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The Synthesis of Polymers by Modification Methods

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The present state of the syntheses of polymers by modification methods is considered and the characteristics of the polymer modification reactions, determined by the specific macromolecular features of the polymers, are discussed. The applicability of the concept of the heterounit structure to polymers obtained by the modification procedure is demonstrated. Typical groups of reactions modifying natural and synthetic polymers and their features are specified and the characteristics of such reactions, involving substitution, structure formation, degradation, addition, elimination, isomerisation, and exchange, are considered. The prospects for the development of modification processes as a leading trend in the field of the synthesis of polymers are described.
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I. INTRODUCTION

The modification of polymers is one of the ways of synthesising high-molecular-weight compounds, which, together with polymerisation and polycondensation, has been used for a long time to synthesise polymers.

Whereas the polymerisation and polycondensation reactions are processes based on the conversion of monomers into polymers, the third procedure (modification) is a process based on the interconversion of polymers (Fig.1).

Consequently, *chemical modification of polymers is a process in which the initial polymer is subjected to physical or chemical influences, as a result of which it is converted into a new polymer with a different chemical structure*†.

The polymer modification reaction was first achieved by the French worker Braconnot, who obtained nitrocellulose in 1833 by treating cellulose with nitric acid[1]. Similar reactions were later carried out on a series of natural polymers. Different derivatives of cellulose, starch, proteins, rubber, and other natural polymers were obtained[2]. Subsequently synthetic polymers such as poly(vinyl chloride), polystyrene, polyethylene, and others began to be subjected to modification reactions at an increasing frequency[2].

Such wide-scale use of the modification reactions is due to the fact that the initial polymers do not meet all the practical requirements as regards their properties. Thus many insoluble polymers can be converted by modification into soluble high-molecular-weight compounds. A striking example of this kind is provided by cellulose, whose esters are readily soluble in organic solvents; chlorinated poly(vinyl chloride) and polyethylene become readily soluble. The introduction of carboxy- and amino-groups into polystyrene imparts to it acid and basic properties respectively, which are essential for ion-exchange resins. The introduction of nitrate ester groups into cellulose imparts explosive properties to the latter. The introduction of phosphate groups as well as chlorine, fluorine, bromine, and certain other elements into polymers renders them incombustible.

Thus the modification of polymers constitutes an extremely universal method whereby it is possible to vary within a wide range their physical and chemical properties in the desired direction. Because of this, the modification of polymers has now become one of the most important procedures whereby a large number of polymers are synthesised both in the laboratory and in industry. In industry modification processes have found extensive applications in the synthesis of many polymers, produced on a large scale, such as nitrocellulose, acetylcellulose, other cellulose esters and ethers, poly(vinyl alcohol), acetals of poly(vinyl alcohol), chlorinated poly(vinyl chloride), chlorinated and sulphochlorinated polyethylene, and others. There is no doubt that in the future modification will acquire still greater importance in industry.

The aim of the present review is to outline the present state of the modification processes and the likely prospects for their utilisation. The characteristics of the polymer modification reactions, determined primarily by their macromolecular nature, are considered at the beginning of the review. A feature of polymers such as their heterochain structure, which in many respects determined their characteristic set of physical and chemical properties, merits particular attention. Next, typical reactions used at present for the modification of polymers are described.

II. CHARACTERISTICS OF POLYMER MODIFICATION REACTIONS

A characteristic feature of the polymer modification processes is the fact that all reactions of this kind do not as a rule go to completion and are accompanied by side reactions, which has a significant influence on the course of the process and its results. This is caused by the influence of a number of significant physical and chemical factors, manifested in a specific manner in various polymer modification reactions. Such factors include the influence of the nature of the reagents and catalysts, the structure and degree of crystallinity of polymers, temperature, the nature of the solvent, and others. Ultimately, the reactions therefore result in a mixture of macromolecules of different structure, each of which contains different units in a wide variety of combinations. The final polymer is chemically inhomogeneous, i.e. has a heterounit structure[3].

† According to this definition, the copolymerisation of monomers should not be classified as chemical modification of polymers.

Consequently reactions in the polymer chain obey much more complex rules than the analogous reactions of low-molecular-weight compounds. The explanation is that not only the structure of the reacting groups but also a number of specific influences, determined by the macromolecular nature of one or both reactants, play a significant role here. The chain effect, the effect of the neighbouring group, and configurational, conformational, electrostatic, and supermolecular effects are usually isolated from such influences as the most significant[3-5].

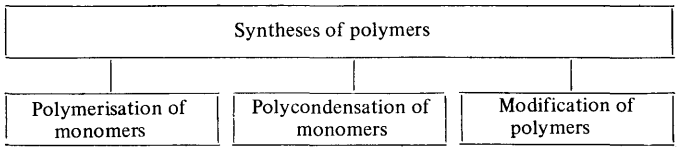
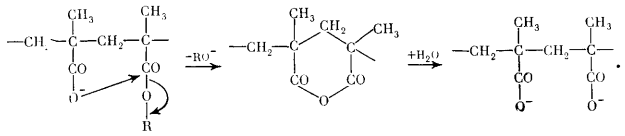


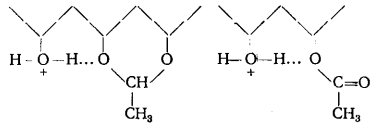
Figure 1. Different processes leading to the synthesis of polymers.

The relative steric disposition of different groups in the polymer chain has a significant steric or electrostatic (polar) influence on their reactivity. This influence can be shown both in the activation and passivation of neighbouring groups. The increase of the rate of reaction under the influence of a neighbouring group, known as "anchimeric assistance", is exhibited mainly when five- or six-membered rings can be formed. Thus it is observed for succinate esters. In exactly the same way, owing to the steric proximity of a neighbouring group, isotactic poly(methyl methacrylate) hydrolyses faster than the syndiotactic and atactic polymers, because in the isotactic polymer the neighbouring functional groups are distributed more favourably for their interaction with one another, leading to the formation of an intermediate cyclic anhydride[6,7]. The distribution function of the compositions of polymers has been considered in a number of investigations[8,9].

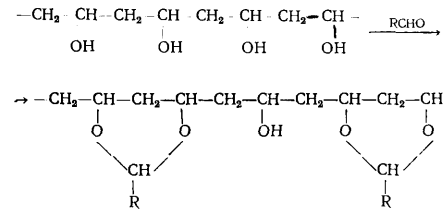
As already stated, one of the causes of the formation of anomalous units in polymer modification processes is the influence of neighbouring units which have already reacted (the "neighbour effect")[10]. A characteristic example of the acceleration of the reaction by the "neighbour effect" is the hydrolysis of the methacrylate–methacrylic acid copolymer[11]:



In the case of the partially hydrolysed poly(vinyl acetate) or polyvinylacetal this interaction takes place via the formation of a hydrogen-bonded ring[12], which facilitates the hydrolysis of acetals and acetates by increasing their reactivity[13] via the mechanism



As a result of the "neighbour effect", not all the initial hydroxyls in poly(vinyl alcohol) are converted into the acetal by treatment with aldehydes. According to Flory's calculations[14], approximately 13.53% of the hydroxyls should remain unsubstituted:



As another example, one may take polyethylene, which is readily chlorinated up to a chlorine content of 60%, whereupon the reaction slows down and, after the attainment of a chlorine content of 73%, ceases, although theoretically the chlorine content could reach 85.5%.[15] The explanation is that CCl_2 groups are not formed and the first stage proceeds with formation of the $-CH_2CHCl-$ groups up to a chlorine content of 56.8%. The next stage consists in the formation of the $-CHClCHCl-$ groups up to a chlorine content of 73.2%, whereupon the chlorination reaction stops. The retarding effect of the chlorine atoms in the $-CHCl-$groups on the chlorination of neighbouring CH groups can be accounted for by the inductive effect[13,16].

