oxidation by oxygen during preparation [108].

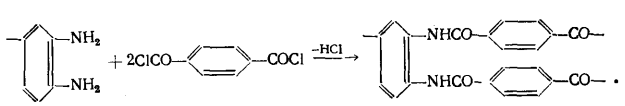
Although the laws of non-equilibrium polycondensation, like the structure of the polymers obtained, have been investigated less thoroughly, we shall consider some examples showing that heterounit polymers are formed in this process. Branched polymers may be produced by direct acylation or by a rearrangement analogous to the Fries rearrangement. Thus in the synthesis of polyarenoates branching may occur in conformity with the equation [109]



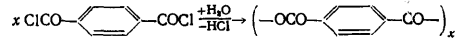
The resulting phenolic hydroxyl in then able to react with an acid chloride to form a branch. Acylation can cause branching as a result of the reaction



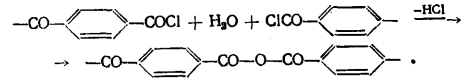
Branching can occur in the reactions of the dichlorides of dicarboxylic acids with tetramines, bis-*o*-amino-phenols, and bis-*o*-amino-thiols:



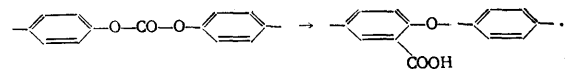
The action of water on a solution of such a dichloride in triethylamine yields a polyanhydride of terephthalic acid [110]:



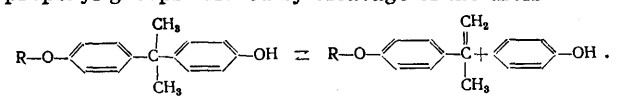
Therefore the presence of traces of moisture in the low-temperature polycondensation of acid chlorides with dihydric phenols may lead to the appearance of anhydride groups in the macromolecule by the reaction



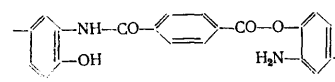
Schnell [111] considered it possible that a Kolbe type of side-reaction leading to the formation of branched and cross-linked structures may occur in the preparation of polycarbonates from diphenyl carbonate:



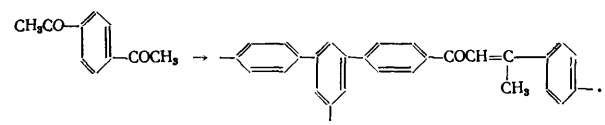
He also considers [112] that branching may result from the polymerisation of polycarbonates involving terminal isopropenyl groups formed by cleavage of the diols



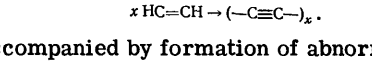
When dichlorides of dicarboxylic acids undergo polycondensation with biaminophenylmethanediols or bisaminophenylmethanedithiols (in which the amino-group is *ortho* to the hydroxy- or mercapto-group), their analogues and homologues, reaction can occur in two directions with the formation of abnormal units of isomeric structure, e.g.



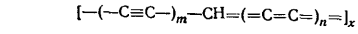
In the polycyclocondensation of diketones the phenyl rings may be accompanied by aliphatic units remaining from incomplete cyclisation [113]:



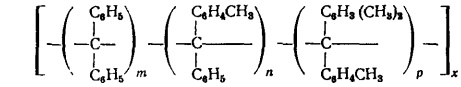
The oxidative dehydropolycondensation of acetylene yields a linear form of polymeric carbon, which is a third allotropic modification of carbon termed "carbyne" [114]:



This is accompanied by formation of abnormal units and block copolymers having the structure



A side-reaction in the polyrecombination of diphenylmethane is methylation of the benzene rings by the action of methyl radicals, so that the resulting polymer contains tolyl and xylyl groups [115]



Polycyclisation is one of the most important types of reactions in non-equilibrium polycondensation [116]. It occurs in two stages: the linear polymer formed initially then undergoes cyclisation, and is thus converted into a

ring–chain polymer. However, several examples have shown that the second stage is almost always incomplete. One reason is increasing rigidity of the chain causing steric hindrance to cyclisation. This is shown in an increase in the activation energy of cyclisation during the process, as illustrated by Fig. 2, in which are plotted results of the cyclisation of a polyhydrazide [117]. The reason for this increase in activation energy and consequent decrease in rate of polycyclisation is the stiffening of the polymer macromolecules caused by the formation of oxadiazole rings, since this diminishes the mobility of the units necessary for them to overcome the stereochemical obstacles to cyclisation. Therefore the macromolecules of the resulting ring–chain polymer always retain some proportion of uncyclised units as a residue of incomplete cyclisation: i.e. these are abnormal units in the resulting heterounit polymer.

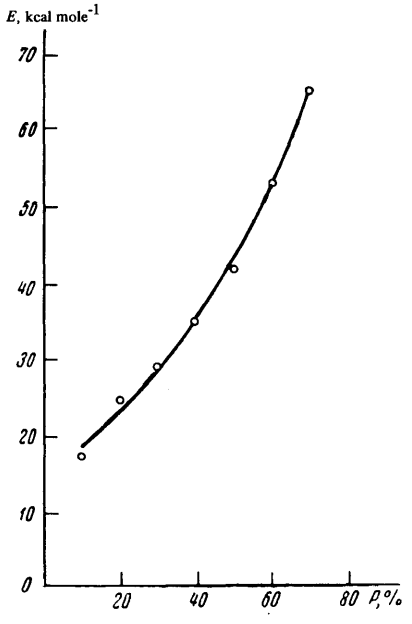
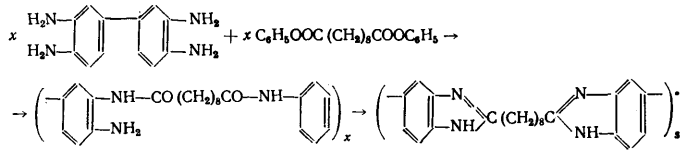
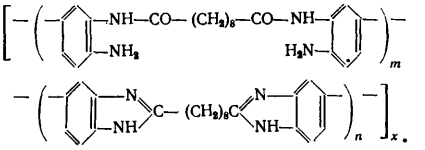


Figure 2. Variation of activation energy for the cyclodehydration of a polyhydrazide of diphenylphthalidedicarboxylic acid with completeness of conversion P.

Thus the polycondensation of aromatic bis-*o*-diamines with diphenyl esters of aromatic dicarboxylic acids leads to the formation of polybenzimidazoles:

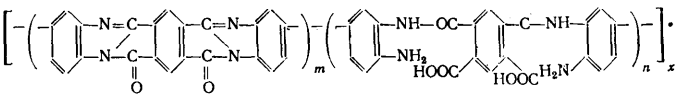


At any stage in this reaction, however, the product is a heterounit polymer containing amino-amide and benzimidazole units in the macromolecule, so that its structure is more correctly represented by the formula [118,121,122]

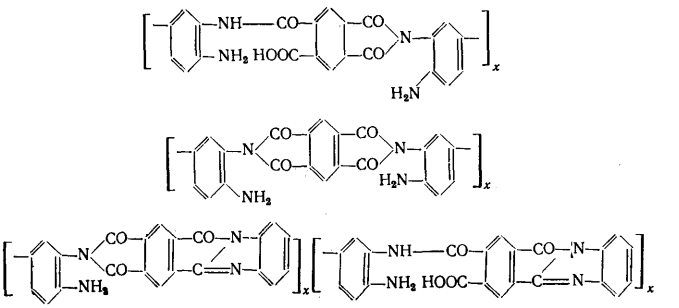


Examination of polybenzimidazoles which have been dehydrated at 270°C showed that they contained about 69% of benzimidazole and 31% of amino-amide units [121].

