CHEMICAL DEFECT OF HETERO-UNIT POLYMERS AND ITS EFFECTS

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ABSTRACT

Consideration of various routes to the synthesis of polymers leads us to a conclusion that all reactions of such types are accompanied by various side reactions which are responsible for chemical defect of the macromolecule of the resulting polymer.

The chemical defect consists primarily in the presence of anomalous units which differ in their structure from most units forming this macromolecule. Such polymers with anomalous units, it is proposed, should be called 'hetero-unit' polymers.

Many known reactions for the preparation of high molecular weight compounds by the polymerization and polycondensation of low molecular weight monomers and by the modification of various polymers are discussed in this report.

Polymers resulting from these reactions are shown to be hetero-unit polymers, since they contain chemically defective units in the chain. The following formula is proposed for denoting the hetero-unit polymers

$$-\!\!\left[(M)_{\boxed{m}}-(A)_{\boxed{n}}\right]_x$$

The anomalous units have considerable effect on the chemical and physical properties of the polymers.

Most high molecular weight compounds known at the present time are 'hetero-unit' polymers; 'single-unit' polymers, i.e. those without anomalous units, are rare exceptions. This fact should be taken into consideration when studying the relation between the properties of polymers and their structure. On the other hand the methods for synthesis of various polymers should be improved to obtain polymeric structures without defect.

The specific character of high molecular weight compounds was explained by their molecular chain structure composed of recurring units described by the formula $-(A)_x$.

Such a macromolecular concept secured the rapid development of polymer chemistry and continues to contribute to it at the present time. It could explain many specific features of polymers, those of their chemical reactions and physical properties.

However, further development of science and engineering nowadays poses more and more complicated problems and requirements for polymeric materials, without which modern techniques cannot function.

In order to solve these problems one must know the structure of all units of the macromolecule and their mutual arrangement to be able to control the ratio of hetero-units and to determine the conditions and ways of introducing them into the molecule of hetero-units polymers.

It would be no overstatement to say that the modern stage of development of polymer science is that in which the synthesis, investigation and application of hetero-unit polymers characterized by molecular heterogeneity are predominant directions. And the above-mentioned problems of modern science and engineering can be solved only in this way.

Heterogeneity of the hetero-unit polymers is largely caused by a chemical defect of the macromolecule of the polymer[1–3].

In general, the chemical defect of the macromolecular structure results from the incorporation of anomalous units differing structurally from the basic ones.

It is known that any chemical reaction is accompanied by the formation of a greater or lesser amount of byproducts along with the main compounds. Usually, the yield of the main product points to the share of the main reaction. The byproducts are removed by purification and consequently do not affect the quality of the main products, decreasing the yield of the latter only. However, in the case of polymer formation all byproducts remain in the resulting polymer as anomalous units, and this is one of the causes of the chemical defect of the polymer. Although we denote the general formula of the polymer as $-(\mathrm{M})-_{x}$, where M is the monomer residue, this is, nevertheless, an idealized formula. It would be better to use for description of the real polymer the formula $-[(\mathrm{M})_{\boxed{m}}-(\mathrm{A})_{\boxed{n}}]-_{x}$, where A is the anomalous unit, and M are the normal units[1–3].

Let us briefly discuss the types of chemical defect of macromolecules and the manner of formation of the corresponding anomalous units.

(1) Formation of anomalous units during polymerization and polycondensation processes due to crosslinking, branching, and side-group formation.

(2) Difference in the 'head-to-head' or 'head-to-tail' combinations of the units in the course of polymerization and polycondensation.

(3) In radical polymerization, the double bonds can be formed either in the chain or in the side branches.

(4) As a result of branching tertiary atoms of hydrogen or halogen can be produced.

(5) Isomerization during polymerization and polycondensation.

(6) Formation of anomalous units due to the difference in the configuration of the asymmetric carbon atoms (tacticity) which compose the chain of the macromolecule.

(7) Formation of anomalous units due to the difference in the configuration of the groups with central, axial, and planar asymmetry.

(8) Difference in geometrical isomerism of the units formed in the polymerization of dienes and of those containing disubstituted cycles.

(9) Difference in the structure of the units owing to conformation asymmetry and hindered rotation of the units (rotational isomerism).

(10) Anomalous units formed by incomplete trimerization in the polycyclotrimerization of dienes.

(11) Anomalous units as residues of incomplete formation of carbo- or heterocycles in polycyclization or polycyclocondensation.

(12) Formation of anomalous units by copolymerization and copolycondensation.

(13) Anomalous units resulting from irregular substitution and other chemical reactions of units in the macromolecule (chlorination, oxidation, dehydration etc.).

(14) Anomalous units resulting from the random arrangement of the crosslinks in three-dimensional crosslinked polymers.

(15) Anomalous units resulting from statistical arrangement of the units with different configuration in atactic polymers.

(16) Graft and block copolymers as one of the types of defective macromolecules.

(17) Aromatic groups in the aliphatic chain, as well as aliphatic units irregularly arranged among the aromatic groups.

(18) Hydroaromatic units arranged among the aromatic groups as a result of incomplete aromatization and hydrogenation.

(19) Different arrangement of the substituents in the aromatic cycle (*o*-, *m*-, *n*-, etc.).

(20) Formation of anomalous units in the macromolecules of naturally occurring polymers.

Let us consider several routes to the formation of chemical defects in macromolecules in the synthesis and transformations of polymers.

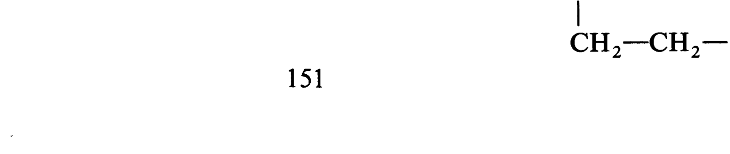
1. FORMATION OF ANOMALOUS UNITS IN POLYMERIZATION PROCESSES

In polymerization processes of the unsaturated compounds proceeding by a radical or ionic mechanism such reactions as recombination of macroradicals, intra- and intermolecular chain transfer, isomerization of the unit etc. leading to the formation of anomalous units take place. In the first case, the anomalous group —CHX—CHX is formed as a result of recombination

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

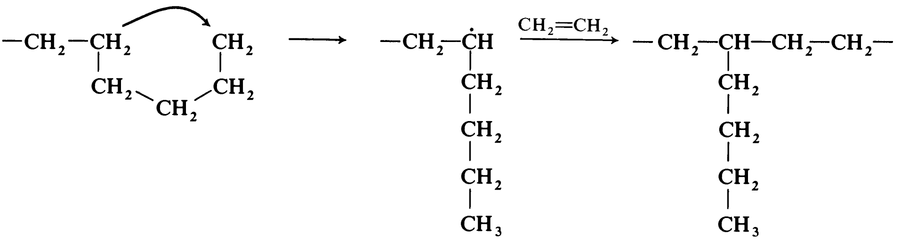
In the second case, long and short branches and side groups of various lengths appear as a result of the chain transfer.

Such units are produced by the chain transfer reaction and, therefore, it is suggested that they are present in all polymers obtained by radical polymerization. For some polymers of this type the presence of such units has been confirmed experimentally^4. Long branches are formed by intermolecular chain transfer according to the reaction

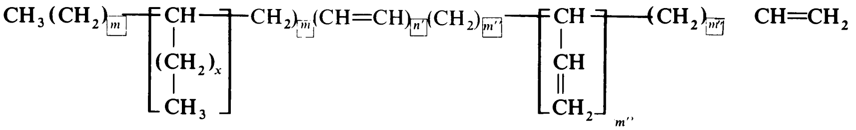


$$-CH_2-CH_2-CH_2-CH_2-\xrightarrow{R^{\cdot}}-CH_2-CH_2-\dot{C}H-CH_2 \xrightarrow{CH_2=CH_2} -CH_2CH_2-\underset{\displaystyle CH_2-CH_2-}{\underset{|}{C}H}-CH_2-$$

Short branches are produced by intramolecular chain transfer according to the equation[5]



Because of this, polyethylene obtained by radical polymerization (low density polyethylene) contains such side groups as ethyl or butyl, and also longer branches. Moreover, its macromolecule has double bonds both in the main chain and in the side branches[6]. Consequently, the real structure of polyethylene can be schematically represented as follows

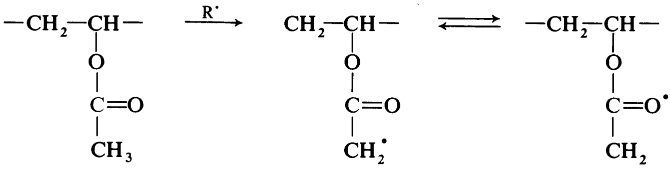


$$CH_3(CH_2)_{m}\left[\begin{array}[t]{c}CH\\|\\(CH_2)_x\\|\\CH_3\end{array}\right](CH_2)_{m}(CH=CH)_{n'}(CH_2)_{m'}\left[\begin{array}[t]{c}CH\\|\\CH\\\|\\CH_2\end{array}\right](CH_2)_{m''}\quad CH=CH_2$$

where $n = 20–40$, $n' = 1–2$, $n'' = 1–2$, $x = 1–1000$ for the low density polyethylene, and $n = 1–2$, $n' = 1–2$, $n'' = 1–2$, $x = 0–10$ for the high density polyethylene.

Investigations on the copolymerization of ethylene with vinylacetate have shown that the degree of branching increases with temperature[5].

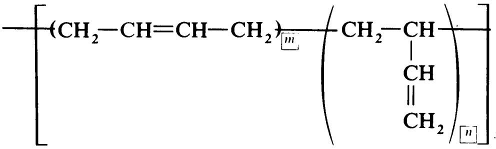
With polyvinylacetate, branches resulting from chain transfer through the acetyl group are possible[7]



$$-CH_2-\begin{array}[t]{c}CH-\\|\\O\\|\\C=O\\|\\CH_3\end{array}\xrightarrow{R^{\cdot}}CH_2-\begin{array}[t]{c}CH-\\|\\O\\|\\C=O\\|\\CH_2^{\bullet}\end{array}\rightleftarrows-CH_2-\begin{array}[t]{c}CH-\\|\\O\\|\\C=O^{\bullet}\\|\\CH_2\end{array}$$

The polymerization of diene compounds is a process rather sensitive to the conditions. Therefore, polymers with various structures can be produced. Dolgoplosk and Tinyakova[8] studied the mechanism of diene polymerization and the microstructure of the resulting polymeric chain and showed that the polymerization of butadiene can lead to the formation of polymers containing units bonded in the 1,2- and 1,4-positions, to *cis*- and *trans*-configurations, as well as to cyclic units and some other structures.