Thus in substitution reactions the "neighbour effect" as well as the steric and electrostatic influence of the initial side groups play a significant role[13].

Examples are known in which different effects are superimposed. Thus the alkaline hydrolysis of polymethacrylamide does not go to completion[17] and the methacrylamide–methacrylic acid copolymer hydrolyses with greater difficulty the smaller its methacrylamide content[18]. The loss of reactivity by the amide groups in these cases occurs both as a consequence of their being blocked by two ionised carboxy-groups and as a result of the electrostatic repulsion by the latter of hydroxide ions which catalyse the hydrolysis[19].

Attention should be drawn to the fact that, in order to characterise fully the polymer formed as a result of chemical modification, it is important to establish not only the presence of anomalous units and their number but also their sequence in the polymer macromolecule. Thus the frost resistance and physical properties of vulcanised rubbers are determined not only by the ratio of the *cis*- and *trans*-units but also by their sequence in the macromolecules[20]. Yet another example is provided by chlorinated polyethylene containing 56% of chlorine, the properties of which differ appreciably from those of poly(vinyl chloride) with the same chlorine content[21]. In the former case we have an irregular and in the latter a regular arrangement of chlorine atoms, as can be seen from the formulae of these polymers:

$$-CH_2-CH_2-CHCl-CHCl-CH_2-CH_2-;\ (-CH_2-CHCl-)_x.$$

Polyethylene chlorinated in solution in carbon tetrachloride and in an aqueous suspension has different arrangements of chlorine atoms and, for the same content of the latter, these two types of polymers have appreciably different properties[22].

It has been found that the hydrolysis of isotactic polyacrylonitrile converts it into an atactic polymer[23], while polymethacrylate esters hydrolyse without change of configuration[24], which constitutes a specific illustration of the influence of the steric structure on the chemical properties of these polymers and particularly on the structure of their reaction products.

When the causes responsible for the chemical inhomogeneity of the products, i.e. the formation of heterounit polymers, are considered, one should bear in mind that the physical structure of the initial polymer plays a by no means subsidiary role[25,26]. Its role is particularly significant when the reaction takes place in a heterogeneous system. This is necessary when there is no suitable solvent for the reaction or when one has to retain the initial form of the polymer, as, for example, in the treatment of fibres and films. Finally, the tendency towards the manufacture of polymers with the greatest possible elimination of all solvents has been recently assuming an increasing importance. Together with economical and ecological causes, this is associated with the fact that reactions in solution are sensitive to the nature of the solvent and to the properties of the solution, which can be significantly reflected in the degree of conversion and in the structure of the modification products formed.

The compatibility of the polymers is also significant, because, as the reaction proceeds, their composition changes very considerably with a corresponding alteration of their properties. Incompatibility can cause phase separation or coiling of the chains. As a result of the latter, the reaction is localised on the surfaces of compact coils or becomes diffusion-controlled. The accessibility of the functional groups of the polymer to the low-molecular-weight reagent is thus altered, which affects the degree of the modification reaction and the structure of the product[27].

Factors such as the supermolecular structure of the polymers, the orientation of the macromolecules in solution, and the solubility and compatibility of the polymers and reagents in solutions also exert a considerable influence on the result of reactions involving substitution in macromolecules. The influence of the supermolecular structure of the polymer in a reaction carried out in a heterogeneous system, where the solid polymer is acted upon by liquid reagents, is associated with the fact that the rate and degree of conversion depend on the rate of diffusion of the liquid reagent into the bulk of the polymer structure. This diffusion takes place more readily in an amorphous polymer and in the amorphous regions of crystalline polymers. Macromolecules in the amorphous regions react faster and are more fully acted upon by chemicals than macromolecules in the ordered crystalline state.

The hydrolysis of poly(ethylene terephthalate)[28], the chlorination[29] and oxidation[30] of polyethylene, the grafting of styrene onto polyamides[31], and the heterocyclisation of polyhydrazides to polyoxadiazoles[32] proceed much more readily in the amorphous regions than in the crystalline regions, since the orientation of polymer chains in the latter hinders both the accessibility of the macromolecules to the reagents and the interaction of the functional groups of the macromolecules with one another.

It has been shown for the sulphochlorination of polyethylene that the number of sulpho-groups which have entered the polymer corresponds to the degree of crystallinity of the latter determined by X-ray diffraction[33]. It has been found that the degree of acetylation of cellulose also depends markedly on the supermolecular and morphological structures of the initial cellulose[25,34]. The degree of crystallinity of cellulose affects not only the distribution of the substituted groups along the chain of the macromolecule but also the mode of substitution in the glucose residues. Thus, although the primary hydroxy-group at the sixth carbon atom is more reactive, the heterogeneous xanthate substitution reaction takes place preferentially at the less reactive secondary hydroxyls attached to the second or third carbon atoms. The explanation is that the hydroxyl at the sixth carbon atom is blocked by intramolecular and intermolecular hydrogen bonds[35,36].

The study of the oxidation and chlorination of isotactic poly-4-methylpentene showed that these processes take place preferentially at the bends in the chains, since the lowest activation energy is required at these sites as a consequence of internal stresses[37].

The nature of the reagents is also very important. Thus acetic anhydride and nitric acid react with all the hydroxy-groups of cellulose, while trityl chloride reacts only with the primary groups[38]. The reaction temperature also plays a significant role. All possible polymer modification reactions take place more readily at temperatures above the glass point of the polymer[39].

In view of the above characteristics of the reactions in heterogeneous systems, in chemical modification reactions an attempt is made to dissolve the polymers or at least to obtain them in a gel, i.e. in a swollen state, which facilitates the substitution process[40–42].

Substitution reactions in solution, i.e. in a homogeneous system, take place faster and result in a more complete substitution of the functional groups and a more uniform disposition of the substituting groups along the chain than in a heterogeneous system. Thus acetylation of poly(vinyl alcohol) in a homogeneous solution makes it possible to obtain a virtually fully substituted product, while a considerable number of unsubstituted hydroxy-groups remain after acetylation in a heterogeneous system[42]. The distribution of free hydroxy-groups and correspondingly acetyl groups in the cellulose acetate obtained under homogeneous conditions is more regular than in the acetate obtained under heterogeneous conditions[43]. Since a single treatment of the polymer with the reagent does not lead to complete substitution, the treatment must be frequently repeated. Fig.2 shows how the content of methoxy-groups in methylated cellulose depends on the number of repeated treatments[44].

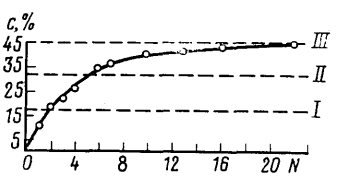


Figure 2. Dependence of the content of methoxy-groups (*c*) in methylated cellulose on the number of repeated treatments: I) monomethylcellulose; II) dimethylcellulose; III) trimethylcellulose. The continuous curve represents the variation of the content of methoxy-groups in the specimen.

As already mentioned, the polymer modification reactions never go to completion and they therefore lead to heterounit polymers containing the initial units as well as the final and intermediate units. The study of the resulting polymers shows that the substituents are usually distributed at random along the polymer chain. Fig.3 illustrated the distribution of substituents for different degrees of substitution.

III. THE HETEROUNIT STRUCTURE OF POLYMERS OBTAINED BY THE MODIFICATION PROCEDURE

One of the characteristic features of the modification reactions is their failure to reach completion, as a consequence of which some of the initial functional groups do not react and remain in the unchanged state. At the same time there is a possibility of a wide variety of side reactions, which also lead to the formation of units of a different chemical type and give rise to chemical heterogeneity in the macromolecules, referred to as the heterounit structure of polymers[45–48].