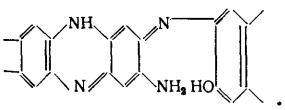
The structure of pyrrones—products of the reaction between tetracarboxylic anhydrides and bis-*o*-diamines—has also been studied very carefully in view of the especially high thermal stability expected [123–129]. Application of a thermodynamic method by Rabinovich et al. [123] established that the pyrrone macromolecule contains 66% of benzoylenebenzimidazole and 34% of amino-amide units, the latter remaining from incomplete cyclisation. Their structure is therefore represented more accurately by the formula



It must be borne in mind, of course, that this formula contains only the two extreme structures: several intermediate structures may also be present, formed in the passage from the amido-amino-acid to the benzoylenebenzimidazole, e.g.



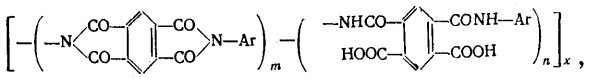
Incomplete cyclisation has also been suggested in the ladderlike polyquinoxalines obtained by Stille and Mainen [130] from 2,5-dihydroxy-*p*-benzoquinone and benzene-1,2,4,5-tetra-amine, so that the chain should contain units of the two types



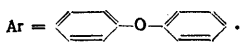
A similar hypothesis was put forward by Okeda and Marvel for polyquinoxalino-oxazines [131] and polyquinoxalino-thiazines [132].

Polypyromellitimides also contain a considerable quantity of uncyclised units. Thus Bruck [133] found that the polypyromellitimide obtained from bis-*p*-amin[illegible]yl ether contained only 78% of imide units, with 22% of

amido-acid units remaining uncyclised, so that a more correct formula for this heterounit polymer is



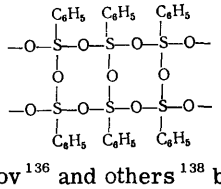
where



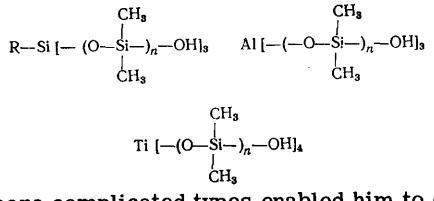
Investigation of several polyheteroarylenes obtained recently has revealed the presence of a considerable quantity of uncyclised units also in polyquinoxalines [130], polybenzoxazoles [134], polyoxadiazoles [117], polypyridines [135], etc.

Thermal dehydrocyclisation—a process widely applied to the synthesis of various thermostable polymers—represents a novel type of pyrolysis involving the elimination only of water. Genuine pyrolysis is often a polycondensation process occurring with the elimination of volatile products—water, carbon dioxide, carbon monoxide, hydrogen, methane and other saturated and unsaturated hydrocarbons, and benzene and other aromatic compounds—the composition of which varies with the temperature and the conditions of pyrolysis. The non-volatile product of pyrolysis is coke or graphite, whose structure and properties also depend on the structure of the starting materials and the conditions of pyrolysis.

The polycondensation of monomers containing three or more functions leads to the formation of branched and cross-linked polymers containing abnormal units. Andrianov [136,137] showed with several polymers that the functionality and the structure of the initial monomers play a very important role. Thus a three-dimensional polymer with a regular arrangement of rings can be obtained [137] by the polycondensation of cruciform polytitano-organosiloxane oligomers. An especially detailed investigated was made of the ladderlike polymer of structure

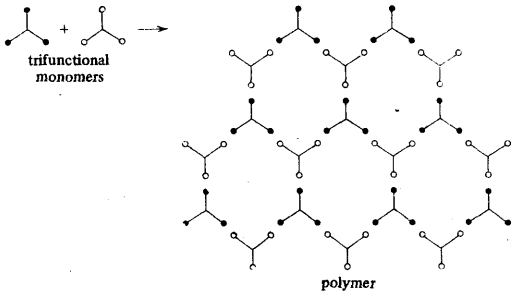


obtained by Andrianov [136] and others [138] by the hydrolysis of phenyltrichlorosilane. Its macromolecule contains defects consisting in incomplete ring closure [139]. In the case of three-dimensional polymers it is very important to ensure maximum regularity of the network structure, which is achieved by using tri- and tetra-functional oligomers having the same side-chains [137]. Thus Andrianov's use of oligomers of the type



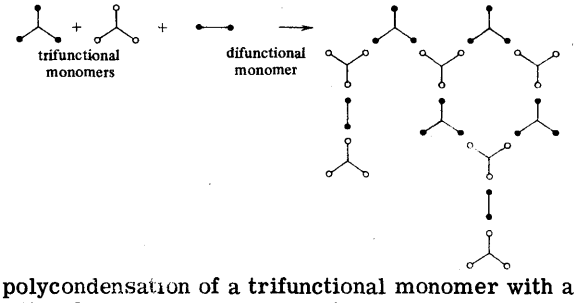
and also more complicated types enabled him to obtain polymers having a regular network structure [137].

Defects of two kinds—rings (loops) and long side-chains attached at only one end to branch points of the network—may appear on formation of a network structure [140]. The structure of the initial substances is evidently of especial importance. Thus an extremely regular network could probably be obtained by the polycondensation of two trifunctional monomers [141]:

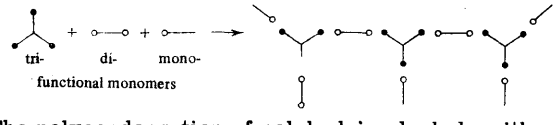


In the work cited above Andrianov proved experimentally the possibility of obtaining such regular structures [136,137].

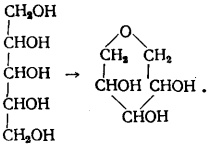
The regularity of the three-dimensional framework undoubtedly breaks down in the polycondensation of trifunctional with difunctional and especially with monofunctional monomers, which makes such a system chemically imperfect owing to the appearance of many abnormal units, as shown below. The picture for the polycondensation of trifunctional monomers when one of them has been replaced by a difunctional monomer will be



The polycondensation of a trifunctional monomer with a difunctional monomer and a monofunctional monomer can be depicted



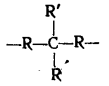
The polycondensation of polyhydric alcohols with dicarboxylic acids will be accompanied by the side-reactions considered above, together with substitution, cyclisation, etc. leading to the formation of abnormal units [142]. An interesting case of the formation of heterounit polymers was observed by Kiselev and Lubman [143] in the polycondensation of xylitol with phthalic anhydride, when abnormal units resulted from secondary dehydration with the formation of cyclic ethers:



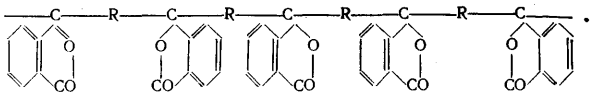
Most polymers obtained by polycondensation methods contain symmetrical units, so that the stereoregularity of their structure does not attract the attention of investigators. As with polymerisation methods, however, it must be envisaged that stereoregular polymers can be prepared by polycondensation. The first necessary condition for achieving this aim is, of course, the use of polymers capable of forming asymmetric units. This has already

been realised in practice by starting with optically active monomers, which enable polymers to be obtained with a sterically regular alternation of units.

Use is generally made of monomers having two different and two identical substituents of the type

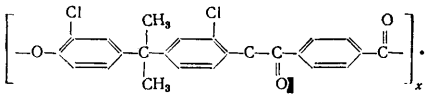


but this yields polymers having a structure analogous to that of atactic polymers, i.e. with sterically non-equivalent units. Consequently these units can also be regarded as abnormal relative to each other, and such polymers as heterounit. An example of this type is supplied by the "atactic" polyarenoates of phenolphthalein and various dicarboxylic acids, which have the schematic formula

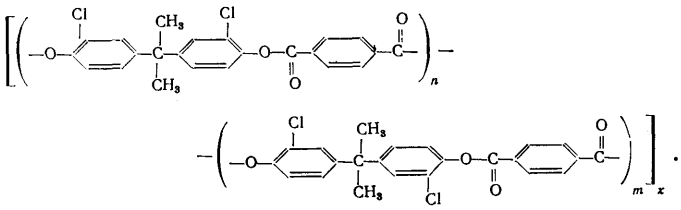


As we shall see later, this view of its structure is supported by its physical properties [144].