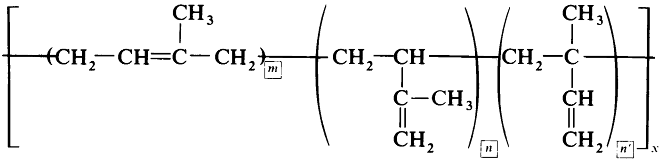
In the case of the polymers of isoprene, 3,4-units can additionally be formed[9]. Hence, in the diene polymers we observe a variety of anomalous units. For instance, the first sorts of synthetic rubber prepared by the Lebedev method[10] using polymerization of butadiene under the action of metallic sodium are polymers containing butadiene units bonded in the 1,2- and 1,4-positions both to *cis*- and to *trans*-configurations[11]



$$\left[\mathrm{(CH_2{-}CH{=}CH{-}CH_2)}_m\left(\mathrm{CH_2{-}\underset{\substack{|\\ CH\\ \|\\ CH_2}}{CH}}\right)_n\right]_x$$

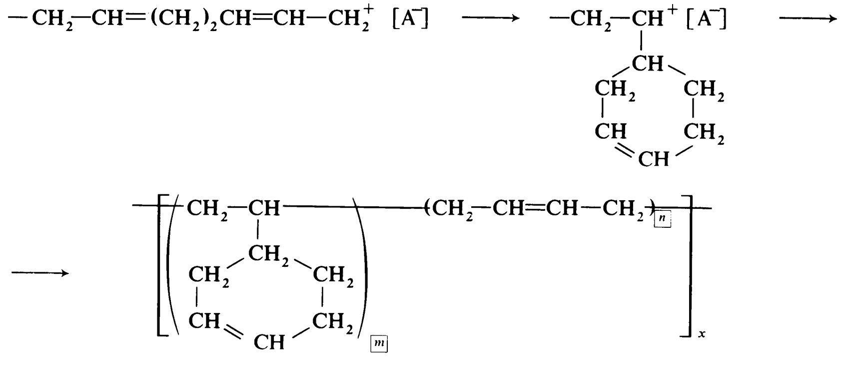
The polymers of butadiene and isoprene obtained in the presence of organometallic catalysts contain much less anomalous units. Thus, polyisoprene produced in the presence of the complex [$TiCl_4 + Al(C_2H_5)_3$] and in the presence of lithiumalkyl catalysts contains 96 per cent of *cis*-1,4-units[12, 13].

Polyisoprene prepared in the presence of π-allyl nickel iodide contains 95 per cent of 1,4-*trans*-units, 1 per cent of 1,2-units, and 4 per cent of 3,4-units. Its structure can be represented as follows[14]

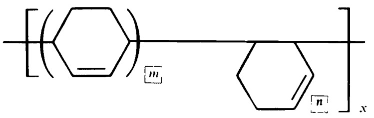


$$\left[\mathrm{(CH_2{-}CH{=}\overset{\substack{CH_3\\|}}{C}{-}CH_2)}_m\left(\mathrm{CH_2{-}\underset{\substack{|\\ C-CH_3\\ \|\\ CH_2}}{CH}}\right)_n\left(\mathrm{CH_2{-}\underset{\substack{|\\ CH\\ \|\\ CH_2}}{\overset{\substack{CH_3\\|}}{C}}}\right)_{n'}\right]_x$$

In the cationic polymerization of butadiene Dolgoplosk *et al.*[8, 15] observed the formation of six-membered cycles according to the equation



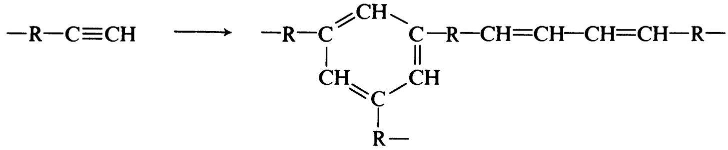
Depending on the nature of the catalyst, the polymerization of 1,3-cyclohexadiene yields polycyclohexene with various degrees of chemical defect. In the presence of organometallic and Ziegler catalysts a polymer with 1,2- and 1.4 units is formed[16]



When π-allylnickel iodide is used as a catalyst, a polymer containing 83 per cent of 1,4-units forms[14].

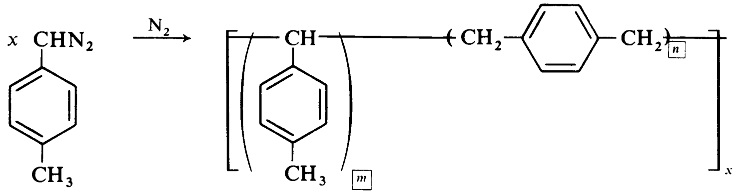
Atactic polymers formed by both radical and ionic polymerization belong to the compounds consisting of hetero-units and having some other randomly-arranged l-units, which is generally characteristic of the polymers prepared by radical polymerization[17]. Natta showed[18] that the difference in the unit structure falls into the field of stereochemistry. Indeed it would be better to consider the atactic polymers as statistical copolymers of the d- and l-forms unlike the regular copolymer of these forms, i.e. the corresponding syndiotactic polymer.

In the course of polycyclotrimerization of bis-acetylene derivatives, which gives polyphenylenes, defect units are formed which are a residue of the incomplete cyclization proceeding according to the equation[19]

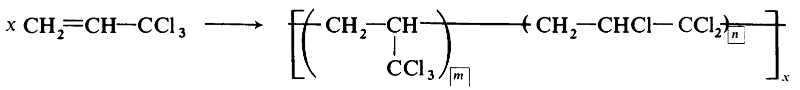


2. ANOMALOUS UNITS AS A RESULT OF ISOMERIZATION OF UNITS IN THE COURSE OF POLYMERIZATION

In the course of some polymerization processes the isomerization of the resulting units can be observed. This gives hetero-unit polymers of two and more types. For instance, Korshak *et al.*[20] showed that in the polymerization of 4-methylphenyldiazomethane isomerization leading to an appreciable amount of the *p*-xylylene units takes place along with the formation of normal 4-methylbenzylidene units. Because of this the structure of the resulting polymer will be as follows

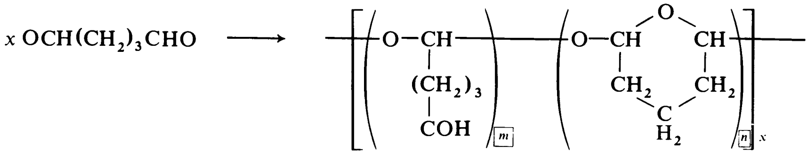


Suprun *et al.* found[21] that the polymerization of 3,3,3-trichloropropene-1 by isomerization accompanied by the transfer of the chlorine atom yields a hetero-unit polymer of the following structure

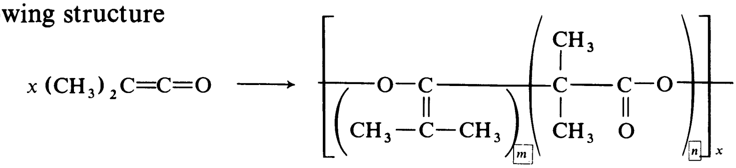


$$x\,CH_2{=}CH{-}CCl_3 \longrightarrow \left[\left(CH_2{-}\underset{CCl_3}{CH}\right)_m\left(CH_2{-}CHCl{-}CCl_2\right)_n\right]_x$$

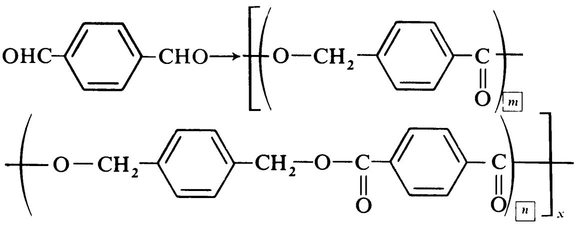
The polymerization of glutaric aldehyde proceeds by two routes to give a hetero-unit polymer of such a structure[22] as



According to the data of Natta *et al.*[23] dimethylketone polymerizes in the presence of trimethylaluminium to yield polyketone–polyacetal of the following structure

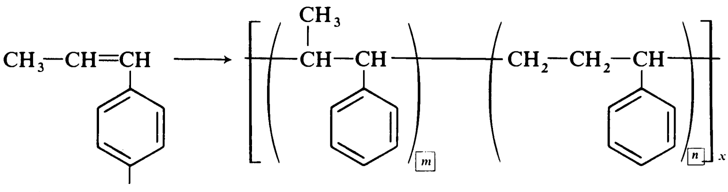


An unusual course has also been observed for the polymerization of terephthalic aldehyde in the presence of organometallic compounds of aluminium and zinc to yield hetero-unit polyesters of the following structure[24]



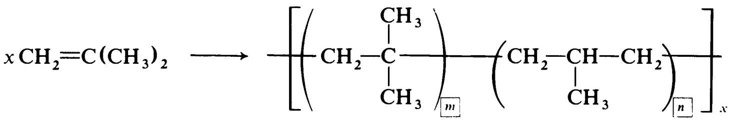
Ionic polymerization of some vinyl compounds, substituted styrenes and vinylpyridines often proceeds as a migration polymerization with hydrogen transfer to give hetero-unit polymers containing carbo- and heterocycles and other anomalous units in the main chain[25, 26].

The first reaction of this type of isomerization polymerization with hydrogen transfer would probably be the polymerization of β-methylstyrol[28] studied by Staudinger[27] which results in the case of β-methylstyrol in a hetero-unit polymer of feasible structure

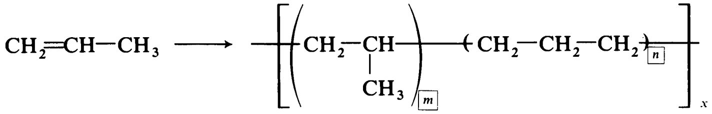


Kennedy[28] showed that a similar polymer can also be produced by the cationic polymerization of allylbenzene.

Topchiev *et al.*[29] showed that the isomerization polymerization of isobutylene leads to the formation of the following hetero-unit polymer

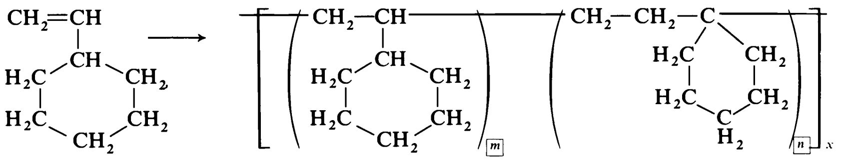


It has been shown[30] that with propylene a hetero-unit polymer is formed which is similar to the copolymer of ethylene and propylene and has the following structure



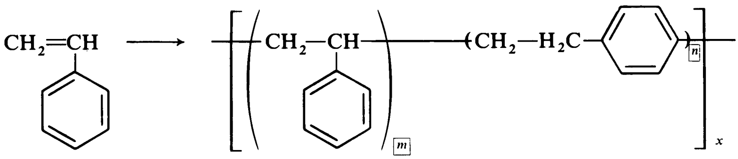
$$CH_2{=}CH{-}CH_3 \longrightarrow \left[\left(CH_2{-}\underset{CH_3}{CH}\right)_{\boxed{m}}\left(CH_2{-}CH_2{-}CH_2\right)_{\boxed{n}}\right]_x$$

Vinylcyclohexene in ionic polymerization gives a hetero-unit polymer containing, along with the normal units, also anomalous units in which the cyclohexene cycle is in the polymeric chain[31]

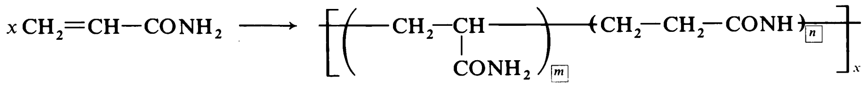


Anomalous units of such a type are characteristic of the cardo polymers.