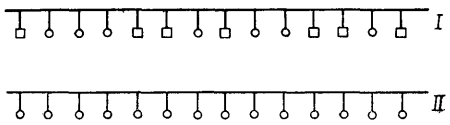


Figure 3. Distribution of substituents in the macromolecule for different degrees of substitution of the functional groups: I) partial, irregular substitution in heterounit polymers; II) complete substitution.

The heterounit polymers obtained as a result of various modification reactions differ by the presence of anomalous units in the macromolecule, i.e. are chemically heterogeneous. Whereas the structure of a normal homounit polymer can be represented by the usual formula $-(-M-)_x-$, the macromolecule of a heterounit polymer contains anomalous A units:

$$-M-M-M-A-M-M- \quad .$$

Consequently the structure of a heterounit polymer can be represented by the following formula in the general case:

$$-[-(-M-)_{\overline{[m]}}-(-A-)_{\overline{[n]}}-]_x$$

where M are normal units, A are anomalous units, and $[\overline{m}]$ and $[\overline{n}]$ are coefficients indicating a statistical distribution of the units in the macromolecule of the heterounit polymer obtained by one of the modification methods[45–48].

As an example, one may quote the formula of heterounit cellulose nitrate[49]:

$$-[-C_6H_7O_2(OH)_3-]_{\overline{[m]}}-[-C_6H_7O_2(OH)_2(ONO_2)-]_{\overline{[n]}}$$
$$-[-C_6H_7O_2(OH)(ONO_2)_2-]_{\overline{[p]}}-[-C_6H_7O_2(ONO_2)_3-]_{\overline{[q]}} \quad .$$

Thus we may expect the presence of units of at least four different types in the macromolecules of this cellulose ester, disregarding the anomalous units which might have been present in the initial cellulose.

Yet another example of a heterounit polymer is provided by chlorinated polyethylene, the general structure of which can be expressed by the following formula:

$$-(-CH_2-CHCl-)_{\overline{[m]}}(-CH_2-CH_2-)_{\overline{[n]}}-(-CHCl-CHCl-)_{\overline{[p]}} \quad .$$

Naturally the coefficients depend on the degree of the modification and its conditions.

Fig. 4 illustrates the fundamental reactions—both normal reactions and secondary reactions—which can occur in the modification of polymers and which we designate as the "set of modifying reactions". The data in Fig. 4 readily lead to the conclusion that the causes responsible for the heterounit structure of the products of the modifying reactions are fairly numerous. It is therefore not surprising that all the modification methods lead to the formation of chemically heterogeneous heterounit polymers. This conclusion is very significant, because it relates the structure of polymers to their properties[50].

It had been shown earlier for a large number of polymers that the heterounit structure is a factor which exerts a very significant influence on the entire set of physical and chemical properties of heterounit polymers[45]. Thus a statistical distribution of units of different chemical types in the macromolecules of heterounit polymers is frequently responsible for their ready solubility, a decrease of the melting point and thermal stability, an increase of elasticity, and the simultaneous decrease of strength[46].

On the basis of the concept of the heterounit structure, the modification reactions must be represented with allowance for the formation of anomalous units. For example, the nitration of cellulose can be represented thus:

$$-[-C_6H_7O_2(OH)_3-]_x \xrightarrow{HNO_3}$$
$$\rightarrow -[-C_6H_7O_2(OH)_3-]_{\overline{[m]}}-[-C_6H_7O_2(OH)_2(ONO_2)-]_{\overline{[n]}}$$
$$-[-C_6H_7O_2(OH)(ONO_2)_3-]_{\overline{[p]}}-[-C_6H_7O_2(ONO_2)_3-]_{\overline{[q]}} \quad .$$
$$x = m + n + p + q$$

The hydrolysis of poly(vinyl acetate) can be represented by the equation

$$-\left[-CH_2-\underset{OCOCH_3}{CH}-\right]_x- \xrightarrow{H_2O} -\left[-CH_2-\underset{OCOCH_3}{CH}\right]_{\overline{[m]}}-\left[-CH_2-\underset{OH}{CH}-\right]_{\overline{[n]}} \quad .$$
$$x = m + n$$

The chlorination of polyethylene is described schematically by the following equation:

$$-[-CH_2-CH_2-]_x \xrightarrow{Cl_2}$$
$$\rightarrow -[-CH_2-CH_2-]_{\overline{[m]}}-[-CH_2-CHCl-]_{\overline{[n]}}-[-CHCl-CHCl-]_{\overline{[p]}} \quad .$$
$$x = m + n + p$$

Naturally, this type of expanded representation of the modification reactions requires much space and for the sake of economy we shall henceforth represent only the extreme units in the chain of transformations occurring in the modification processes.

IV. TYPICAL CHEMICAL POLYMER MODIFICATION REACTIONS

Polymer modification processes are based on the use of a series of chemical reactions. In considering the polymer modification reactions known at the present time, one should note their large number and wide variety. Among these reactions, there are both processes based on the interactions of polymers with low-molecular-weight reagents and reactions of polymers with polymers. To facilitate the discussion of these reactions, we combined them into seven groups in terms of their chemical similarity. Examples of typical reactions in each group are given in Table 1, which shows that a series of different reactions are widely used in polymer modification processes. Here we encounter both substitution and elimination reactions, on the one hand, and reactions involving addition to multiple bonds, structure formation, and degradation of polymers, on the other. In addition, reactions involving the isomerisation of macromolecules and extremely unusual exchange type reactions of heterochain polymers are used for this purpose.

An interesting feature of all these reactions is that each has a specific influence on the structure of the polymer