When bulky substituents are present, polyarenoates are produced having different crystal forms depending on the nature of the solvent. Thus the polyarenoate of 2,2-bis-*m*-chloro-*p*-hydroxyphenylpropane and terephthalic acid obtained in the presence of pyridine is crystalline and gives narrow signals in the nuclear quadrupole resonance spectrum, indicating the predominance of one crystalline form [85], so that this polymer can be regarded as stereoregular. It probably has the structure



When this reaction is conducted in dioxan and other solvents, a heterounit polymer is formed containing both crystallographic conformations, which can be represented by the formula



Thus this reaction is an example of the synthesis of a stereoregular polymer by stereospecific polycondensation.

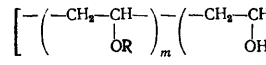
5. Appearance of Abnormal Units during Copolycondensation

Copolycondensation, like copolymerisation, results in the formation of "heterounit polymers" containing units differing in structure. Polymers having macromolecules of varying degrees of imperfection are obtained depending on the nature and the quantity of the monomers taken. The use of monomers having three or more functions enables polymers to be obtained containing substituent groups and side-chains, as well as cross-linked three-dimensional structure. A more detailed description of the structure of the copolymers obtained is outside the scope of the present paper, so that reference will be made to the monograph on this topic [75].

6. Formation of Various Abnormal Units during the Substitution, Oxidation, and other Reactions of Macromolecules

Heterounit polymers can be obtained also as a result of substitution in the macromolecule of hydroxy-groups, hydrogen atoms, halogen atoms, and other atoms or groups by halogenation, oxidation, metallation, and other reactions. Since such reactions never go to completion, a heterounit polymer is obtained containing the initial units, together with the final and intermediate substitution products. The distribution of substituents resulting from substitution is usually random.

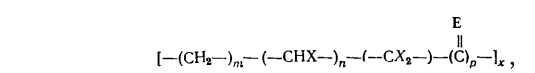
An extremely clear example of reactions of this kind is the polymerlike substitution in the hydroxy-groups of cellulose, polyvinyl alcohol, starch, and other polymers containing easily replaceable hydrogen atoms, which are usually only partly replaced by various groups. As a result of this, polyvinyl alcohol forms a heterounit polymer having the structure [145]



A still more complicated situation is found in cellulose ethers, which may contain four types of units [146]

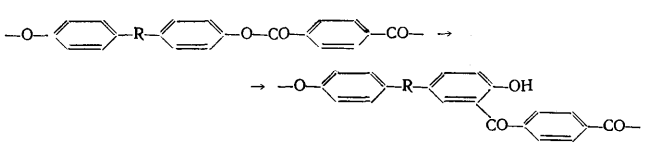


The same consideration applies to the huge number of heterounit polymers of various types, whose chains may contain two, three, or more different units in various proportions. They include both copolymers obtained by the copolymerisation of different monomers, which we have discussed previously, and heterounit polymers formed by the replacement in a homopolymer of hydrogen or other atoms or even whole groups as a consequence of such reactions as oxidation, chlorination, hydrochlorination, dehydrochlorination, esterification, alkylation, acylation, sulphonation, nitration, metallation, etc. These reactions yield heterounit polymers containing, together with the original monomer units, irregularly arranged mono- and di-substituted units, which can be represented for a substituted polyethylene by

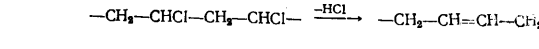


where X = Cl, Br, I, F and E = O, S.

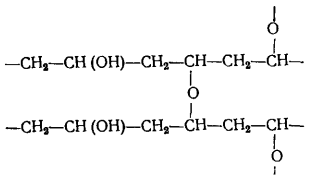
Abnormal units and consequent chemical imperfection may result also from various reactions leading to the formation of heterounit polymers—the Fries rearrangement in polyarenoates, the elimination of hydrogen chloride from poly(vinyl chloride) and other halogenated polymers, the removal of water from polyvinyl alcohol and from polymethacrylic acid, etc. The Fries rearrangement



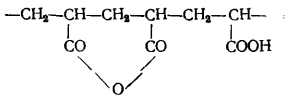
takes place when polyarenoates are exposed to ultraviolet radiation or are treated with aprotic acids [147]. The elimination of a hydrogen halide from halogenated polymers results in the appearance of double bonds [148,149]:



Dehydration of polyvinyl alcohol leads to cross-linking by ether bonds



and the polymer becomes insoluble [150]. Elimination of water from polymethacrylic acid converts it into the cyclic anhydride [151]

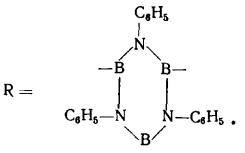


An interesting and very peculiar case of the formation of a heterounit polymer is the isomerisation of polyethers containing bishydroxymethyl-*o*-carborane residues into polyethers of bishydroxymethyl-*m*-carborane, which occurs on prolonged heating in an inert atmosphere [152]:

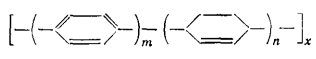
$$(-R-OCH_2-CB_{10}H_{10}C-CH_2O-)_x \rightarrow (-R-OCH_2-CB_{10}H_{10}C-CH_2O-)_x,$$

ortho *meta*

where

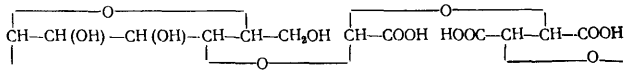


Marvel's synthesis of polyphenylene [27] involves a stage of polymerisation of cyclohexa-1,3-diene followed by dehydrogenation of the resulting polycyclohexene. The latter reaction is incomplete, so that actually the product is not poly-*p*-phenylene but the heterounit polymer

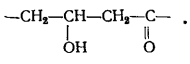


containing phenylene and cyclohexene units.

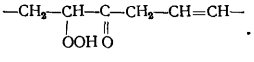
The oxidation of polymers results in the formation of heterounit polymers whose macromolecules contain carboxyl, ketone, alcohol, and other groups formed by oxidation of a monomer unit. Thus oxidised cellulose



comprises [146] units containing carboxy-groups formed both by oxidation of terminal primary alcohol groups and by cleavage of a pyran ring. Marvel and Denoon [153] showed that oxidised polyvinyl alcohol contains keto-groups



Oxidised polyethylene contains peroxy- and keto-groups together with double bonds [154]:



Nearly every polymer is oxidised on standing in air for a long time, and therefore contains aldehyde and ketonic groups, carboxyls, and peroxy-groups [155].

Marvel and Sampel [156] showed that dehydrochlorination of poly(vinyl chloride) leads to the formation of double bonds in the chain and the appearance of a dark colour in the polymer [156].

An immense number of heterochain polymers of varying structure—e.g. polyamides, polyesters, poly(amide–esters), etc.—have quite polar bonds in their chain, and therefore readily undergo exchange reactions with analogous heterochain polymers to form heterounit polymers. The products have the same structure and properties as copolymers synthesised from the corresponding initial monomers [157].