The isomerization polymerization of styrene yields a polymer containing both the styrene and *p*-xylylene units of a structure[32]

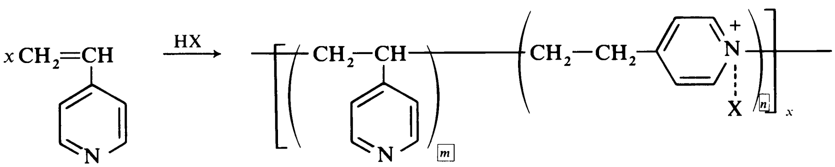


Acrylamide isomerizes in the presence of basic catalysts and gives a hetero-unit polymer[26]

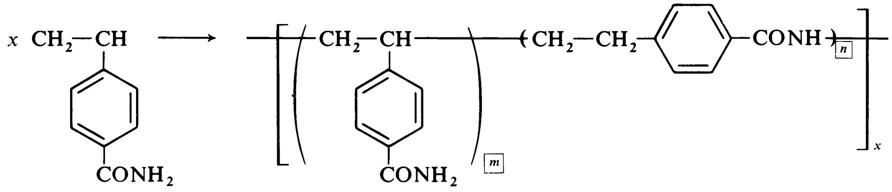


$$x\,CH_2{=}CH{-}CONH_2 \longrightarrow \left[\left(CH_2{-}\underset{CONH_2}{CH}\right)_{\boxed{m}}\left(CH_2{-}CH_2{-}CONH\right)_{\boxed{n}}\right]_x$$

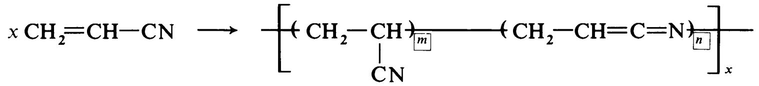
The polymerization of 4-vinylpyridine in the presence of acids proceeds with hydrogen migration to give a polymer containing pyridiniumethyl units[33]



The anionic polymerization of vinylbenzamide yields a hetero-unit polymer containing normal and anomalous units in various ratios[26]



The x-ray[34] or high-speed electron action[35] polymerization of acrylonitrile yields a hetero-unit polymer containing up to ten per cent of keteneimine structures



$$x\,CH_2{=}CH{-}CN \longrightarrow \left[(CH_2{-}\underset{CN}{CH})_{\boxed{m}} \text{---} (CH_2{-}CH{=}C{=}N)_{\boxed{n}} \right]_x$$

3. FORMATION OF ANOMALOUS UNITS BY COPOLYMERIZATION

The copolymerization reaction leads to the formation of copolymers containing other units in various amounts and ratios, and because of that they are considered to be hetero-unit polymers. It should be emphasized that in this case both the amount of other units and their arrangement are of particular importance. Thus, the regular alternation of units gives not a copolymer, but a true homopolymer with long units, as for instance in the copolymerization of sulphur dioxide with unsaturated compounds which leads to the formation of polysulphones

$$xSO_2 + x\,CH_2{=}CHR \rightarrow {-}(CH_2{-}CHR{-}SO_2)_x{-}$$

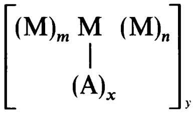
or in the migration copolymerization of diols or diamines with diisocyanates which leads to the formation of polyurethanes or polyureas:

$$-(O{-}CH_2{-}CH_2{-}O{-}CO{-}NHC_6H_4NHCO)_x-$$

$$-(CH_2{-}CH_2{-}NH{-}CO{-}NHC_6H_4NH{-}CO{-}NH)_x-$$

Among the above-mentioned types of copolymers the copolymers with regular alternation of units should be considered as homopolymers. Their structure can be represented by the following general formula: $-(M{-}A)_x-$, while in the case of statistical copolymers which are also hetero-unit polymers the general formula of their structure will be as follows: $-[(M)_{\boxed{n}}(A)_{\boxed{m}}]_x$, where $n = 1, 2, 3$, etc., $m = 1, 2, 3$, etc. and $n \neq m$. Consequently, the regular copolymer is again formed with $n = m$. The block-copolymer will be represented by the same general formula but $n \neq m$, $n > 10$, and $m > 10$.

For the graft copolymer the general formula will be



$$\left[(M)_m \underset{(A)_x}{\underset{|}{M}} (M)_n \right]_y$$

where $n + m > 1000$, $y = 1$–10 and upwards, $x > 10$.

A more detailed discussion of copolymerization and the properties of copolymers is beyond the scope of this report; we shall restrict ourselves to the above-mentioned examples which illustrate the fact that the great majority of copolymers are hetero-unit polymers.

4. FORMATION OF ANOMALOUS UNITS IN THE COURSE OF POLYCONDENSATION

In the course of investigations of the common tendencies of polycondensation reactions two groups of polycondensation processes have been revealed, which differ essentially in the mechanism of their reactions and which have been called 'equilibrium' and 'non-equilibrium' polycondensation. In discussing separate examples of reactions of each of these polycondensation types these differences should, therefore, be taken into consideration[36–38].

In the polycondensation reaction hetero-unit polymers can be formed in various ways.

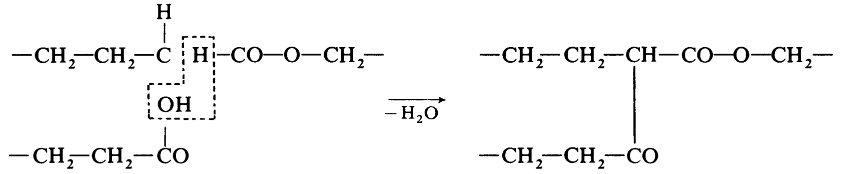
Similar to the reactions considered above and taking place in various polymerization reactions, in the course of polycondensation reactions are also possible which lead to the formation of anomalous units: units containing side groups and branches, crosslinks, anomalous groups in the main chain, and all possible stereochemically different units leading to the formation of macromolecules with a structure similar to that of the atactic, isotactic and syndiotactic polymers prepared by stereospecific polymerization. The term 'tacticity' as applied to the polycondensation polymers has its specific meaning[39]. This term is applied to units containing carbon atoms with two different substituents, to *cis*- and *trans*-isomers with multiple bonds and a twice substituted cycle, as well as to groups with central axial and planar asymmetry. In this case, in complex polymeric structures stereoregular structures can also result from the stable conformations[40]. An important cause of the formation of anomalous units is also the residue of uncyclized units in polycyclization and polycondensation.

Let us consider some cases of the formation of hetero-unit polymers in the course of equilibrium polycondensation.

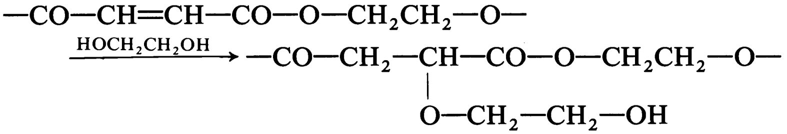
For instance, the equilibrium polycondensation of ethyleneglycol with terephthalic acid or its dimethyl ester in the presence of most catalysts leads[41] to the formation of polyethyleneterephthalate which melts at 256°C. But the use of the sulphuric acid gives a lower melting polyester due to the formation of the hetero-unit polymer containing ether bonds

$$\left[(OCH_2CH_2OCOC_6H_4CO)_{m}(OCH_2CH_2OCH_2CH_2OCOC_6H_4CO)_{n}\right]_x$$

Staudinger and Schmidt[42] observed the formation of branched polyesters on prolonged heating of the reaction mixture. They explain this phenomenon by dehydration proceeding according to the scheme



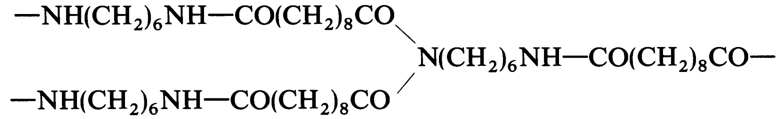
If in the polycondensation unsaturated monomers such as maleic or fumaric acids are used, during the polyesterification the addition of glycol to the double bond takes place to form esters of hydroxyethoxysuccinic acid according to reaction[43]



$$\mathrm{-CO-CH{=}CH-CO-O-CH_2CH_2-O-} \xrightarrow{\mathrm{HOCH_2CH_2OH}} \mathrm{-CO-CH_2-}\underset{\underset{\mathrm{O-CH_2-CH_2-OH}}{|}}{\mathrm{CH}}\mathrm{-CO-O-CH_2CH_2-O-}$$

In the polycondensation with glycols maleic acid isomerizes to fumaric acid, which results in polyesters which are hetero-unit polymers, but can also be considered as copolymers of maleic and fumaric acids[44]. The conversion depends both on the glycol nature and the conditions of polycondensation and can be as high as 70–90 per cent.

On prolonged heating in the melt during synthesis the polyamides give branched products of the following structure

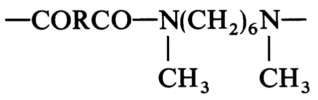


Such observations were made by Champetier and other authors for both aliphatic and aromatic polyamides[45, 46].

Thomas showed[47] that on preparation of polyamides from diamines and dicarboxylic acid ethers at elevated temperatures alkylation of diamine is possible

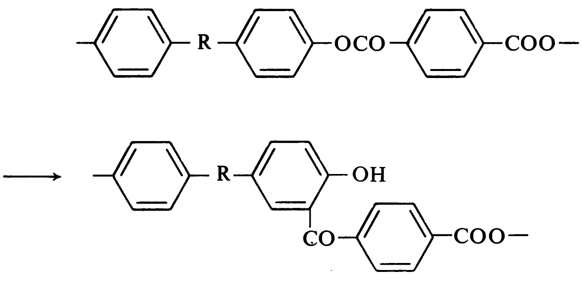
$$\mathrm{H_2NRNH_2 + 2R^{\bullet}COOCH_3 \rightarrow CH_3NHRNHCH_3 + 2R^{\bullet}COOH}$$

which leads to the formation of methyl side groups of the polyamide



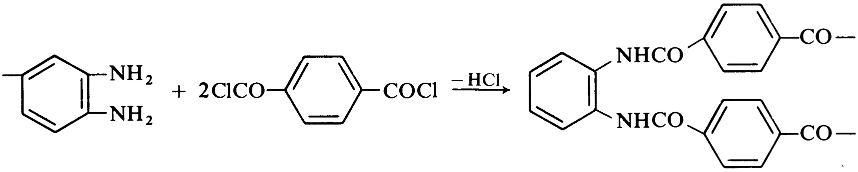
$$\mathrm{-CORCO-}\underset{\mathrm{CH_3}}{\mathrm{N}}\mathrm{(CH_2)_6}\underset{\mathrm{CH_3}}{\mathrm{N}}\mathrm{-}$$

In non-equilibrium polycondensation branched polymers can result from direct acylation or a rearrangement similar to the Friese rearrangement. Thus, in the synthesis of polyarylates the branches can be formed as follows[48]

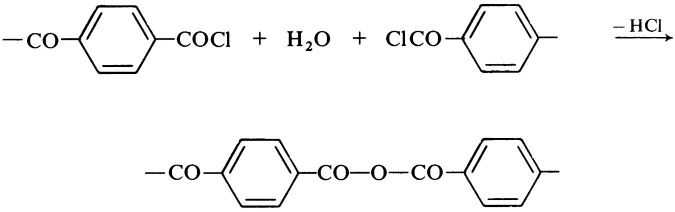


Phenol hydroxyl can further react with acid chloride to give branches.