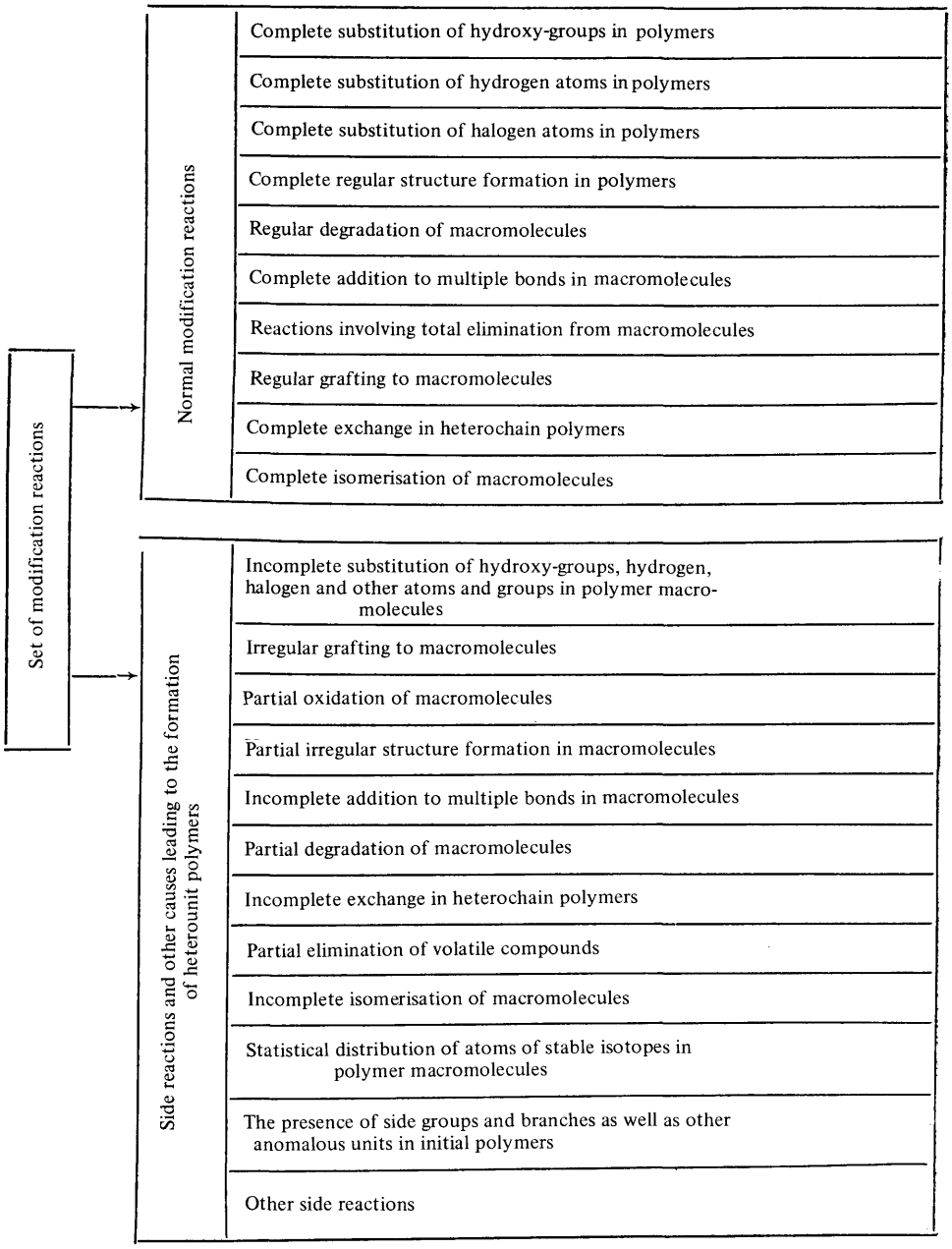


Figure 4. The set of modification reactions.

macromolecule formed as a result of the modification. Fig. 5 illustrates schematically the changes in the structure of macromolecules occurring as a result of the modification processes. It shows that in reactions of type (1) the structure of the polymer chain is retained, as in fact should have been the case in reactions of the polymer-analogue type to which these processes belong. In all the remaining types of reactions the structure of the macromolecule changes significantly. The remaining modification reactions cannot therefore be included in the class of polymer-analogue transformations.

In considering the modification reactions, one must bear in mind not only their chemical nature but also the way in which they are carried out (in solution, in the melt, in an emulsion, and in the solid), since the result of the process depends significantly on its conditions.

1. Polymer Modification Reactions Involving Substitution

We shall now consider in detail reactions of each type, examples of which are given in Table 1. We shall begin their consideration with the widely used substitution reactions.

The substitution reactions in Table 2 can be subdivided into the following subgroups: (1) substitution of a hydroxy-group by acyl and alkyl groups as well as inorganic acid residues; (2) substitution of a hydrogen atom by deuterium, a halogen, halogeno-, nitro-, phosphino-, and sulpho-groups, as well as alkyl groups in grafting reactions; (3) hydrolysis of derivatives of polymeric carboxylic acids; (4) substitution of a halogen and other groups for a hydroxy- or amino-group; (5) oxidation of side groups.

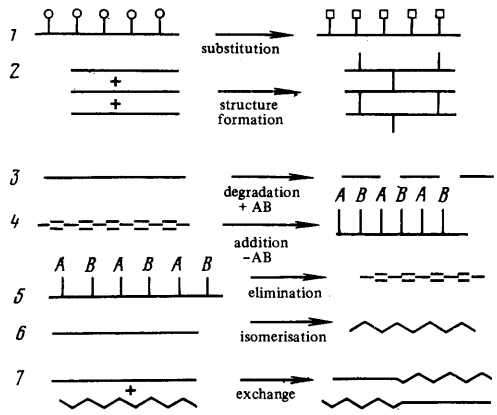


Figure 5. The change in the structure of macromolecules as a result of the modification reaction (the numbers of the reactions have the same significance as in Table 1).

Table 1. Examples of typical chemical polymer modification reactions.

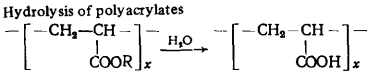
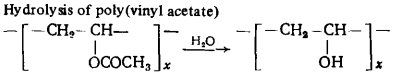
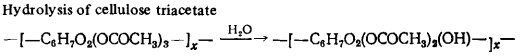
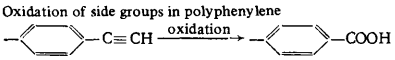
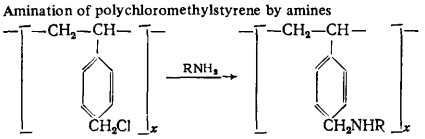
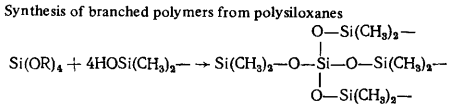
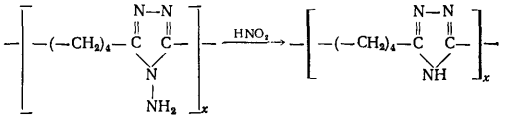
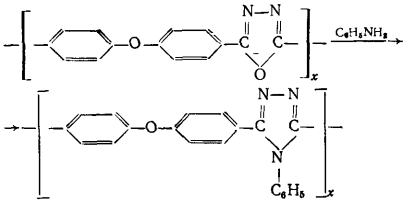
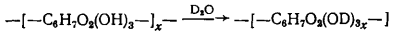
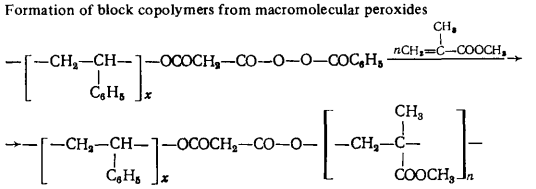
Name and equation of modification reaction	References
Substitution of atoms and groups in macromolecule $-[-C_6H_7O_2(OH)_3-]_x- \xrightarrow{HNO_3} -[-C_6H_7O_2(ONO_2)_3-)_x-$	1
Structure formation in polymers $-CH_2-CH_2-CH_2- \xrightarrow{h\nu} -CH_2-\underset{\displaystyle CH_2-CH-CH_2-}{\overset{\displaystyle |}{CH}}-CH_2-$	51
Degradation of macromolecules $-[-CH_2-CH=CH-CH_2-CH_2-]_x- \xrightarrow{WCl_4(CH_3)_2Si(CH_2)_2Si(CH_3)_2}$ $\rightarrow -[-CH_2-CH=CH-CH_2-CH_2-]_{x/n}-$	52
Reactions involving addition to multiple bonds in macromolecule $-[-CH_2-CH=CH-CH_2-]_m- \xrightarrow{+Cl_2} -[-CH_2-\underset{Cl}{\overset{|}{C}}H-\underset{Cl}{\overset{|}{C}}H-CH_2-]_m-$	53
Reactions involving elimination from macromolecules $-(-CH_2-CCl_2-)_x- \xrightarrow{-HCl} -(-C\equiv C-)_x-$	54
Isomerisation reactions of macromolecules $-[-C\equiv C-C\equiv C-]_x- \rightarrow =[=C=C=C=C=]_x=$	55
Exchange reactions of heterochain polymers $-R-\overset{+}{COO}-R- \quad -R-COO\ R'$ $-R'-\overset{+}{COO}-R'- \rightarrow -R'-\overset{+}{COO}-R-$	56

These reactions have certain common features consisting in the nature of the alteration of the structure and the properties of the resulting polymers. We may note that the replacement of a hydroxy-group in the polymer by an acid residue or an alkyl group makes the polymer soluble in inorganic solvents; the substitution of hydrogen by a halogen has a similar influence. In contrast, the substitution of an alkyl group in an ether by a hydroxy group impairs the solubility of such a polymer in organic solvents.