Heating a mixture of polyhexamethylenedipamide and poly-6-hexanoamide yields mixed polyamides having the same properties as those obtained by the reaction of hexamethylenediammonium adipate with ϵ-caprolactam [97]. In the same way, heating a mixture of three polyamides—polyhexamethylenedipamide, polyhexamethyleneazelaamide, and poly-ϵ-caproamide—results in a mixed polyamide with the properties of the polymer obtained by polycondensation of the corresponding starting materials [157]. When a mixture of two polyesters is heated, a heterounit polymer is formed with the same properties as in the corresponding copolymer obtained from the initial monomers [158,159]. Similarly, a poly(amide–ester) was obtained by heating a mixture of a polyamide and a polyester [160].

Another interesting feature of exchange reactions between two heterochain polymers is that, together with the statistical copolymer which is the final result of such a process, block copolymers appear in the early stages [97]. We obtain a mixture of various copolymers with abnormal units depending on the stage at which the reaction is halted, as shown in Fig. 3.

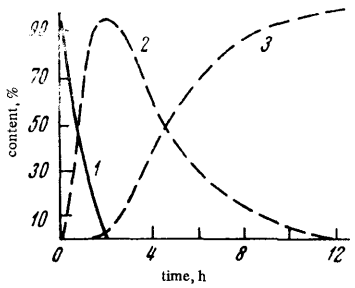
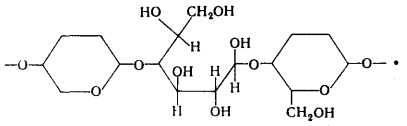


Figure 3. Variation in composition of a mixture of two heterochain polymers during heating: 1) homopolymers; 2) block copolymers; 3) random copolymer.

The formation of cross-linked polymers by various types of vulcanising reactions also produces chemically defective macromolecules [73,161,162]. Thus polyethylene, when heated with a peroxide [161], exposed to radiation [162], or treated with other chemical reagents becomes initially branched, and then an insoluble, infusible, cross-linked three-dimensional product. This type of imperfection resulting from chemical or radiation treatments occurs in many polymers, and is widely used in technology. The network produced in vulcanising and similar cross-linking processes is in most cases irregular, and usually results in chemically defective heterounit polymers.

7. Natural Polymers containing Abnormal Units

The examples we have been considering have been drawn mainly from synthetic polymers. In conclusion, therefore, we will cite examples of chemically imperfect macromolecules in natural polymers. Pacsu[163] and Strepikheev[164] showed that such an important natural polymer as cellulose contains, together with cyclic units, abnormal, acyclic units, as in the formula



Natural rubber contains 97–98% of *cis*-1,4-units and a small quantity (2–3%) of *trans*-units with units of different structure[22]. Deoxyribonucoeic acid, which plays such an outstanding part in the transmission of inherited characters, can also contain abnormal units in the chain, whose presence leads to the appearance of mutations and inherited diseases[165,166]. Thus abnormal units appear in appreciable quantities even in the synthesis of polymers in living organisms.

The above examples show that almost all known methods for synthesising and modifying polymers result in the formation of compounds that are heterounit polymers and contain chemically defective macromolecules. In practice, therefore, we are always dealing with heterounit polymers whose macromolecules contain abnormal units.

III. EFFECT OF ANOMALOUS MONOMER UNITS ON CHEMICAL PROPERTIES OF HETEROUNIT POLYMERS

The presence of abnormal units in the chain of a heterounit polymer should undoubtedly have a significant influence on the whole complex of its inherent chemical and physical properties. Primary importance will, of course, attach to the nature and number of abnormal units and their arrangement in the polymer chain. Very little information is yet available which could clearly illustrate the details of such effects, but the general picture has become quite distinct.

Let us consider individual examples of how the chemical properties of a polymer may vary under the influence of abnormal units. The differences between the chemical properties of heterounit polymers and those of the ideal polymer containing only one type of unit, taken as the initial standard for comparison, is larger the more the abnormal units differ from the main units constituting the macromolecule. Thus the formation of a branch in the radical polymerisation of vinyl compounds leads to the appearance in the macromolecule of units containing tertiary hydrogen atoms and side-chains, which are anomalous for this structure. The consequence is diminished resistance to oxidation, since tertiary hydrogen atoms are oxidised very easily, and therefore become points from which chain oxidation reactions begin, leading to degradation of the polymer[167].

Investigation has in fact shown that the thermal degradation of branched polyethylenes is initially considerably more rapid than that of the linear polymers (Fig. 4)[168]: only at 60% breakdown of the polymer do the rates of degradation of the two polyethylenes become equal. It is interesting that the rate of degradation of branched polyethylenes increases with increase in the degree of branching, i.e. in the content of side-chains, as is evident from Fig. 5.[169] Similarly, the branching of polymers containing aromatic rings diminishes their thermal stability, since benzene rings containing three substituents are more easily oxidised, being weak spots in the macromolecule.

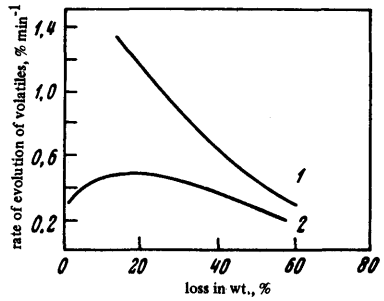


Figure 4. Rate of evolution of volatile products during the heating at 400°C of polyethylene: 1) branched; 2) linear.

The presence of monomer units linked "head to head" in vinyl polymers results in the appearance of anomalous groupings containing adjacent halogen atoms or hydroxy-groups, as e.g. in poly(vinyl chloride) or polyvinyl alcohol[153]



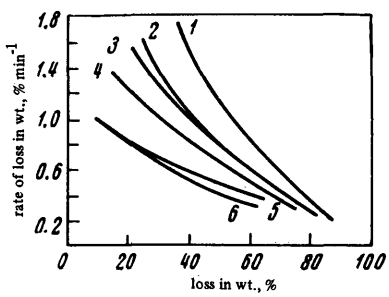
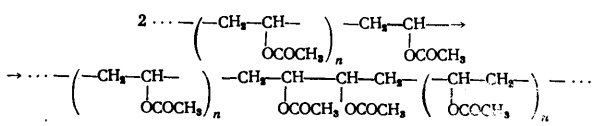
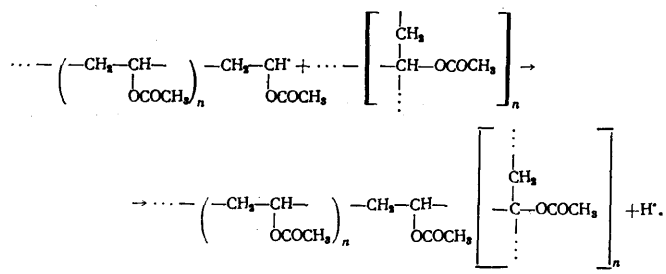


Figure 5. Rate of loss in weight at 400°C for specimens of branched, high-pressure polyethylene having different contents of side-groups (CH_3 per 100 CH_2): 1) 8.7; 2) 6.9; 3) 6.0; 4) 5.6; 5) 3.9; 6) 3.7.

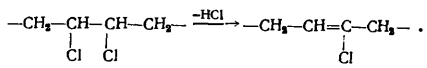
The latter polymer is found to contain ~1% of 1,2-groupings[170], which differ in chemical properties from 1,3-groupings typical of these polymers[153,170]. Such 1,2-groupings may be formed[170] as a result both of the recombination of macroradicals



and of chain transfer



The effect of such anomalous units was shown very clearly in an investigation of the thermal stability of two polymers of vinyl chloride and of vinylidene chloride, in which the units were arranged "head to head" and "head to tail" [171]. Fig. 6 shows that decomposition was slower in the former than in the latter case. The explanation is that, although the first stage in the reaction is more rapid for a "head to head" polymer, it leads to the formation of a stable structure resembling chloroprene, by the reaction



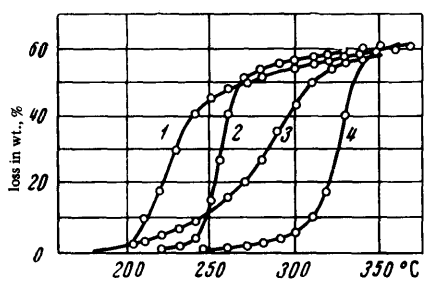
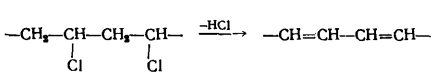


Figure 6. Thermal breakdown of:
1) "head to tail" poly(vinylidene chloride);
2) "head to tail" poly(vinyl chloride);
3) "head to head" poly(vinyl chloride;
4) "head to head" poly(vinylidene chloride).