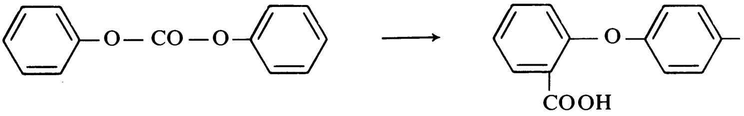
In the reaction of dicarboxylic acid dichloride with tetramines, bis-(*o*-hydroxyamines), and bis-(*o*-thioamines) the branches can be formed by the following reaction[49]



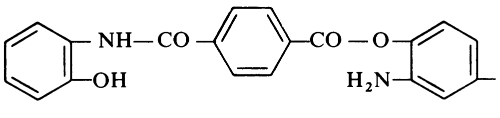
In the case of low temperature polycondensation of acid chlorides with bis-phenols the presence of moisture traces can give rise to the formation of anhydride groups in the macromolecule



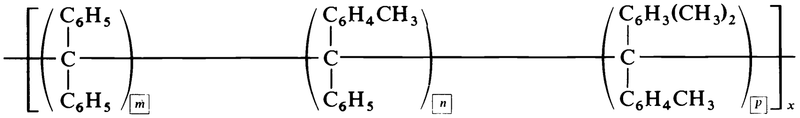
Schnell suggests[50] that in the preparation of polycarbonates from diphenylcarbonate a side reaction of the Kolbe type is possible, which yields branched and crosslinked structures



In the polycondensation of dicarboxylic acid dichlorides with bis-(*o*-hydroxyaminophenyl)methane, bis-(*o*-thioaminophenyl)methane and their analogues and homologues the reaction can proceed in two possible directions, which would give anomalous units of the isomeric structure, as for instance



In polyrecombination of diphenylmethane a side reaction of the methylation of benzene cycles by methyl radicals takes place. Because of this the resulting polymer contains tolyl and xylyl groups[51]



$$\left[\left(\begin{array}{c}C_6H_5\\ |\\ -C-\\ |\\ C_6H_5\end{array}\right)_{\boxed{m}}\left(\begin{array}{c}C_6H_4CH_3\\ |\\ -C-\\ |\\ C_6H_5\end{array}\right)_{\boxed{n}}\left(\begin{array}{c}C_6H_3(CH_3)_2\\ |\\ -C-\\ |\\ C_6H_4CH_3\end{array}\right)_{\boxed{p}}\right]_x$$

Polymerization is one of the most important types among the non-equilibrium polycondensation reactions. Polycyclization is a two-stage process: the first stage is the formation of the linear polymer which at the second state undergoes cyclization to form a cyclochain polymer. It has been shown, nevertheless, that the second stage practically never proceeds to completion[2, 3]. One of the causes is the increasing rigidity of the chain, which produces steric hindrances of cyclization. This is evidenced by the fact that the activation energy of cyclization increases in the course of the reaction.

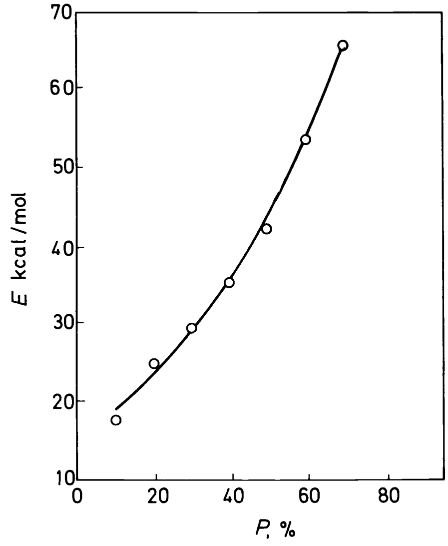
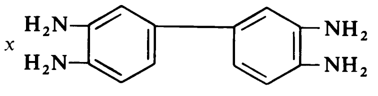


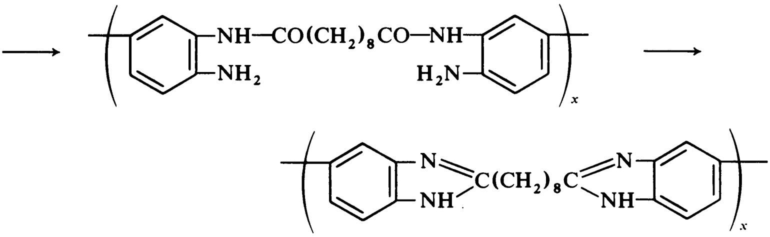
Figure 1. The alteration of activation energy during cyclodehydration of polyhydrazide of diphenylphthalyl dicarboxylic acid versus conversion (*P*).

This is shown in *Figure 1*, where the results of investigations of the cyclization of polyhydrazide are given[96]. The increase of the activation energy and, hence, the decrease of the rate of polycyclization are caused by the increasing rigidity of polymer macromolecules due to the formation of the oxadiazole cycles, since it decreases the mobility of the units, which is necessary to prevent stereochemical hindrances of cyclization. Because of this, in the macromolecules of the resulting cyclochain polymer there is always a certain portion of uncyclized units which are the residue of the incomplete cyclization, i.e. anomalous units in the resulting hetero-unit polymer.

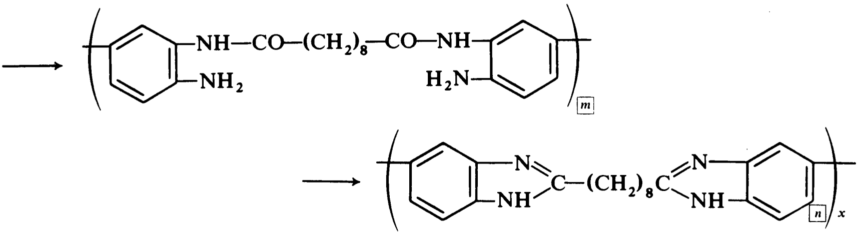
Thus, the polycondensation of aromatic bis-(*o*-diamines) with diphenyl ethers of aromatic dicarboxylic acids leads to the formation of polybenzimidazoles according to the equation



$+ \quad x\,C_6H_5OOC(CH_2)_8COOC_6H_5 \longrightarrow$

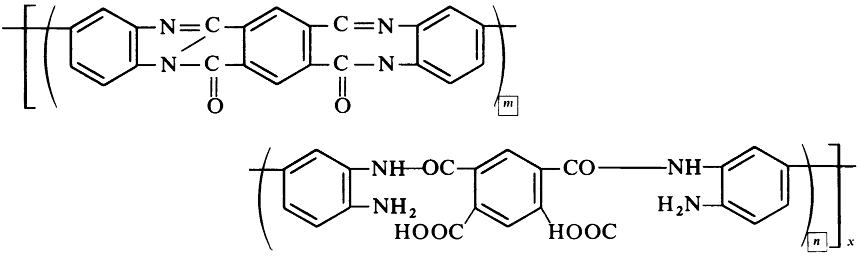


But the polymer obtained by this reaction at any stage is a hetero-unit polymer containing both the aminoamide and benzidazole units in the macromolecule. It would be better, therefore, to describe it by the following formula[52]



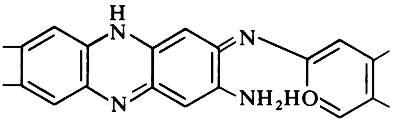
Polybenzimidazoles undergo dehydration at 270°C and contain 69 per cent of benzimidazole and 31 per cent of aminoamide units.

Using the thermodynamic method, Rabinovich and other authors found[53] that the pyrrone macromolecule contains 66 per cent of benzoylbenzimidazole and 34 per cent aminoamide units, which are the residue of incomplete cyclization. Because of this, their structure would be better expressed by the following formula



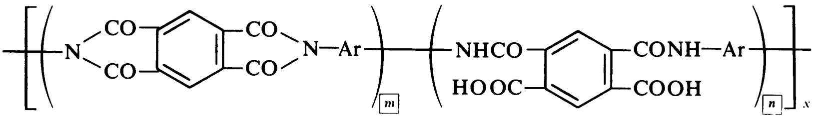
It should certainly be taken into consideration that this formula shows only two extreme structures of the unit. In addition to them several intermediate structures can exist which are forming in the course of transition from the amidoaminoacid to benzoylenebenzimidazole.

In the case of ladder polyquinoxalines obtained by Stille and Mainen[54] from 2,5-dihydroxy-*p*-benzoquinone and 1,2,4,5-tetraaminobenzene it was also proposed that their cyclization was incomplete, which must result in units of two types

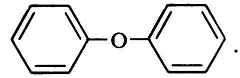


A similar proposal was made by Okada and Marvel about polyquinoxalinooxazines[55] and polyquinoxalinothiazines[56].

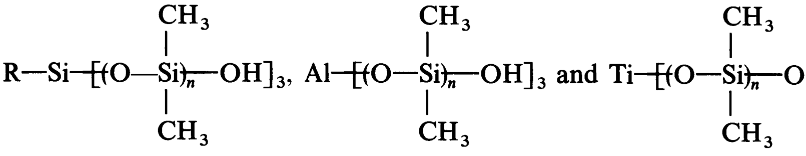
Polypyromelliteimide obtained from 4,4′-diaminodiphenyloxide contains only 78 per cent of imide units, and 22 per cent of amidoacid units are not cyclized[57]. Because of this, the formula of this hetero-unit polymer would be better represented as follows



where Ar denotes



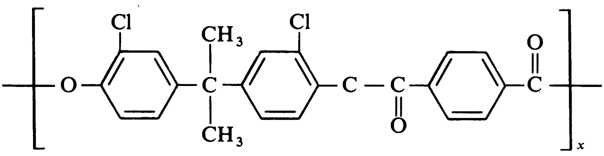
With net polymers it is very important to assure the maximum regularity of the net structure. This can be achieved by using tri- and tetrafunctional oligomers with the same branches. Thus, Andrianov used[58] oligomers of the types



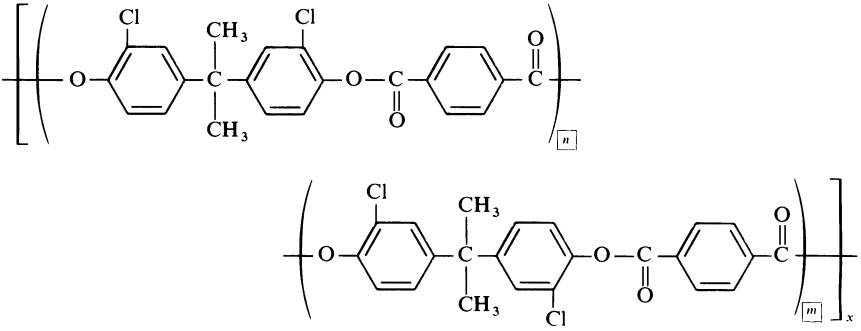
$$R{-}Si{-}[(O{-}\underset{CH_3}{\overset{CH_3}{Si}})_n{-}OH]_3,\quad Al{-}[(O{-}\underset{CH_3}{\overset{CH_3}{Si}})_n{-}OH]_3 \text{ and } Ti{-}[(O{-}\underset{CH_3}{\overset{CH_3}{Si}})_n{-}OH]_4,$$

and more complex compounds and obtained regular net polymers.