Table 2. Examples of polymer modification reactions by substitution.

Name and equation of modification reaction	Refs.
Nitration of cellulose with nitric acid $-[-C_6H_7O_2(OH)_3-]_x- \xrightarrow{HNO_3} -[-C_6H_7O_2(ONO_2)_3-]_x-$	1
Acetylation of cellulose with acetic anhydride $-[-C_6H_7O_2(OH)_3-]_x- \xrightarrow{(CH_3CO)_2O} -[-C_6H_7O_2(OCOCH_3)_3-]_x-$	57
Acetylation of poly(vinyl alcohol) with acetic anhydride $-\left[-CH_2-\underset{OH}{\overset{|}{C}}H-\right]_x- \xrightarrow{(CH_3CO)_2O} -\left[-CH_2-\underset{OCOCH_3}{\overset{|}{C}}H-\right]_x-$	58
Acetylation of poly(vinyl alcohol) with aldehydes $-\left[-CH_2-\underset{OH}{\overset{|}{C}}H-CH_2-\underset{OH}{\overset{|}{C}}H-\right]_x- \xrightarrow{RCHO} -\left[-CH_2-\underset{O}{\overset{|}{C}}H-CH_2-\underset{O}{\overset{|}{C}}H-\right]_x-$ (R = CH_3, C_6H_5)	59
Nitration of poly(vinyl alcohol) with nitric acid $-\left[-CH_2-\underset{OH}{\overset{|}{C}}H-\right]_x- \xrightarrow{HNO_3} -\left[-CH_2-\underset{ONO_2}{\overset{|}{C}}H-\right]_x-$	60
Chlorination of poly(vinyl chloride) with elemental chlorine $-[-CH_2-CHCl-]_x- \xrightarrow{Cl_2} -[-CHCl-CHCl-]_x-$	61
Chlorination of polyethylene with elemental chlorine $-[-CH_2-CH_2-]_x- \xrightarrow{Cl_2} -[-CHCl-CH_2-]_x-$	62
Nitration of polystyrene with nitric acid	63
Chloromethylation of polystyrene with di(chloromethyl) ether	64
Sulphochlorination of polyethylene with sulphur dioxide and chlorine $-[-CH_2-CH_2-]_x- \xrightarrow{SO_2+Cl_2} -\left[-CHCl-\underset{SO_2Cl}{\overset{|}{C}}H-\right]_x-$	65
Grafting by chain transfer in the presence of peroxides $-[-CH_2-CH_2-]_x- \xrightarrow{R^\cdot} -[CH_2-\dot{C}H-]_x- \xrightarrow{H_2C=CHX}$ $\rightarrow -\left[-\underset{CH_2-CHX-}{\overset{CH_2-CHX-}{|}}-CH_2-CH-\right]_x-$	66
Repeated grafting of polyamides under the influence of ozone to obtain "pemosors" (multiple grafted copolymers) $-(-CH_2-)_4-CONH- \xrightarrow{O_3} -CH_2-\dot{C}H-CH_2-CH_2-CONH- \xrightarrow{H_2C=CHX}$ $\underset{CH_2-CHX-CH_2-CHX-}{\overset{CH_2-CHX-CH_2-CHX-}{|}}$ $-CH_2-CH-CH_2-CH_2-CONH- \xrightarrow{O_3} -CH_2-CH-CH-CH_2-CONH- \xrightarrow{H_2C=CHY}$ $\underset{CH_2-CHY-CH_2-CHY-}{\overset{CH_2-CHY-CH_2-CHY-}{|}}$ $\rightarrow -CH_2-CH-CH-CH_2-CONH-$ $\underset{CH_2-CHY-CH_2-CHY-}{\overset{CH_2-CHX-CH-CHX-}{|}}$	67
Grafting by addition of epoxyalkanes to polyamide $-R-CO-NH-R'- \xrightarrow{CH_2-CH_2\ (O)} -R-CO-N(CH_2-CH_2-O-)-R'-$	68

Table 2 (cont'd).

Name and equation of modification reaction	Refs.
Hydrolysis of polyacrylates 	69
Hydrolysis of poly(vinyl acetate) 	70
Hydrolysis of cellulose triacetate 	71
Oxidation of side groups in polyphenylene 	72
Amination of polychloromethylstyrene by amines 	73
Synthesis of branched polymers from polysiloxanes 	75
Conversion of polyaminotriazoles into polytriazoles by treatment with nitrous acid 	76
Conversion of polyoxadiazoles into polytriazoles by treatment with aniline 	77
Deuteration of cellulose with heavy water 	78
Formation of block copolymers from macromolecular peroxides 	79

The majority of polymer modification reactions involving substitution belong to the type designated as polymer-analogue reactions. Their characteristic feature is retention of the main macromolecular skeleton, only the nature of the substituents surrounding the main chain being altered. The specific features of reactions of this type were considered previously.

2. Polymer Modification Reactions Involving Structure Formation

The modification of polymers by structure formation is a process in which the macromolecules pass through a stage with branched structures and are ultimately converted into infusible and insoluble three-dimensional structures. In the first stage of this process the polymer interacts with the cross-linking agent, which leads to the formation of bonds between the macromolecules. An industrial structure formation process, known as vulcanisation, is widely used in the processing of polymers, particularly elastomers. Vulcanisation imparts to rubbers resistance to wear and other mechanical influences and resistance to oxidation and the action of solvents.

Table 3. Examples of polymer modification reactions by structure formation.

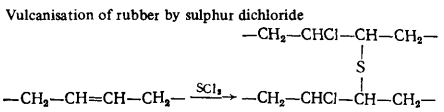
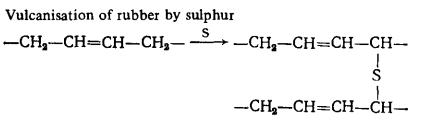
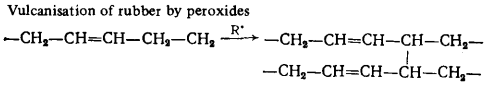
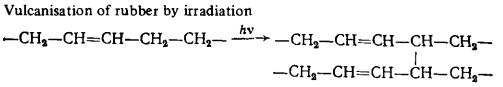
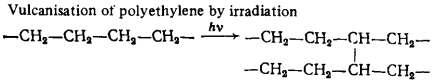
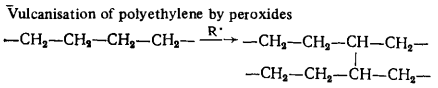
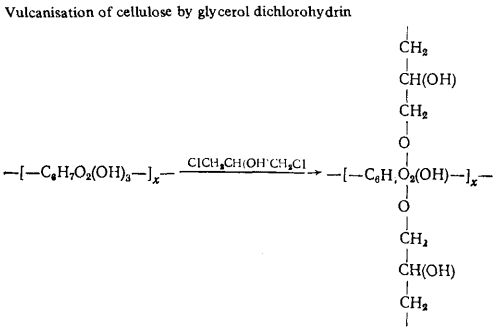
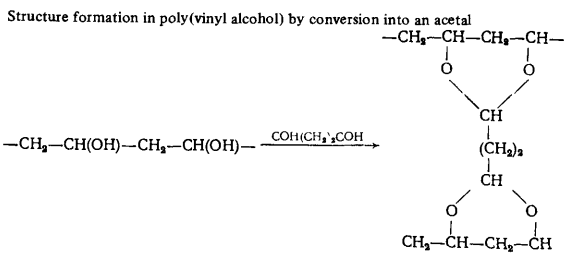
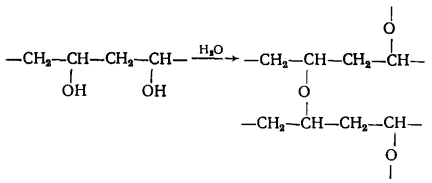
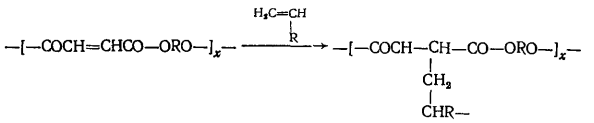
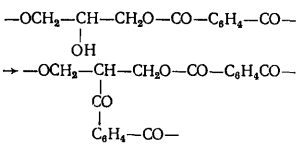
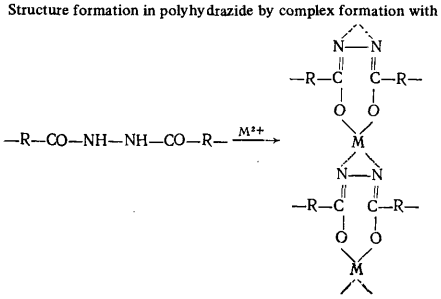
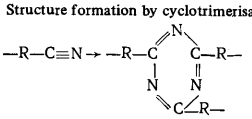
Name and equation of structure formation reaction	Refs.
Vulcanisation of rubber by sulphur dichloride 	80
Vulcanisation of rubber by sulphur 	80
Vulcanisation of rubber by peroxides 	81
Vulcanisation of rubber by irradiation 	82
Vulcanisation of polyethylene by irradiation 	83
Vulcanisation of polyethylene by peroxides 	84
Vulcanisation of cellulose by glycerol dichlorohydrin 	85
Structure formation in poly(vinyl alcohol) by conversion into an acetal 	86