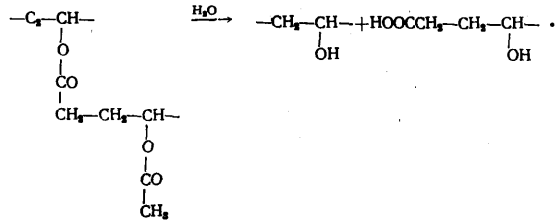
Chain dehydrochlorination is therefore unable to develop further along the macromolecule. In a "head to tail" structure, however, dehydrochlorination



proceeds along the chain until complete. Nevertheless, if abnormal units containing chlorine atoms in the 1,2-positions are present in such a chain, dehydrochlorination will be interrupted.

Examination of poly(vinylidene fluoride) by nuclear magnetic resonance spectroscopy showed that the content of units linked "head to head" varied between 8.6% and 10.6%. [172]

The presence of abnormal units in poly(vinyl acetate) (Section II, 1) results in a decrease in molecular weight on hydrolysis, owing to saponification of the ester bonds [17]:



The polymers of methyl α-chloroacrylate and α-bromoacrylate contain predominantly monomer units linked "head to head" [173]. Monomer units are assumed to be linked in different ways also in polystyrene [54].

Stereochemical relations in the structure of the units in polysaccharides influence their chemical properties especially strongly. Thus natural cellulose and its modification containing 3,6-anhydroglucose as well as glucose units differ in their liability to acid hydrolysis, which according to Rogovin et al. [174] is appreciably lower in cellulose. Similarly, the acetylation of cellulose is slower than that of modified cellulose containing altropyranose units [175]. The presence of anomalous groupings in the cellulose macromolecule, which are more easily hydrolysed than the principal units, facilitates its degradation on hydrolysis, as was shown by Pacsu [163] and by Strepikheev [164]. The increased rate of hydrolysis of cellulose in the first stage is explained by the fact that the abnormal units are "open" structures (Section II, 7), which are less resistant than cyclic structures to acid hydrolysis.

The chemical imperfection of the macromolecules of atactic polymers is shown also in a marked difference in rates of reaction from those of stereoregular polymers [176]. The temperatures at which half the weight of the polymer is lost on heating for 35 min (including heating to this temperature in 15 min) are 295° and 312°C for atactic and isotactic poly(propylene oxide) respectively, and the corresponding activation energies are 20 and 45 kcal mole^{-1}. [176] Similarly, atactic and isotactic polystyrene have activation energies for pyrolysis of 24.5 and 42 kcal mole^{-1}. [177]

The temperature characteristics—primarily the thermal stability—are among the most important indications of the chemical stability of a polymeric structure. The presence of defective units resulting from incomplete cyclisation diminishes the thermal stability of polymers [1,2]. Fig. 7 illustrates the results of a dynamic thermogravimetric analysis showing that a pyrrone is more thermostable than the corresponding poly(amide–aminoacid). However, the observed difference may depend on the dominant importance of dehydration in the acid. Fig. 8 therefore shows the quantities of water and carbon dioxide evolved at various temperatures. Differences are observed not only for water but also for carbon dioxide [127]. Evolution of the latter from the polymeric acid not only begins at a lower temperature than in the case of the pyrrone (200° and 300°C) but also occurs in far larger quantity. It can thus be accepted that defectiveness of the polymer structure consisting of the presence of abnormal units is one cause of the diminution in the thermal stability of polymers [1,127,178].

Polyphenylene, obtained by Marvel's method [27] of dehydrogenating poly-1,4-cyclohexene, has low thermal stability, which is explained by the presence of incompletely aromatised cyclohexene units in its macromolecules.

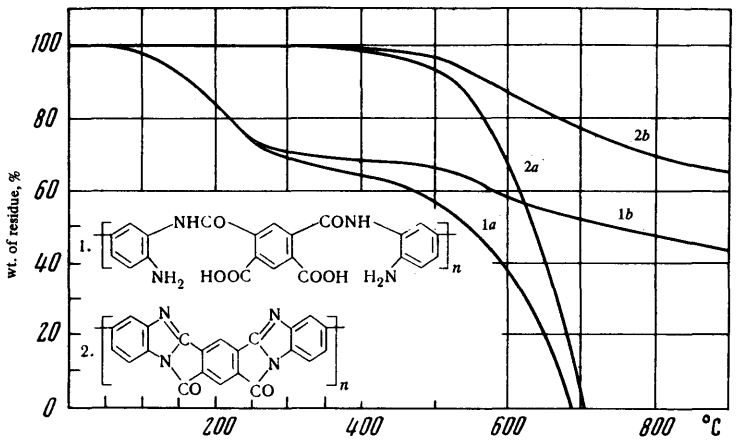


Figure 7. Dynamic thermogravimetric analysis (rate of heating 5 deg min^{-1}) of:
1*a*) poly(amide–amino acid) in air; 1*b*) poly(amide–amino acid) in helium;
2*a*) polybenzoylenebenzimidazole in air; 2*b*) polybenzoylenebenzimidazole in helium.

Hitherto we have been seeing in most cases examples in which the presence of abnormal units impairs the properties of the polymer and is therefore undesirable. However, as we shall see below, there are also cases in which abnormal units improve the thermal, thermo-oxidative, and chemical stability of a polymer.

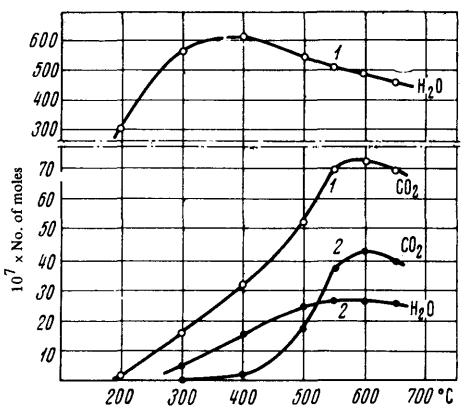


Figure 8. Evolution of water and carbon dioxide in the pyrolysis (15 mg in argon for 8 min) of:
1) poly(amide–amino acid); 2) pyrrone.

The presence of anomalous groupings has a very significant effect on the rate of the thermal depolymerisation of polyvinyl compounds, in most cases slowing it down significantly, as Dolgoplosk and other investigators have shown [179] on several polymers. This self-inhibition of the thermal decomposition of copolymers was shown by Dolgoplosk et al. [179,180] to be due to the difference in activity of the free radicals formed at the end of the chain. If if the radical ...–B· is more reactive, detachment of an A unit will require the consumption, not only of the energy evolved on addition of the monomer A, but also additional energy equal to the difference in energy between the two radicals, i.e. the energy of ...–B· minus the energy of ...–A·; breakdown is then retarded at the stage –A–B–A–A–A–.... If, however, the radical ...–B· is the less reactive, the slowing down occurs at the stage ·B–A–A–A–.... The depolymerisation rate curves in Fig. 9 support this deduction [180].