Polyarylate obtained from bis(4-hydroxy-3-chlorophenyl)-2,2-propane and terephthalic acid in the presence of pyridine is crystalline and gives narrow signals of n.q.r. spectra. This is indicative of the presence of predominantly one crystalline form of the polymer[40], and this permits considering this polymer as stereoregular. Its structure will probably be



But if this reaction is carried out in dioxane solution and other solvents, a hetero-unit polymer can be obtained, which contains both crystalline conformations



Thus, this reaction can exemplify the synthesis of a stereoregular polymer by stereospecific polycondensation.

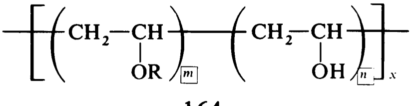
5. FORMATION OF ANOMALOUS UNITS IN COPOLYCONDENSATION PROCESSES

Both copolycondensation and copolymerization lead to the formation of hetero-unit polymers containing units of various structures. Depending on the nature and amount of the monomers polymers with different degrees of defect of the macromolecules are produced. The use of tri- and polyfunctional monomers provides a means for obtaining polymers containing side groups and branches, as well as crosslinked and three-dimensional structures.

6. FORMATION OF VARIOUS ANOMALOUS UNITS BY SUBSTITUTION, OXIDATION AND OTHER REACTIONS OF MACROMOLECULES

Hetero-unit polymers can also be obtained by replacement in the macromolecule of the hydroxyl groups, hydrogen atoms, halogens and other atoms or groups via halogenation, oxidation, metalation etc. Since such reactions never proceed to completion, they result in a hetero-unit polymer, containing initial units along with end and intermediate products of the substitution reaction.

A rather striking example of such a reaction type is the polymer-analogous substitution in the hydroxyl groups of cellulose, polyvinyl alcohol, starch and other polymers containing easily substituted hydrogen atoms which can usually only partially be replaced by various groups. In this case polyvinyl alcohol gives such a hetero-unit polymer[60].

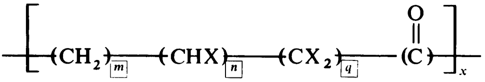


$$\left[\left(CH_2-\underset{OR}{CH}\right)_{\boxed{m}}\left(CH_2-\underset{OH}{CH}\right)_{\boxed{n}}\right]_x$$

A still more complicated case may be observed with the esters of cellulose, when units of four types can be formed[61].

$$-\left\{\left[C_6H_7(OH)_3\right]_{\boxed{m}}-\left[C_6H_7(OH)_2(OR)\right]_{\boxed{m'}}-\left[C_6H_7(OH)(OR)_2\right]_{\boxed{m''}}-\left[C_6H_7(OR)_3\right]_{\boxed{m'''}}\right\}-$$

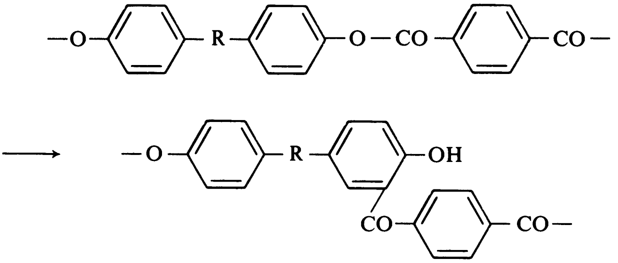
Substitution reactions result in hetero-unit polymers containing both initial units, and mono- and disubstituted randomly-arranged units



$$-\left[(CH_2)_{\boxed{m}}-(CHX)_{\boxed{n}}-(CX_2)_{\boxed{q}}-(\overset{\overset{O}{\|}}{C})\right]_x-$$

Let us give some examples.

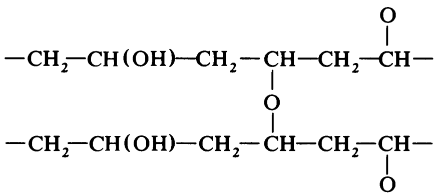
The Friese rearrangement occurs by u.v. radiation or by the action of aprotic acids[62].



Separation of hydrogen chloride from polyvinylchloride and other halogen-containing polymers gives double bonds[63].

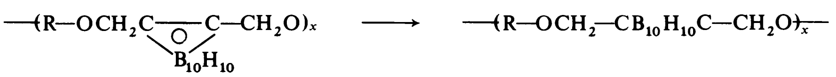
$$-CH_2-CHCl-CH_2-CHCl- \xrightarrow{-HCl} -CH_2-CH{=}CH-CH_2Cl-$$

Dehydration of polyvinyl alcohol yields crosslinks at the expense of the ether bonds, and the former becomes insoluble[64].



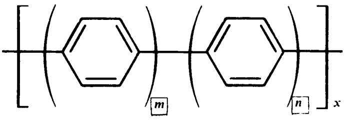
$$\begin{array}{c}
-CH_2-CH(OH)-CH_2-\underset{\underset{\displaystyle O}{|}}{CH}-CH_2-\overset{\overset{\displaystyle O}{|}}{CH}- \\
| \\
-CH_2-CH(OH)-CH_2-CH-CH_2-\underset{\underset{\displaystyle O}{|}}{CH}-
\end{array}$$

Rather interesting and peculiar is the formation of a hetero-unit polymer by the isomerization of polyesters containing residues of bis-hydroxymethyl-*o*-carborane to polyesters of bis-hydroxymethyl-*m*-carborane. It takes place on prolonged heating of the former in an inert atmosphere[65].

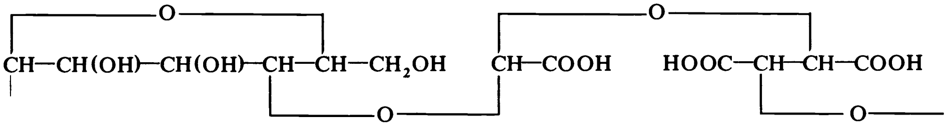


$$-(R-OCH_2\underset{\underset{B_{10}H_{10}}{\diagdown O \diagup}}{C-C}-CH_2O)_x \longrightarrow -(R-OCH_2-CB_{10}H_{10}C-CH_2O)_x-$$

According to Marvel and Hartzell[16], the synthesis of polyphenylenes proceeds through polymerization of cyclohexanediene-1,3 followed by dehydration of the resulting polycyclohexene. The latter reaction proceeds incompletely, which gives, because of this, not the polyphenylene-1,4 but a hetero-unit polymer containing phenylene and cyclohexene units

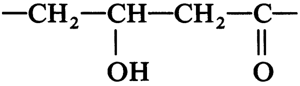


The oxidation of polymers leads to the formation of hetero-unit polymers. Their macromolecules contain carboxyl, ketone, alcohol and other groups formed by oxidation of the unit. Oxidized cellulose contains such units[61]



$$\mathrm{CH{-}CH(OH){-}CH(OH){-}CH{-}CH{-}CH_2OH \quad CH{-}COOH \quad HOOC{-}CH{-}CH{-}COOH}$$

Marvel *et al.*[66] showed that the oxidized polyvinyl alcohol contains ketogroups



$$-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-\underset{\displaystyle O}{\underset{\|}{C}}-$$

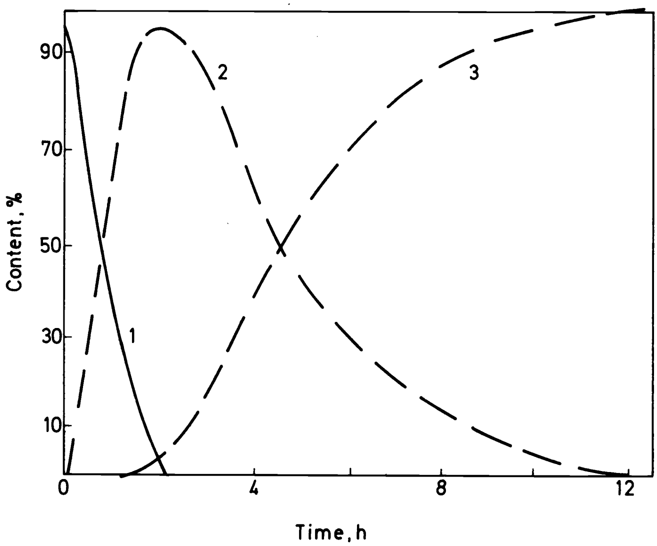
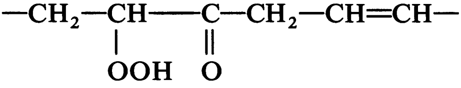


Figure 2. The alteration of composition of the mixture of two heterochain polymers during heating: 1, content of homopolymers; 2, content of block copolymers; 3, content of statistical copolymer.

Oxidized polyethylene contains peroxide, ketone groups and double bonds[67]

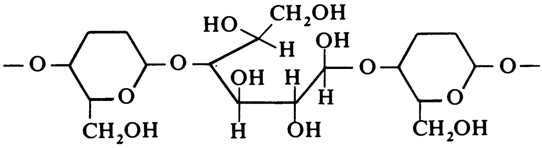


$$-CH_2-\underset{OOH}{\underset{|}{CH}}-\underset{O}{\underset{\|}{C}}-CH_2-CH=CH-$$

The exchange reactions of two heterochain polymers are also of interest, because they give block copolymers at the first stages along with a statistical copolymer, the end product of the process[46]. Depending on the stage at which the reaction is to be terminated, a mixture of different copolymers with anomalous units can be prepared, as shown in *Figure 2*.

7. ANOMALOUS UNITS IN NATURALLY OCCURRING POLYMERS

The above examples illustrated predominantly synthetic polymers. In conclusion we shall comment, therefore, on the chemical defect of macromolecules of naturally occurring polymers. Pacsu[68] and Strepikheev[69] showed that cellulose has, in addition to cyclic units, some anomalous opened units



Natural rubber contains 97–98 per cent of *cis*-1,4-units and a small amount (2–3 per cent) of *trans*- and other units[12].

8. EFFECT OF ANOMALOUS UNITS ON THE CHEMICAL PROPERTIES OF POLYMERS

Undoubtedly, the presence of anomalous units in the chain of the hetero-unit polymer must essentially affect the total chemical and physical properties. Of great importance in this case are the nature and amount of the anomalous units and their arrangement in the polymer chain.

Thus, the above-mentioned branching in the radical polymerization of vinyl compounds gives rise to the formation of units anomalous for this unit structure, which contain tertiary hydrogen atoms and side branches. Due to this fact the resistance to oxidation decreases, since tertiary hydrogen atoms can be very easily oxidized, and they become centres where the oxidative processes begin which result in the degradation of the polymer[70]. Indeed, thermal degradation of branched polyethylenes has been shown to proceed much more rapidly than that of the linear products (*Figure 3*)[71]. The degradation rate of branched polyethylenes increases with branching, that is with the content of side groups, as shown in *Figure 4* (cf. ref. 72).