Table 3 (cont'd).

Name of equation of structure formation reaction	Refs.
Structure formation in poly(vinyl alcohol) by dehydration 	58
Structure formation in unsaturated polyesters by copolymerisation with monomers 	87
Structure formation in Glyptals by treatment with dicarboxylic acids or their derivatives 	88
Structure formation in polyhydrazide by complex formation with metal ions 	89, 106
Structure formation by cyclotrimerisation of nitriles 	90

Examples of reactions involving structure formation in polymers are presented in Table 3, which shows that peroxide and radiation vulcanisations are widely used for modification by structure formation. In addition, in the case of rubbers vulcanisation by sulphur and its derivatives is used.

The cross-linking effect of bifunctional reagents and reagents with a larger number of functional groups is used for cellulose, poly(vinyl alcohol), and other polymers. As a result of these reactions, branching takes place initially and is followed by structure formation in polymers with different degrees of cross-linking, determined by the number of links between branching nodes (a), as shown below in Fig.6. Each branching node can then contain between three and eight and more branches (Fig.7).

In the limit the structured polymer has a molecular weight equal to that in the entire volume which it occupies. However, there is a possibility also of another type of structure formation, where the initial macromolecule contains in each unit a group capable of combining, as a result of the reaction, with one end of another macromolecule. A branched polymer, also occupying the entire space, is then formed. The structure of such a polymer branched to the maximum extent is illustrated in Fig.8. It is in essence a regularly grafted copolymer.

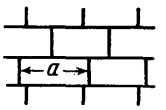


Figure 6. Schematic representation of a three-dimensional polymer.

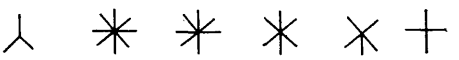


Figure 7. Schematic representation of the possible branching.

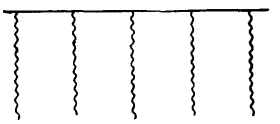


Figure 8. Schematic representation of a regularly branched polymer.

The data in Table 3 show that the structure formation reaction is used to modify different polymers as a procedure involving the conversion of linear polymers into three-dimensional structures. The cross-linked three-dimensional polymers formed are stronger, are insoluble, and exhibit a greater thermal stability than the initial linear polymer: this accounts for the wide-scale employment of this modification method, particularly in the rubber industry.

3. Polymer Modification Reactions Involving Degradation

Degradation is a process directly opposed to structure formation and is used to decrease the molecular weight of polymers. Degradation is widely used as a polymer modification method, particularly in the processing of natural polymers such as rubber and cellulose. With the aid of degradation by mechanochemical and oxidative methods, one obtains polymers with the optimum size of the macromolecules. Table 4 presents examples of certain polymer degradation reactions.

The degradation of carbochain polymers is carried out by a mechanical procedure (on rollers or other machines). In the case of cellulose oxidative degradation by atmospheric oxygen is used. In metathetical reactions in the presence of tungsten- or molybdenum-containing catalysts the carbon–carbon double bonds also become extremely labile and capable of degradative transformations[52].

The data in Table 4 show that hydrolysis, acidolysis, and aminolysis are widely used degradation reactions of heterochain polymers, which lead to the rupture of polar bonds such as ether, amide, acetal, etc. bonds.

4. Polymer Modification Reactions Involving Addition

Addition reactions are used as a procedure for the modification of polymers. When polymers contain multiple carbon–carbon bonds, halogens, oxidants, hydrogen, and other reagents can add to them. At the same time, there also exist metathetical reactions via the addition to carbon–carbon double bonds in unsaturated cyclo-olefins as well as the addition of epoxyalkanes to ester linkages.

Table 4. Examples of polymer modification reactions by degradation.

Name and equation of degradation reaction	Refs.
Mechanical degradation of polyethylene $-CH_2-CH_2-CH_2-CH_2-CH_2- \rightarrow -CH_2-CH_3+CH_2=CH-CH_2-$	91
Mechanical degradation of rubber $-[-CH_2-CH=CH-CH_2-]_x- \rightarrow -[-CH_2-CH=CH-CH_2-]_{x/n}-$	92
Oxidative degradation of cellulose $-[-C_6H_7O_2(OH)_3-]_x- \xrightarrow{O_2} -[-C_6H_7O_3(OH)_3-]_{x/n}-$	93
Acidolysis of polyesters $-R-COO-R'- \xrightarrow{R''COOH} -R-COOH+R''-COOR'-$	94
Acidolysis of polyamides $-R-CO-NH-R'- \xrightarrow{R''COOH} -R-COOH+R''-CONH-R'-$	95
Aminolysis of polyesters $-R-COO-R' \xrightarrow{R''NH_2} -R-CONH-R''+HOR'-$	94
Aminolysis of polyamides $-R-CONH-R'- \xrightarrow{R''NH_2} -R-CONHR''+H_2N-R'$	95
Esterolysis of polyesters $-R-COO-R'- \xrightarrow{R''-COO-R'''} -R-COO-R'''+R''-COO-R'-$	94
Hydrolysis of cellulose $-[-C_6H_7O_2(OH)_3-]_x- \xrightarrow{H_2O} -[-C_6H_7O_2(OH)_3-]_{x/n}-$	93
Hydrolysis of polyesters $-R-COO-R'- \xrightarrow{H_2O} -RCOOH+HOR'-$	94
Hydrolysis of polyamides $-R-CONH-R'- \xrightarrow{H_2O} -R-COOH+H_2N-R'-$	95
Depolymerisation of unsaturated polymers under the influence of catalysts of metathetical reactions $-[-CH_2-CH=CH-CH_2-CH_2-]_x \xrightarrow{WCl_4(CH_3)_2Si(CH_2)_2Si(CH_3)_2} -[-CH_2-CH=CH-CH_2-CH_2-]_{x/n}-$	52
Hydrolytic degradation of β-propiolactone copolymers $\ldots-CH_2-\underset{\displaystyle CH_2Cl}{\overset{\displaystyle CH_2Cl}{\overset{|}{C}}}-CH_2-OCH_2-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-(OCH_2-CH_2-\overset{\displaystyle O}{\overset{\|}{C}})_n-OCH_2-\ldots \xrightarrow{H_2O}$ $\rightarrow \ldots-CH_2-\underset{\displaystyle CH_2Cl}{\overset{\displaystyle CH_2Cl}{\overset{|}{C}}}-CH_2-OCH_2-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-OH+H[OCH_2CH_2COO]H+HOCH_2-\ldots$	96

Table 5 presents examples of different reactions involving addition to polymers. Polymers modified by the addition of halogens usually become more soluble and chemically stable. The data in Table 5 show that the addition of halogens, hydrogen, or oxygen to polymers having double bonds in the macromolecule is one of the most important modification methods. Such addition leads to heterounit polymers.