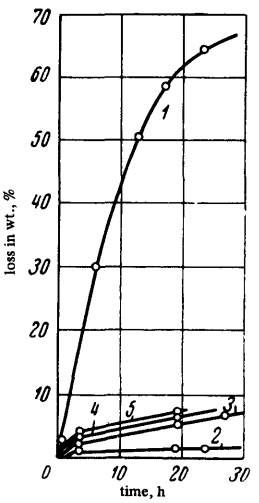
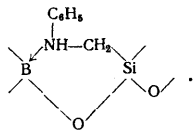


Figure 9. Kinetics of the degradation in air at 200 °C of copolymers of methyl methacrylate with:
1) poly(methyl methacrylate) alone; 2) citraconamide (40%); 3) methylmethacrylamide (40%); 4) hydroxymethylmethacrylamide (7%); 5) methacrylic acid (15%).

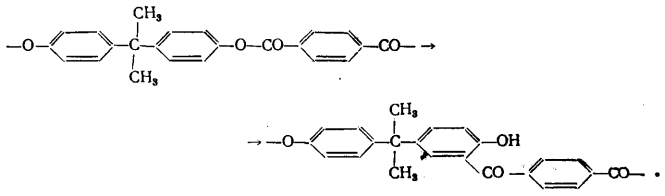
Because of this, copolymers of formaldehyde are also more thermostable than the homopolymer [181]. For the same reason polysilaphenylenesiloxanes are thermally more stable than polysiloxanes [182]. In these cases the

presence of foreign units has a favourable effect, by improving the thermal stability of the polymers.

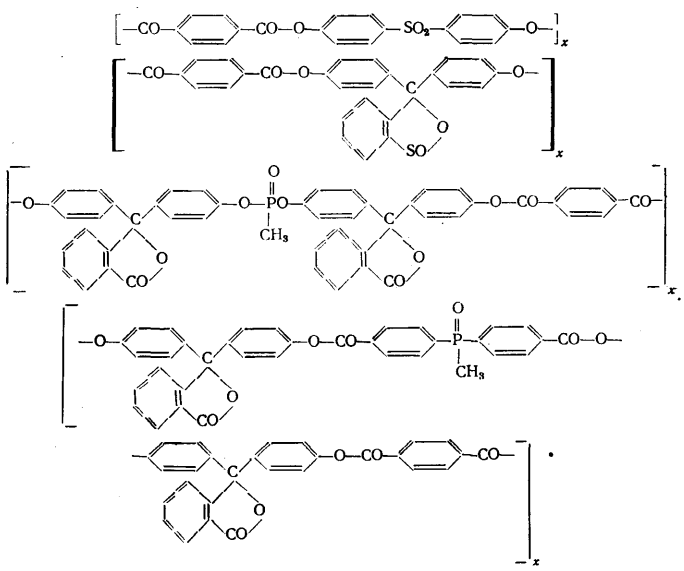
Andrianov's work [183], showing the substantial change in the properties of polymers produced by the introduction of small quantities of "alloying" additives, is most valuable for an understanding of the role of abnormal units. Thus he showed [184] that the presence of anilinomethyl groups attached to silicon greatly increases the hydrolytic stability of polyboraorganosiloxane copolymers, owing to formation of a donor–acceptor bond between boron and nitrogen



We find a similar situation in "self-protecting" polymers [147]. Under the influence of radiation or catalysts, self-protecting polyarenoates undergo the Fries rearrangement, with the formation [109,147] of hydroxybenzophenone units:



The presence of such groupings enhances appreciably the photochemical and the thermal stability of the polymers. A similar improvement in thermal stability is observed on the introduction into polyarenoates of units containing sulpho-groups and phosphine groupings, as in the compounds



Rafikov et al. [185,186] showed that the presence of such groups in these polyarenoates greatly increases their resistance to the action of light and heat.

IV. EFFECT OF ANOMALOUS MONOMER UNITS ON PHYSICAL PROPERTIES OF HETEROUNIT POLYMERS

The physical properties of polymers are also extremely sensitive to the presence of abnormal units, since the latter usually disturb the packing of the polymer chains, which interferes with their crystallisation and the formation of the most compact structures. This is very significant, since structure is a factor governing the physical and especially the mechanical properties of polymers [187]. The presence of abnormal units therefore diminishes the mechanical strength of fibres, films, and other articles made from a given polymer, and conversely raises the solubility and lowers the melting and softening points: i.e. their presence diminishes the heat resistance of polymers. In contrast to this, flawless polymers, containing no abnormal units, should obviously ensure denser packing of the chains, easy crystallisation of the polymer, very strong fibres, films, and other goods, high heat resistance, and sparing solubility.

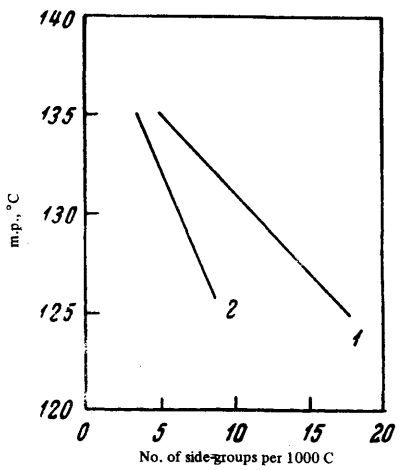


Figure 10. Melting-points of polymethylenes containing different quantities of alkyl groups: 1) methyl; 2) ethyl.

Some support for this suggestion may be found in Preston's work [188], which showed that fibres made from ordered copolymers have higher mechanical strength than fibres made from disordered copolymers with more imperfect heterounit macromolecules. This is suggested also by the effect of side-chains on the properties of polymers. Fig. 10 shows that increase in the content of methyl and ethyl groups lowers the melting point of copolymers [189], ethyl groups being the more effective.

The physical properties of three types of polyethylene (Table 3) show a fall in melting point and decreases in density and crystallinity with increasing degree of branching. The effect of abnormal units is exhibited especially clearly in polymers of butadiene and isoprene: *cis*-1,4-polymers possess the greatest elasticity; the presence of *trans*-1,4- and 1,2-units has an adverse influence on their properties.

Further support may be obtained from data on the effect of the relative imperfection of the structure of a polymer on its temperature characteristics, i.e. its heat resistance and thermal stability. Thus the glass and melting points of copolymers vary significantly with the quantity of the second monomer added [191-193]. Figs. 11 and 12 show a quite clear regularity for copolymers containing only small quantities of the second monomer. Fig. 11 shows the dependence of the glass point of vinyl polymers on the content of a second monomer [191]; Fig. 12 shows the composition dependence of the melting point of mixed polyamides [192,193]. In most cases both glass and melting points fall with increasing content of the second monomer, i.e. with increase in the number of abnormal units in the polymer chain. Since these temperatures depend on the strength of intermolecular forces, and hence on the degree of ordering of the macromolecules, their fall indicates that the second monomer diminishes the degree of order in the polymer and hence the forces of interaction between the macromolecules.

Table 3. Physical properties of various polyethylenes [190].

Property	Polymethylene	High-density polyethylene	Low-density polyethylene
Melting-point, °C	135	125	105—115
Density at 20°C, g cm^{-3}	0.97	0.95	0.92
Crystallinity, %	95	85	60—70

As we have seen, chemical defectiveness of the polymer structure may have a twofold effect on the physical properties: it may either weaken or strengthen intermolecular forces. This applies also to the rigidity of the macromolecules. In this case both the size and the polarity of a substituent are obviously significant. Fig. 13 shows how an abnormal unit containing a side-group or a branching affects the ordering of the macromolecules. The steric effect of a substituent will be in some measure proportional to its size. The final effect should depend also on the quantity of abnormal units. The influence of polarity will obviously be more clearly developed the more polar is the abnormal substituent in comparison with the main substituents, as is evident in a copolymer of vinyl chloride with acrylonitrile.