The presence of 'head-to-head' units in vinyl polymers leads to the

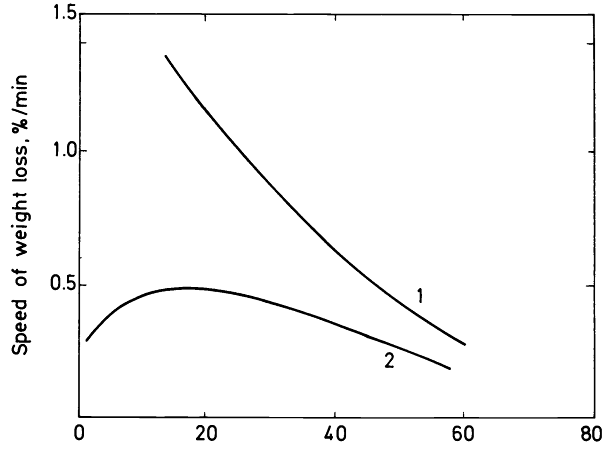


Figure 3. Speed of isolation of volatile products under heating (400°C) of branched (1) and linear (2) polyethylene.

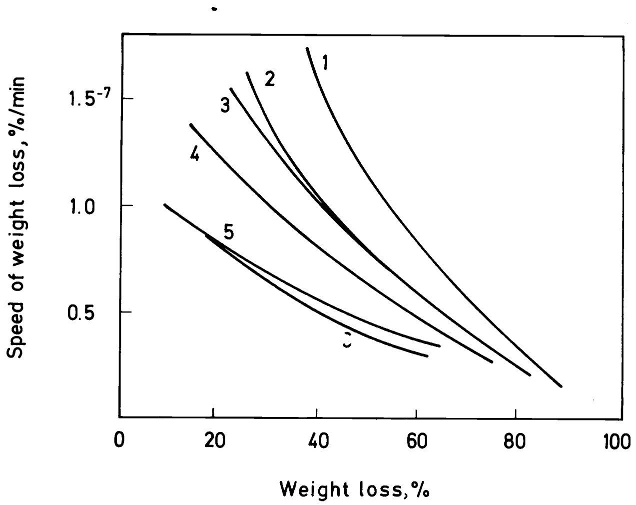
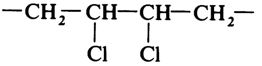
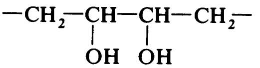


Figure 4. Speed of weight loss under heating (400°C) of branched high pressure polyethylene with different content of side groups (amount of CH_3-groups per 100 CH_2-groups): 1—8.7; 2—6.9; 3—6.0; 4—5.6; 5—3.9; 6—3.7.

formation of anomalous units containing adjacent halogen atoms and hydroxyl groups, as for instance in the case of polyvinylchloride or polyvinylalcohol[66]



$$-CH_2-\underset{Cl}{CH}-\underset{Cl}{CH}-CH_2-$$



$$-CH_2-\underset{OH}{CH}-\underset{OH}{CH}-CH_2-$$

Polyvinylalcohol has been found to contain one per cent of 1,2-groups[73]. The 1,2-groups can result from both the recombination of macroradicals[73] and the chain transfer reaction.

The effect of such anomalous units was particularly clearly shown on an example of thermal stability of the polymers of vinylchloride and vinylidenechloride with 'head-to-tail' and 'head-to-head' units[74].

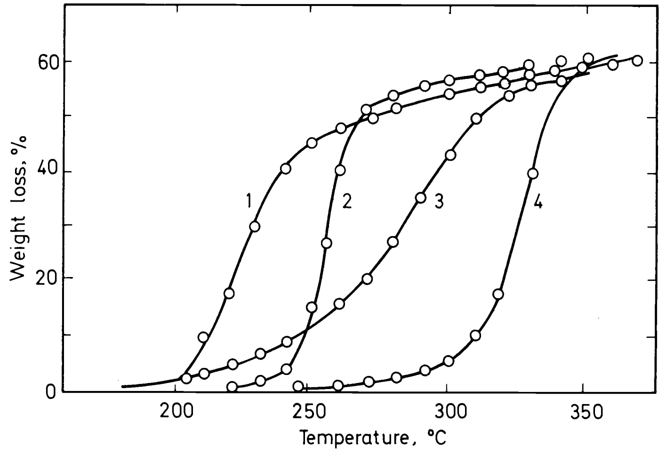
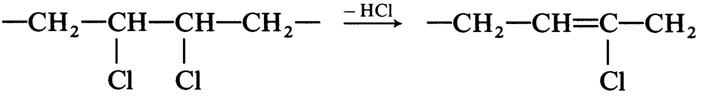


Figure 5. Thermal degradation of polyvinylidenechloride with 'head-to-tail' (1) and 'head-to-head' (4) units and polyvinylchloride with 'head-to-tail' (2) and 'head-to-head' units (3).

It was found that in the former case the degradation proceeds at a slower rate than in the latter (*Figure 5*). This can be explained by the fact that although the first stage of the reaction for the 'head-to-head' polymer proceeds more rapidly, it yields a stable structure similar to that of chloroprene

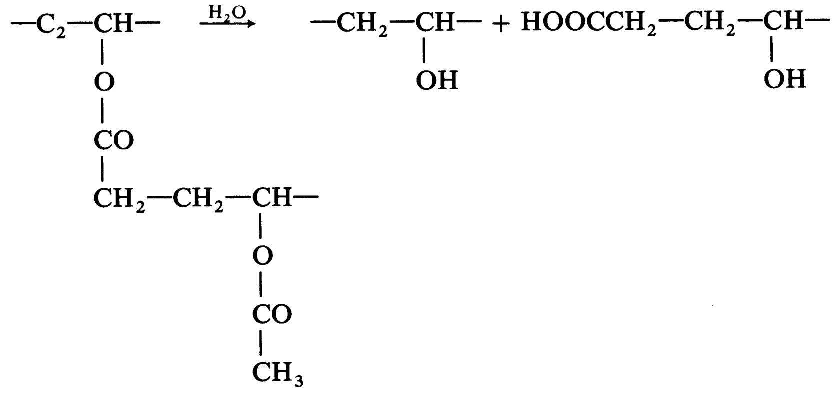


$$-CH_2-\underset{Cl}{CH}-\underset{Cl}{CH}-CH_2- \xrightarrow{-HCl} -CH_2-CH{=}\underset{Cl}{C}-CH_2$$

Because of this, the development of the chain reaction of dehydrochlorination along the polymer macromolecule is impossible.

The n.m.r. spectra showed that the 'head-to-head' units in polyvinylidenechloride vary[75] from 8.6 to 10.6 per cent.

The presence of anomalous units in polyvinylacetate decreases the molecular weight on hydrolysis due to the saponification of the ester bonds[7]



$$-C_2-\underset{\substack{|\\ O\\ |\\ CO\\ |\\ CH_2-CH_2-\underset{\substack{|\\ O\\ |\\ CO\\ |\\ CH_3}}{CH}-}}{CH}- \xrightarrow{H_2O} -CH_2-\underset{\substack{|\\ OH}}{CH}- + HOOCCH_2-CH_2-\underset{\substack{|\\ OH}}{CH}-$$

The presence of anomalous units, which hydrolyse more easily than the basic units, facilitates the degradation of the macromolecule on saponification, as shown by Pacsu[68] and Strepikheev[69].

The chemical defect of the macromolecules of atactic polymers results also in the fact that the rates of chemical reactions in stereoregular and atactic polymers differ greatly according to the data of Madrosky and Straus[76].

The temperature at which the polymer loses half its weight on heating for 35 min including the heating below this temperature for 15 min is 295°C for atactic poly(propyleneoxide) and 312°C for isotactic poly(propyleneoxide), the activation energy of these processes being 20 kcal/mol for the former and 45 kcal/mol for the latter[76].

The activation energy of pyrolysis is 24.5 kcal/mol for atactic polystyrene and 42 kcal/mol for the isotactic compound[77].

The presence of the defect units in the macromolecule, which are residues of an incomplete cyclization process, decreases the thermal stability of the

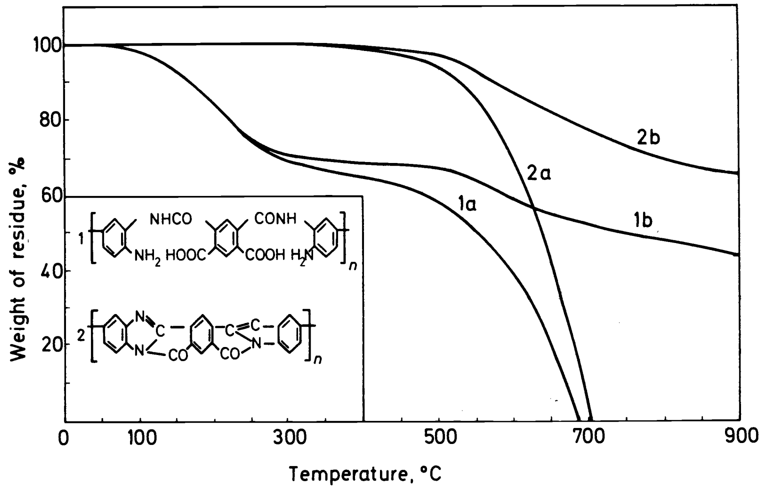


Figure 6. Dynamic thermogravimetric analysis of the pyrrone (2) and the corresponding polyamidoaminoacid (1) in air (a) or in helium (b). The speed of heating is 5°C per minute.

polymers[1-3]. *Figure 6* shows some results of the dynamic thermogravimetric analysis of pyrrone and of the corresponding polyamidoaminoacid[78]. The latter has a lower thermal stability. But this difference may depend on the predominant degradation in the former case. *Figure 7* shows the amounts of water and carbon dioxide formed at various temperatures. It is seen from *Figure 7* that the difference is observed both in the case of water and of carbon dioxide. Not only does the separation of carbon dioxide from polyamidoaminoacid begin at a lower temperature (200°C) compared to pyrrone (300°C) but also its extent for the former polymer is much larger. Thus, it can be believed that the defect of the polymer structure, that is the presence of anomalous units, is one of the facts which tend to decrease the thermal stability of polymers[3, 78, 79].

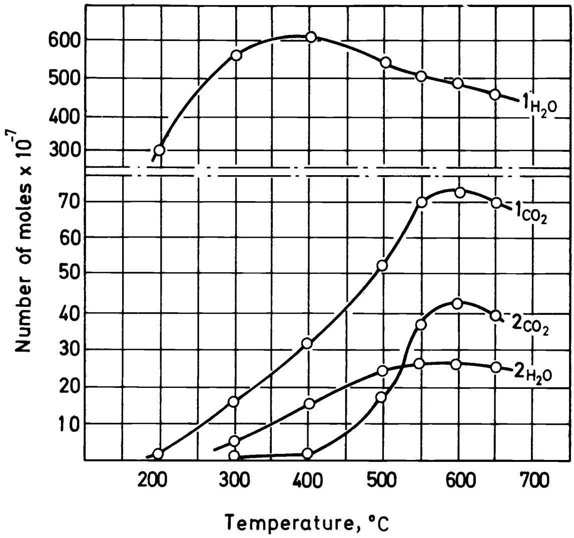


Figure 7. Isolation of water and carbon dioxide under pyrolysis of the pyrrone (2) and the corresponding polyamidoaminoacid (1) in argon (time—8 min; weight of specimen—15 mg).