As an example of the formation of a heterounit polymer, we may quote the rubber chlorination reaction:

$$-[-CH_2C(CH_3)=CH-CH_2-]_x- \xrightarrow{Cl_2} \rightarrow -\left[-CH_2-C(CH_3)=CH-CH_2-\right]_{[\bar{m}]}-\left[-CH_2-C(CH_3)(Cl)-CH(Cl)-CH_2-\right]_{[\bar{n}]}-$$

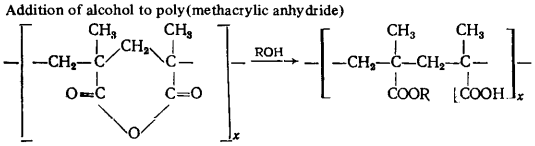
$$x = m + n$$

An analogous process occurs in the synthesis of block copolymers from polyethers, having terminal hydroxy-groups, and di-isocyanates. In this case the addition involves the double bonds of the di-isocyanates.

Table 5. Examples of polymer modification reactions by addition.

Name and equation of addition reaction	Refs.
Chlorination of rubber with elemental chlorine $-CH_2-CH=CH-CH_2- \xrightarrow{Cl_2} -CH_2-CHCl-CHCl-CH_2-$	53
Addition of epoxyalkanes to polyesters $-R-COO-R- \xrightarrow{H_2C-CHR'\ (O)} -R-CO-OCH_2-CH(R')-O-R-$	97
Addition of cyclo-olefins to polydienes in a metathetical reaction $-CH_2-CH=CH-CH_2- \xrightarrow{WCl_4(CH_3)_2Si(CH_2)_2Si(CH_3)_2} -CH_2-CH=CH-(CH_2)_n-CH=CH-CH_2-$	98
Addition of trioxan to polydioxolan $-CH_2-O-CH_2-CH_2-O- \xrightarrow{(CH_2O)_3} (-CH_2O-)_4-CH_2-CH_2-O-$	99
Hydrogenation of polyphenylene-ethylene $-[-CH_2-CH_2-C_6H_4-]_x- \xrightarrow{H_2} -[-CH_2-CH_2-C_6H_{10}-]_x-$	100
Addition of di-isocyanates to polyesters $-COR'CO-ORO-H \xrightarrow{O=C=N-R''-N=C=O} -COR'C(=O)-ORO-CO-NHR''-NH-CO-ORO-COR'CO-$	101
Introduction of xanthate groups into cellulose by treatment with carbon disulphide $-[-C_6H_7OH)_2(ONa)-]- \xrightarrow{xCS_2} -\left[-C_6H_7O_2(OH)_2-OC(=S)-SNa\right]_x-$	102
Addition of cuoxam to cellulose $-[-C_6H_7O_2(OH)_3-]_x- \xrightarrow{[Cu(NH_3)_4(OH)_2]} -\left[-C_6H_7O_2(OH)(OH\rightarrow Cu^{2+}\leftarrow(NH_3)_2)2HO^-\right]_x-$	103
Quaternisation of poly-4-vinylpyridine by treatment with alkyl halides $-[-CH_2-CH(C_5H_4N)-]- \xrightarrow{RBr} -[-CH_2-CH(C_5H_4{}^+NRBr^-)-]-$	104
Epoxidation of polyisoprene by treatment with perbenzoic acid $-CH=C(CH_3)-CH_2- \xrightarrow{R-C(=O)-O-O-H} -CH(O)CH_2-C(CH_3)=$	105
Ozonisation of rubbers $-CH_2-CH=CH-CH_2- \xrightarrow{O_3} -CH_2-CH(O_3)-CH-CH_2-$	107

Table 5 (cont'd).

Name and equation of addition reaction	Refs.
Addition of alcohol to poly(methacrylic anhydride) 	108

The modification of heterochain polyesters by the addition of epoxyalkanes to the latter, which results in the formation of polyesters containing ether linkages, is very unusual[97]. The reactions involving the formation of various complexes of cellulose, polyhydrazides, and other polymers with different metals are very interesting. The ozonisation of rubbers, leading to the formation of unstable ozonides, is widely used in the analysis of rubbers.

Table 6. Examples of the modification of polymers by elimination reactions.

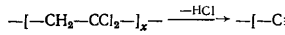
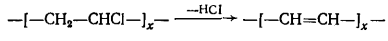
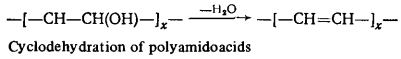
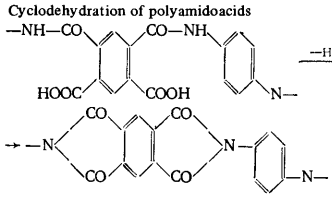
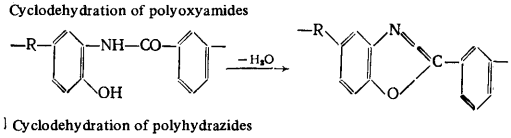
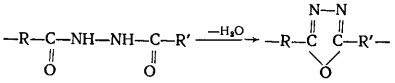
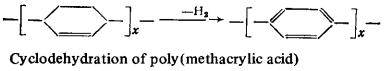
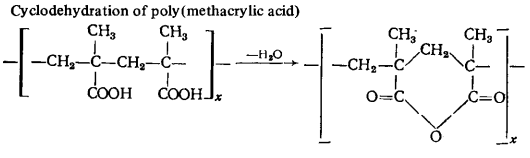
Name and equation of elimination reaction	Refs.
Dehydrochlorination of poly(vinylidene chloride) 	54
Dehydrochlorination of poly(vinyl chloride) 	106
Dehydration of poly(vinyl alcohol) 	42
Cyclodehydration of polyamidoacids 	107
Cyclodehydration of polyoxyamides 	108
Cyclodehydration of polyhydrazides 	109
Dehydrogenation of polycyclohexadiene 	110
Cyclodehydration of poly(methacrylic acid) 	111

Table 6 (cont'd).

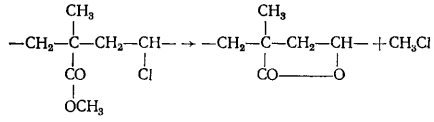
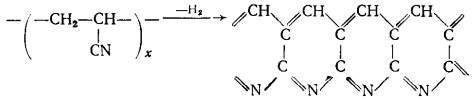
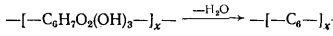
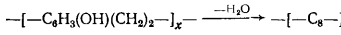
Name and equation of elimination reaction	Refs.
Thermolysis of methyl methacrylate–vinyl chloride copolymer 	112
Pyrolysis of polyacrylonitrile 	113
Pyrolysis of cellulose in order to obtain carbon and graphite fibre 	114
Pyrolysis of phenol-formaldehyde polymer in order to obtain glassy carbon 	115

Table 7. Examples of isomerisation reactions of macromolecules.