A clear example of the immense influence of the stereochemistry of units on the properties of a polymer is provided by the polyamides obtained from *cis*- and *trans*-cyclohexane-1,3-diamines with dicarboxylic acids. Fig. 14 shows the variation in melting point of the mixed polyamides containing various quantities of the *cis*- and *trans*-isomers [194]. The effect of the stereoisomerism is very clearly evident: polyamides obtained from the *trans*-diamine have higher melting points.

Chemical imperfection of the macromolecules is also an important factor governing the ability of polymers to crystallise. The more imperfect is a given heterounit polymer, i.e. the more abnormal units it contains and the more disordered their arrangement, the less is the tendency to crystallise under otherwise similar conditions.

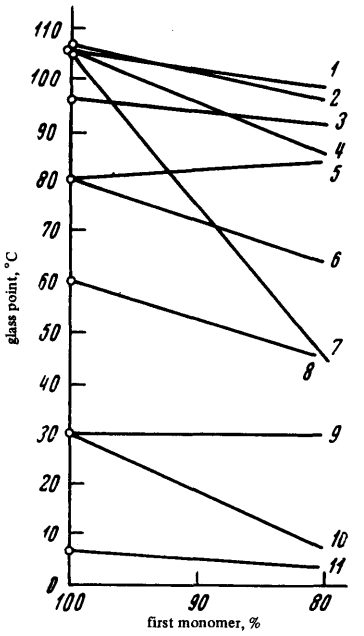


Figure 11. The effect of the nature and the quantity of the second monomer on the glass point of copolymers of:
1) methyl methacrylate with styrene;
2) acrylonitrile with methyl methacrylate;
3) styrene with methyl methacrylate;
4) methyl methacrylate with acrylonitrile;
5) vinyl chloride with acrylonitrile;
6) vinyl chloride with vinyl acetate;
7) methyl methacrylate with butyl acrylate;
8) ethyl methacrylate with butyl acrylate;
9) butyl acrylate with ethyl methacrylate;
10) butyl methacrylate with methyl acrylate;
11) methyl acrylate with butyl methacrylate.

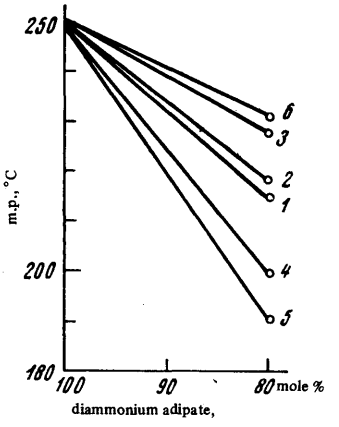


Figure 12. Dependence of melting point of mixed polyamides obtained from hexamethylenediammonium adipate on the nature and the quantity of the second component: 1) hexamethylenediammonium azela-ate;
2) hexamethylenediammonium sebacate;
3) hexamethylenediammonium pimelate;
4) *m*-phenylenediammonium adipate;
5) *m*-tolylenediammonium adipate;
6) 7-aminoheptanoic acid.

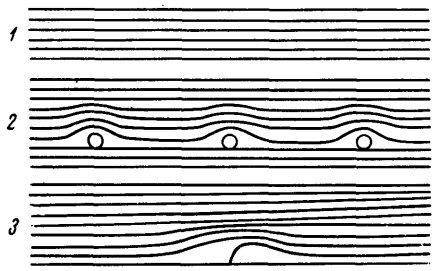


Figure 13. Diagrammatic illustration of effect of chemical defectiveness of macromolecules on their ordering: 1) perfect macromolecules; 2) macromolecules with side-chains; 3) macromolecules with branching.

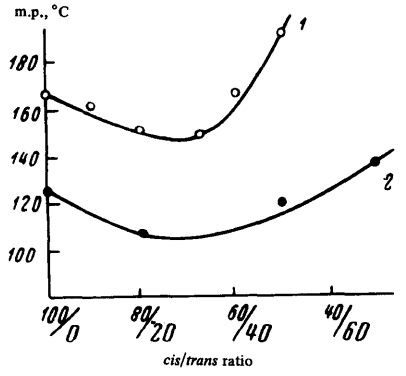
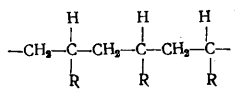
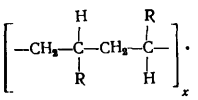


Figure 14. Variation of melting-point with ratio of *cis*- and *trans*-forms of cyclohexane-1,3-diamine for polyamides with: 1) adipic acid; 2) azelaic acid.

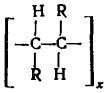
There are several polymers which it has not yet proved possible to obtain in a crystalline state. Among them must first be mentioned the atactic polymers of styrene, methyl methacrylate, propene, vinyl chloride, etc., which are amorphous owing to the disordered arrangement of *dextro*- and *laevo*-units in their macromolecules. In this sense they are also copolymers of the stereoisomeric *dextro*- and *laevo*-forms of the units. When arranged with some regular alternation, however, these same monomer units give readily crystallisable homopolymers—the isotactic polymers



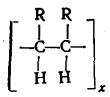
and also a regular copolymer of *dextro*- and *laevo*-forms—a syndiotactic polymer—which, however, can be regarded also as a homopolymer having the longer unit



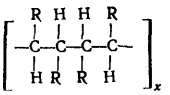
Similarly, the di-isotactic *threo*-polymer



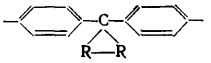
and the di-isotactic *erythro*-polymer



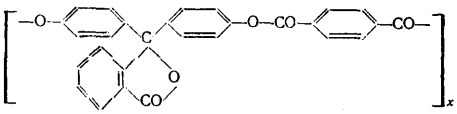
are homopolymers, whereas the disyndiotactic polymer can be regarded either as a copolymer of two different units or as a homopolymer having the longer unit



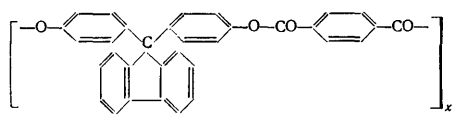
Several polycondensation polymers exhibit a similar effect of monomer structure on ability to crystallise. Thus polyarenoates that are polyesters of dihydric phenols and dicarboxylic acids containing rings and a central carbon atom, of the type



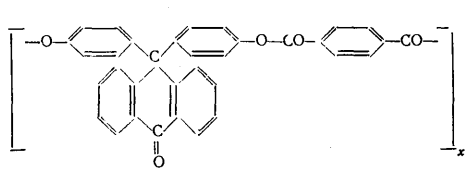
are among the most interesting "card" polymers. They are constructed on the necklace principle: i.e. each unit contains a carbon atom forming part both of the polymer chain and of a side-ring. These polyarenoates are either crystalline or amorphous depending on their structure. Polyarenoates of phenolphthalein having the structure



are non-crystallisable, amorphous polymers [144]. This was explained on the hypothesis that their structure resembles that of atactic polymers: i.e. they have a statistical distribution of an asymmetric substituent (phthalide group) in the repeating unit of such a polyarenoate, which is a heterounit polymer (Section II, 4). Under certain conditions a stereoregular distribution of this substituent could probably be achieved, which would lead to the formation of a crystalline polyarenoate of phenolphthalein. This suggestion is supported by our observation [144] that polyarenoates of card type having a symmetrical cyclic side-substituent are able to crystallise. Examples are the polyarenoates based on 9,9-bis-*p*-hydroxyphenylfluorene (I) and 10,10-bis-*p*-hydroxyphenylanthrone (II)



(I)



(II)

These polyarenoates are crystalline substances, in contrast to those of phenolphthalein.