The polyphenylene obtained by Marvel and Hartzell[16] by dehydration of polycyclohexene-1,4 has a low thermal stability, which can be explained by the presence of incompletely aromatized cyclohexene units in the macromolecules.

In essence, the anomalous groups affect the rate of thermal depolymerization of vinyl polymers, considerably decreasing it in most cases, as shown by Dolgoplosk and other authors[80].

Dolgoplosk *et al.*[80] showed that this effect of self-inhibition of the thermal degradation of copolymers depends on the fact that the free radicals formed at the chain ends differ in their activities. *Figure 8* shows the curves of the kinetics of depolymerization which confirm this conclusion.

Because of this, copolymers of formaldehyde are also more thermally

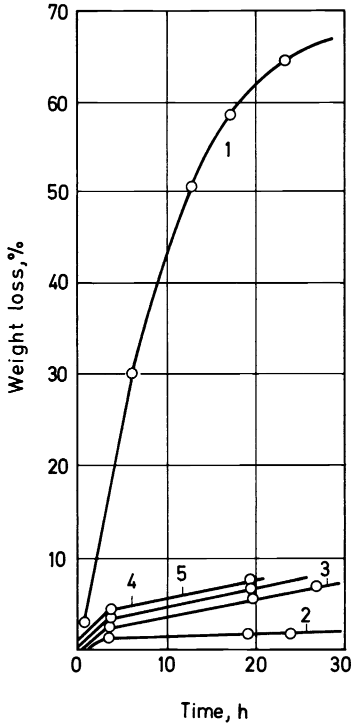
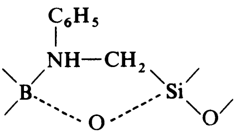


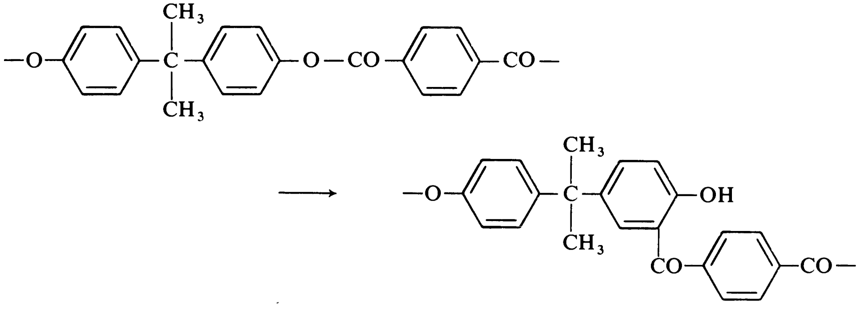
Figure 8. The kinetics of depolymerization of methyl methacrylate copolymers: 1, homopolymer; 2, copolymer with 40% of citracone amide; 3, copolymer with 40% of methyl methacrylamide; 4, copolymer with 7% of methylol methacrylamide; 5, copolymer with 15% of methacrylic acid.

stable than the homopolymer[81]. In this case the presence of another unit plays a positive role in decreasing the thermal stability of the polymer[82].

Of great importance for understanding the role of the anomalous units are the studies of Andrianov. The author points out substantial changes in the properties of polymers due to the introduction of small amounts of 'alloying' agents[83]. Andrianov[84] showed that in polyboronorganosiloxanes the phenylaminomethyl groups bonded with silicon increase considerably the resistance to hydrolysis of the copolymer due to the formation of an acceptor-donating bond between boron and nitrogen



The same can be observed with 'selfprotecting' polymers[62]. Self-protecting polyarylates undergo the Friese rearrangement by the action of radiation or catalysts. Vinogradova *et al.*[48,42] showed that in this case hydroxybenzophenone units are formed



9. EFFECT OF ANOMALOUS UNITS ON THE PHYSICAL PROPERTIES OF HETERO-UNIT POLYMERS

The physical properties of polymers are also rather sensitive to anomalous units, since they usually disturb the packing of the polymeric chains and, hence, impede their crystallization and the formation of denser structures. This is very important, because the structure of polymers is a factor which is responsible for physical and particularly the mechanical properties of polymers[85]. The presence of anomalous units decreases the mechanical strength of fibres, films, and other polymer articles and, vice versa, increases the solubility and decreases the melting and softening temperatures, i.e. decreases the thermal stability of polymers. Here are some examples illustrating these relations.

In contrast to this, polymers without defects and having no anomalous units must probably provide denser packing of chains, easier crystallization of the polymer, higher strength of fibres, films and other articles, high thermal stability and poor solubility. Preston[86] showed that the fibres obtained from ordered copolymers are stronger than those from random copolymers with greater numbers of defective hetero-unit macromolecules. This fact is also confirmed by the effect of the side groups on the properties of the polymer. *Figure 9* shows the relation between the melting point of copolymers and the amount of methyl and ethyl side groups. It can be seen

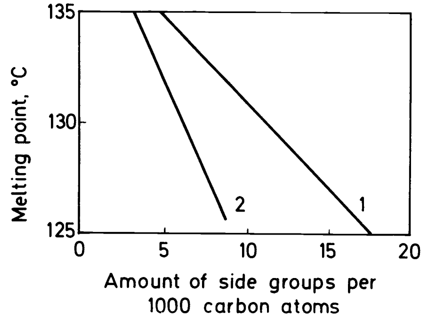


Figure 9. Melting points of polymethylenes with different amounts of methyl (1) and ethyl (2) side groups.

from this figure that the increase in the content of side groups decreases the melting point[87], the ethyl groups being more effective in this respect than the methyl groups.

The physical properties of polyethylene of various degrees of branching differ considerably, since the branching of polyethylene decreases the melting point, the density and crystallinity of the polymer.

The effect of anomalous units is very pronounced in the polymers of butadiene and isoprene. The *cis*-1,4-polymers are most elastic. The *trans*-1,4- or 1-2-units exert a detrimental effect on their properties.

The data indicating the dependence of temperature characteristics of the polymer, i.e. thermal stability and heat resistance, on the degree of defect of the structure confirm this suggestion. For instance, the glass transition temperature and the melting point of copolymers largely depend on the amount of the second monomer introduced into the copolymer[88–90]. If we consider only copolymers which contain a small amount of the second monomer, a rather definite common tendency can be observed (*Figures 10* and *11*).

In *Figure 10* the dependence of the glass transition temperature of vinyl monomers on the content of the second monomer is given[88]. In *Figure 11*

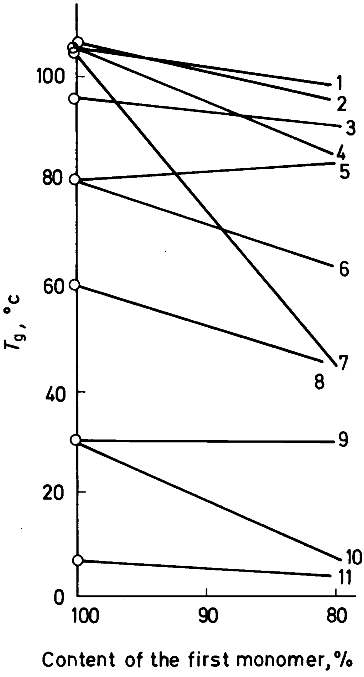


Figure 10. T_g versus structure and content of the second monomer. Copolymers: 1, methyl methacrylate with styrene; 2, acrylonitrile with methyl methacrylate; 3, styrene with methyl methacrylate; 4, methyl methacrylate with acrylonitrile; 5, vinyl chloride with acrylonitrile; 6, vinyl chloride with vinyl acetate; 7, methyl methacrylate with butyl acrylate; 8, ethyl methacrylate with butyl acrylate; 9, butyl acrylate with ethyl methacrylate; 10, butyl methacrylate with methyl methacrylate; 11, methyl acrylate with butyl methacrylate.

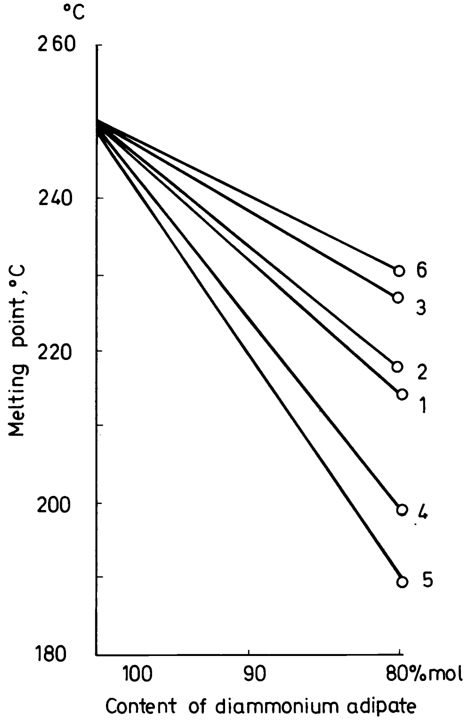


Figure 11. Melting point of copolyamides versus structure and content of the second monomers (the first monomer is hexamethylenediammonium adipate). The second monomer is: 1, hexamethylenediammonium azelate; 2, hexamethylenediammonium sebacate; 3, hexamethylenediammonium pimelate; 4, *m*-phenylenediammonium adipate; 5, *m*-toluenediammonium adipate; 6, ω-aminoenanthic acid.

the change in the melting point of mixed polyamides as a function of the composition is represented[89, 90].

It is seen from the figures that usually the glass transition temperature and the melting point decrease as the content of the second monomer increases, i.e. the amount of anomalous units in the polymer chain increases.

Figure 12 shows the effect of anomalous units containing a side group or a branch on the ordering of the macromolecules. The steric hindrance of the substituents will be to a certain extent proportional to its magnitude. The final effect must also depend on the amount of anomalous units[3].

The effect of polarity will probably be the more distinct the higher the polarity of the anomalous substituent compared to that of the basic substituents, which is exemplified by the copolymer of vinylchloride with acrylonitrile.

A striking example of the profound effect of the stereochemistry of the units on the properties of the polymer can be illustrated by polyamides prepared from *cis*- and *trans*-isomeric *n*-cyclohexylenediamines and dicarboxylic acids. *Figure 13* shows the change in the melting points of copolyamides containing various amounts of *cis*- and *trans*-isomeric

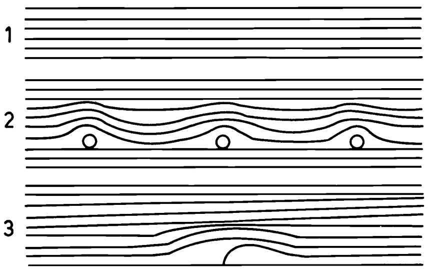


Figure 12. Influence of the chemical defect of macromolecules on their hindrance: 1, defectless macromolecules; 2, macromolecules with side groups; 3, branched macromolecules.

diamines[91]. It is seen that the effect of stereoisomerism is rather distinct. The polyamides from the *trans*-diamine have higher melting points.

The chemical defect of the macromolecules is also an important factor which is responsible for the ability of polymers to crystallize. The more profound the defect of the macromolecules, i.e. the larger the amount of anomalous units and the more randomly they are arranged, the less pronounced is the ability to crystallize, all other things being equal.

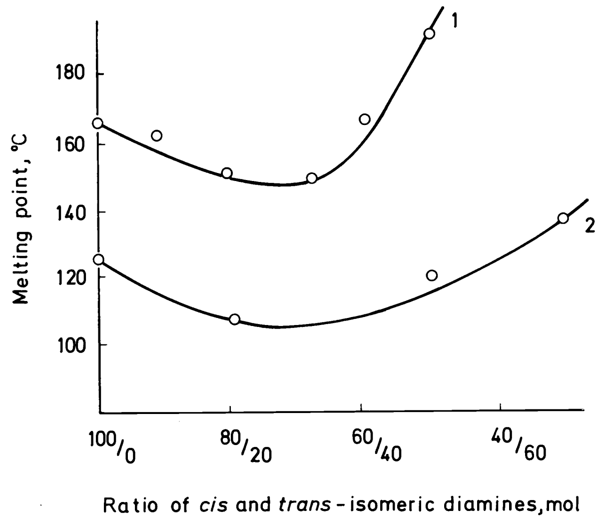
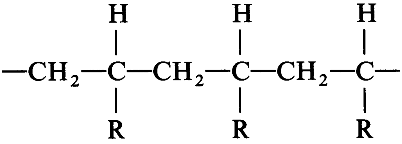
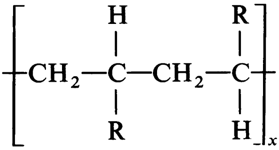


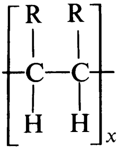
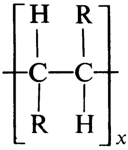
Figure 13. Change in the melting points of copolyamides containing various amounts of *cis*- and *trans*-isomers of 1,3-cyclohexylenediamine: 1, polyamide from adipic acid; 2, polyamide from azelaic acid.

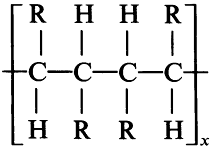
There is a number of polymers which up till now could not be converted into the crystalline state. Among these the following products should be mentioned: atactic polymers of styrene, trimethacrylate, propylene, polyvinylchloride and others. They are amorphous because of the random rearrangement of the d- and l-units in their macromolecules. In this respect they are also statistical copolymers of stereoisomeric d- and l-forms of the units. Nevertheless, the same units when regularly arranged yield easily crystallizable homopolymers, the isotactic polymer


$$-CH_2-\underset{R}{\overset{H}{C}}-CH_2-\underset{R}{\overset{H}{C}}-CH_2-\underset{R}{\overset{H}{C}}-$$

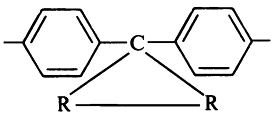
as well as a regularly composed copolymer of d- and l-forms, the syndiotactic polymer, which nevertheless can also be considered as the homopolymer with the following larger units


$$\left[-CH_2-\underset{R}{\overset{H}{C}}-CH_2-\underset{H}{\overset{R}{C}}-\right]_x$$

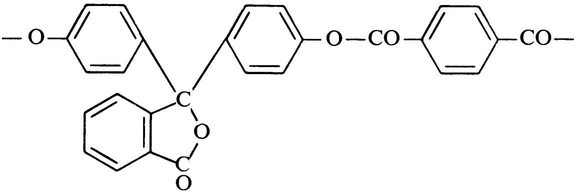
The threo-diisotactic  $\left[-\underset{H}{\overset{R}{C}}-\underset{H}{\overset{R}{C}}-\right]_x$ and erythrodiisotactic  $\left[-\underset{R}{\overset{H}{C}}-\underset{H}{\overset{R}{C}}-\right]_x$ polymers are also homopolymers, while the disyndiotactic polymer can be considered either as a copolymer of two different units or as a homopolymer with one, larger, unit


$$\left[-\underset{H}{\overset{R}{C}}-\underset{R}{\overset{H}{C}}-\underset{R}{\overset{H}{C}}-\underset{H}{\overset{R}{C}}-\right]_x$$

A similar influence of unit structure on the ability to crystallize is shown for polycondensation polymers. Thus, polyarylates which are the polyesters of bisphenols and dicarboxylic acids and which contain cycles with a central carbon atom such as

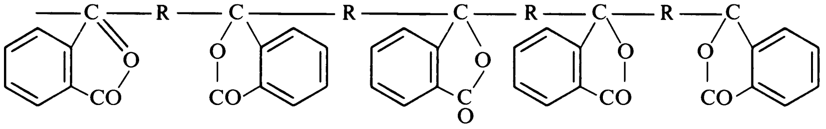


are among the most interesting 'cardo' polymers. They are composed on the necklace principle, i.e. each unit contains a carbon atom which simultaneously lies in the polymeric unit and in the side cycle. Depending on their structure, these polyarylates can be crystalline or amorphous. The following polyarylates of phenolphthalein

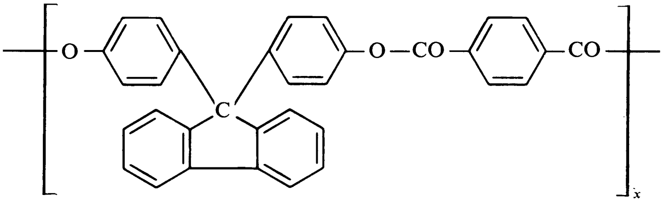


are amorphous, not crystallizable polymers[59]. In order to explain this phenomenon it has been suggested that their structure is similar to that of the atactic polymers, i.e. as in the latter the asymmetrical substituent (the phthalide group) is arranged statistically in the unit of such a hetero-unit polyarylate.

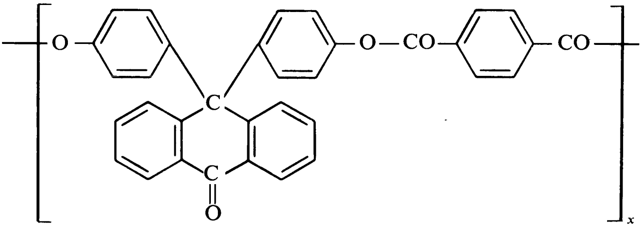
The next formula shows schematically the structure of the 'atactic' polyarylate of phenolphthalein[59]



Under certain conditions, it may be possible to achieve a stereoregular arrangement of this substituent, which leads to the formation of the crystalline polyarylate of phenolphthalein. This assumption is confirmed by the ability of the polyarylate with symmetrical cyclic side substituents of the cardo type to crystallize, found in our laboratory[59]. This can be exemplified by polyarylates based on 9,9-bis-(4-hydroxyphenyl)fluorene (I) and 9,9-bis(4-hydroxyphenyl)anthrone-10 (II) which have the following formulas



(I)



(II)

These polyarylates are crystalline substances unlike the polyarylates of phenolphthalein. Batzer[93] showed that the polyhexamethylene-α,α′-dibutylsebacate does not crystallize in contrast to the crystalline polyhexamethylenesebacate. This is caused by the fact that the polyhexamethylene-α,α'-dibutylsebacate is also a hetero-unit atactic polymer, since the starting acid is reacted in a racemic form. The butyl side groups of the polymer are, therefore, arranged irregularly. The copolymer prepared from sebacic and α,α'-dibutylsebacic acids only begins to crystallize at their ratio of 5 : 1, which corresponds to one butyl group for 54 atoms in the polymer chain. In this case the amount of anomalous units is rather low in order not to hinder the crystallization of the polyester.

The density of polymers changes markedly with increased defect of the macromolecules; the increased content of anomalous units is usually responsible for decreased density. A similar effect is exerted by branching. For instance, the density of the unbranched polymethylene is 0.971, that of the slightly branched low-pressure polyethylene is 0.95–0.96, and that of the highly branched high-pressure polyethylene is 0.92–0.93 (cf. ref. 87).

The solubility is also rather sensitive to the presence of anomalous units in the macromolecule. Usually, the increase in the content of anomalous units and their random arrangement increases the solubility of the polymer. The solubility of many copolymers also increases. Homopolyamides are

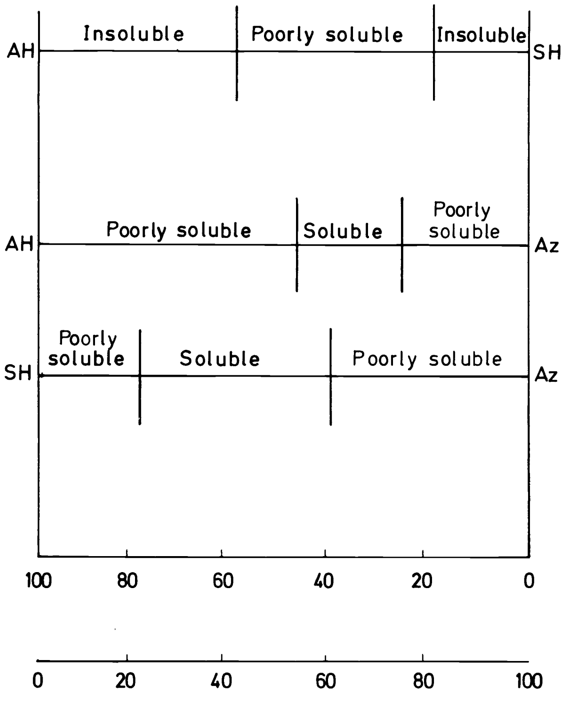


Figure 14. Change in solubility of copolyamides in ethanol with change in their composition: AH is hexamethylenediammonium adipate; SH is hexamethylenediammonium sebacate; AzH is hexamethylenediammonium azelate.

usually soluble only in acids, phenols and acid amides, and their copolymers (copolyamides) are soluble even in aqueous alcohol. *Figure 14* shows the change in solubility of copolyamides with change in their composition[94].

Thus, we have discussed many known reactions for the synthesis of polymers and showed that each of them is accompanied by various side reactions. These reactions result in the formation of anomalous units in the macromolecule, which give rise to the chemical defect of the macromolecular structure characteristic of hetero-unit polymers.

Anomalous units can be formed not only in polymerization and polycondensation but also in copolymerization and copolycondensation.

Various substitution reactions in the polymeric chain also lead to the formation of anomalous units and, hence, to the formation of hetero-unit polymers. There is no doubt that it should be possible to control the amount of anomalous units and their arrangement in the chain, which is one of the important problems of synthetic polymer chemistry.

The great importance of the problem of the chemical defect of the macromolecular structure is connected with the fact that it has a very significant influence on the chemical and physical properties of polymers, as has been illustrated by reference to a number of hetero-unit polymers.

In summary it can be concluded that the above-mentioned examples clearly show the effect of various reactions leading to the formation of anomalous units and, hence, to the formation of hetero-unit polymers having the general formula $-[(\mathrm{M})_{\boxed{m}}(\mathrm{A})_{\boxed{n}}]_x$. This specific feature of polymerization and polycondensation as well as substitution in the polymeric chains has not so far been investigated systematically, and our knowledge in this field is, therefore, incidental. Nevertheless, from the above data a conclusion can be drawn that all real polymers are in practice hetero-unit polymers, and the one-unit polymers, i.e. those without anomalous units, are rare exceptions. This fact should be taken into consideration in investigations of the interrelation between the structure of polymers and their properties, since the idea of hetero-unit polymers as a basic type of polymer structure becomes one of principal importance for polymer chemistry.

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