Similarly, as Batzer showed [195], poly(hexamethylene 2,9-dibutyldecanedioate) does not crystallise, in contrast to the crystalline poly(hexamethylene decanedioate). The reason is that the former polyester is also an atactic heterounit polymer, because the racemic form of the initial acid was taken, so that the polymer has an irregular distribution of butyl groups. The copolymer obtained from decanedioic and 2,9-dibutyldecanedioic acids begins to crystallise only when their proportions are 5 : 1, which corresponds to a content of one butyl group for every 54 atoms in the polymer chain [195]. In this case the presence of abnormal units becomes sufficiently minor not to prevent crystallisation of the polyester.

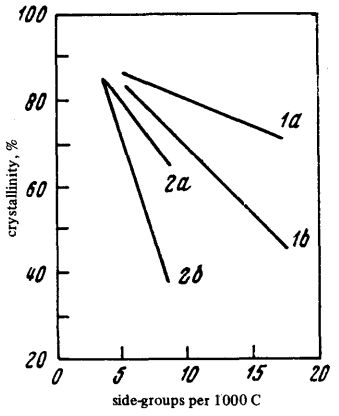


Figure 15. Crystallinity of branched polymethylenes determined by different methods:
1*a*) methyl groups by X-ray examination;
1*b*) methyl groups by differential thermal analysis;
2*a*) ethyl groups by X-ray examination;
2*b*) ethyl groups by differential thermal analysis.

We may recall also that, when carbyne is heated to 1000°C, the abnormal units

$$-C\equiv C-CH=C=C=,$$

split off hydrogen

$$-C\equiv C-CH=C=C= \xrightarrow{-H} -C\equiv C-C\equiv C-C\equiv C-$$

which results in conversion of the polymer into a crystalline form [114]. As a consequence of this reaction, the heat-treatment of carbyne enhances its crystallinity.

A detailed investigation of the dependence of crystallinity on the number of abnormal groups has been made on polymethylenes containing various quantities of methyl or ethyl groups, obtained by copolymerising diazomethane with diazoethane or diazopropane [189]. Fig. 15 shows that ethyl groups have a stronger effect than methyl groups in diminishing crystallinity. The amorphous content is greatly increased by the presence of branching in the polyethylene macromolecules (Fig. 16) [196].

The density of polymers changes significantly with increasing imperfection of the macromolecules: it usually decreases with increase in the content of abnormal units. The presence of branches has a similar effect: thus unbranched polymethylene has a density of 0.971, slightly branched low-pressure polyethylene 0.95–0.96, and strongly branched high-pressure polyethylene 0.92 to 0.93 (Table 4). The densities of copolymers obtained from diazomethane and other diazoalkanes [189] are also given in Table 4, from which it is evident that increase in the number and length of the side-chains diminishes the density of the polymer. The variation in the density of polyethylene with degree of branching illustrated in Fig. 17 shows a decrease in density with increase in content of methyl groups [197].

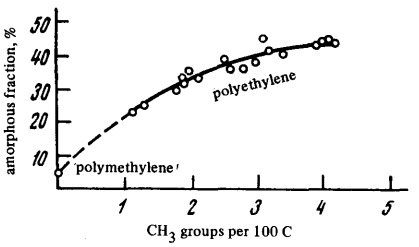


Figure 16. Dependence of content of amorphous material on degree of branching of polyethylene macromolecules.

The solubility of polymers also is extremely sensitive to the presence of abnormal units in the macromolecule: it is usually increased by increase in their content and their disordered arrangement. This is illustrated (Fig. 18) by the dependence of the temperature of dissolution of polymethylenes containing branched macromolecules on the number of branches [16].

Table 4. Properties of copolymers.

Polymeric material	Mode of preparation	Density
Polymethylene	polymerisation of diazomethane	0.971
Polymethylene with side-groups :		
methyl	diazomethane–diazoethane copolymer	0.939
ethyl	diazomethane–diazopropane copolymer	0.952
Polyethylene with ethyl side-chains	ethylene–but-1-ene copolymer	0.957
Crystalline ethylene–propene block copolymer	copolymerisation of ethylene and propene	0.917

Enhancement of solubility is observed also in many copolymers. Homopolyamides usually dissolve only in acids, phenols, and amides, whereas their copolymers and mixed polyamides dissolved even in aqueous alcohol. Fig. 19 shows how the solubility of mixed polyamides varies with their composition [198].

We have thus been considering many of the methods for synthesising polymers known at the present time, and have shown that they are all accompanied by various side-reactions. These result in the formation of abnormal units in the macromolecule, and the consequent chemical defectiveness characteristic of heterounit polymers. Abnormal units appear not only during polymerisation and polycondensation but also in the course of copolymerisation and copolycondensation.

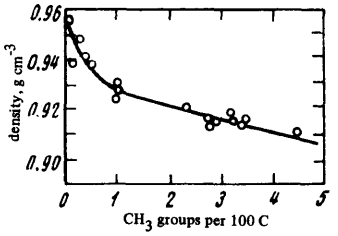


Figure 17. Dependence of density of polyethylene on degree of branching.

Various reactions involving substitution in the polymer chain also lead to the appearance of abnormal units and the formation of heterounit polymers. It is undoubtedly possible to influence the number and distribution of the abnormal units thus formed, which is an important task of synthetic polymer chemistry. The significance of studying the chemical imperfection of the macromolecule structure is that it has a great influence on the chemical and physical properties of polymers, as has been illustrated by the series of examples of heterounit polymers given here.

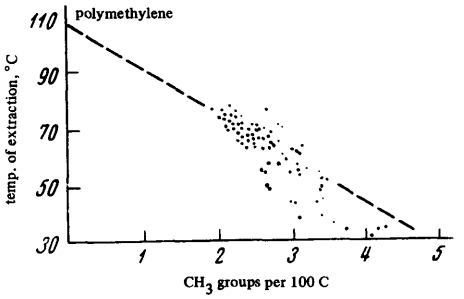


Figure 18. Dependence of temperature of dissolution on degree of branching of polyethylene macromolecules.

Finally we conclude that these examples quite clearly illustrate the effect of various reactions leading to the formation of abnormal units and hence the production of heterounit polymers of general formula $[[M]_m-[A]_n]_x$.

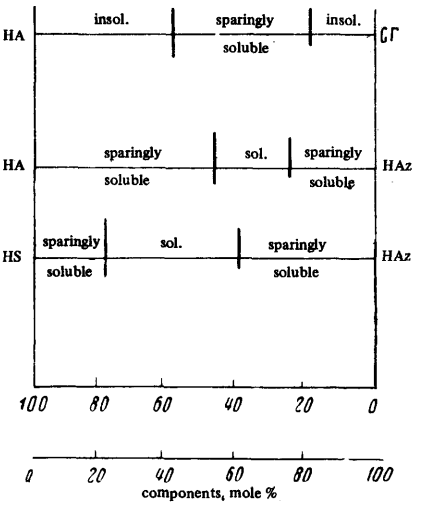


Figure 19. Effect of composition of copolymers on their solubility in ethanol: HA = hexamethylenediammonium adipate; HS = hexamethylenediammonium sebacate; HAz = hexamethylenediammonium azela-ate.

This feature of polymerisation and polycondensation processes, and also of substitution in polymer chains, has not yet been investigated systematically, so that our knowledge in this field is still largely haphazard. However, it can be concluded from the above results that almost all real polymers comprise heterounit macromolecules, while homounit polymers, containing no abnormal units, are rare exceptions. Hence this must be taken into account in considering the problem of the relation between the structure and the properties of polymers, since the concept of heterounit polymers as the main type of polymeric structure acquires fundamental importance for polymer chemistry.

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