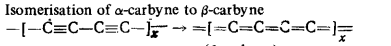
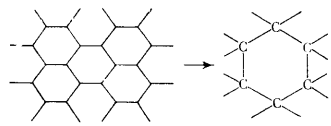
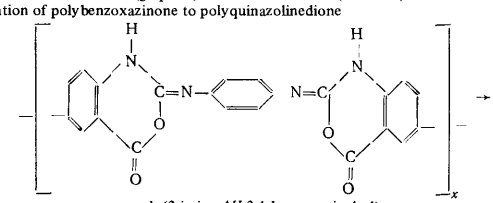
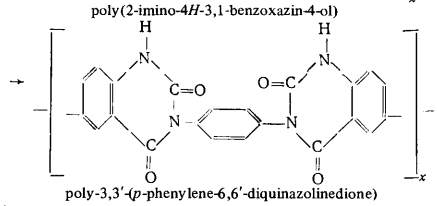
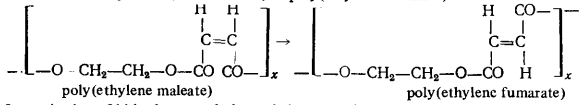
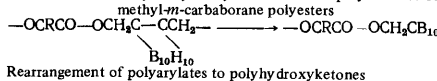
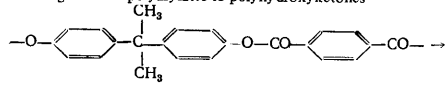
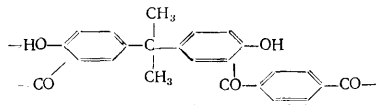
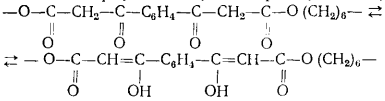
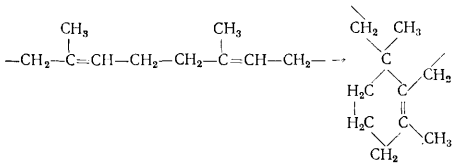
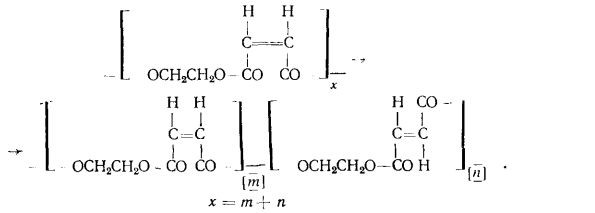
Name and equation of macromolecule isomerisation reaction	References
Isomerisation of α-carbyne to β-carbyne  (α-carbyne) (β-carbyne)	55
Isomerisation of graphite to diamond  (graphite) (diamond)	116
Isomerisation of polybenzoxazinone to polyquinazolinedione  poly(2-imino-4*H*-3,1-benzoxazin-4-ol)  poly-3,3′-(*p*-phenylene-6,6′-diquinazolinedione)	117
Isomerisation of poly(alkylene maleate) to poly(alkylene fumarate)  poly(ethylene maleate) poly(ethylene fumarate)	118
Isomerisation of bishydroxymethyl-*o*-carbaborane polyesters to bishydroxymethyl-*m*-carbaborane polyesters 	119
Rearrangement of polyarylates to polyhydroxyketones 	120

Table 7 (cont'd).

Name and equation of macromolecule isomerisation reaction	Refs.
 Enolisation of poly(hexamethylene terephthalyldiacetate)	121
 Cyclisation of rubber under the influence of acids	122
 Conversion of polycarbaboranes into polyundecaborates	74

poly(alkylene fumarate):



$x = m + n$

7. Polymer Modification Reactions Involving Exchange

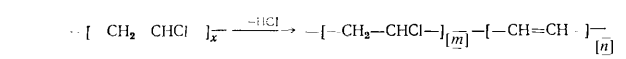
All the modification methods examined previously led to the formation of polymers in which the structure of the initial polymer chain remained unaltered in most cases. In contrast to this, the next modification method, based on the use of exchange reactions between macromolecules, leads to the formation of a polymer containing the units of both initial polymers in the chain. The macromolecules of this polymer therefore constitute in essence a copolymer whose composition corresponds to that of the initial mixture of polymers. Consequently, this modification method also constitutes simultaneously an unusual copolymerisation method.

5. Polymer Modification Reactions Involving Elimination

The elimination of low-molecular-weight substances such as water, alcohols, hydrogen halides, etc. is one of the important polymer modification methods. As a result of the elimination of low-molecular-weight substances, a double or triple bond or even a heterocycle is formed in the macromolecule of the initial polymer.

All these reactions involving the elimination of low-molecular-weight substances are used to modify polymers, as shown in Table 6. According to the data in Table 6, the elimination of such low-molecular-weight substances results in the appearance of multiple bonds in the polymer chain or rings are produced.

As an example of a reaction leading to the formation of a heterounit polymer in such processes, we may quote the dehydrochlorination of poly(vinyl chloride):



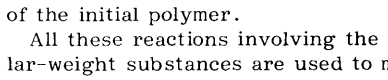
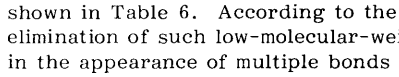
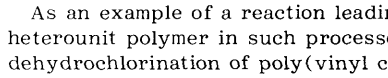
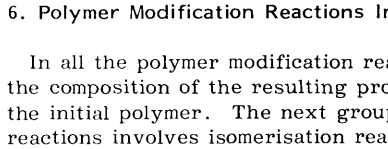
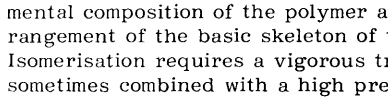
$x = m + n$

6. Polymer Modification Reactions Involving Isomerisation

In all the polymer modification reactions considered above, the composition of the resulting product differed from that of the initial polymer. The next group of polymer modification reactions involves isomerisation reactions which, in contrast to the previous ones, proceed without a change in the elemental composition of the polymer and consist in the rearrangement of the basic skeleton of the macromolecule. Isomerisation requires a vigorous treatment, such as heating, sometimes combined with a high pressure. Table 7 presents examples of polymer isomerisation reactions.

As an example of the formation of a heterounit polymer in isomerisation reactions, we shall consider a more detailed scheme for the transformation of poly(alkylene maleate) into

Table 8. Examples of the modification of polymers by exchange reactions between heterochain polymers.

Name and equation of exchange reaction	Refs.
Exchange reaction between heterochain polyesters 	56
Exchange reaction between heterochain polyamides 	124
Exchange reaction between heterochain polyesters and polyamides 	125
Exchange reaction between polysulphides	126
Synthesis of block copolymers by exchange reaction between heterochain polyamides	127
Formation of block copolymers by the polydisproportionation reaction (metathesis) 	128,129
Synthesis of deuterated polyesters by treating poly(ethylene sebacate) with diethyl 2,3-deuterosuccinate 	130

An important feature of this method is that heterochain polymers with fairly polar bonds between the units can be used as the starting materials for the reaction. On the other

hand, if heteroatoms are incorporated in the composition of the aromatic heterocycles, then polymers of this kind do no undergo exchange reactions[123]. It was believed previously that carbochain polymers are also unsuitable for these reactions, but it has now been established that the metathetical reaction makes it possible to carry out exchange reactions also between carbochain polymers[128,129]. Table 8 presents examples of the modification of polymers by exchange reactions between different polymers.

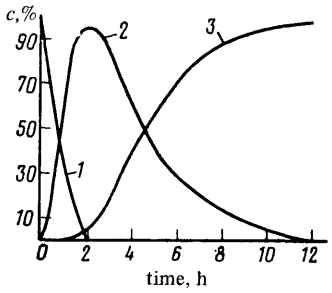


Figure 9. An exchange reaction between two polyamides. Variation of the contents (*c*) of homopolymers (curve *1*), block copolymers (curve *2*), and statistical copolymers (curve *3*).

An interesting feature of the exchange reactions is that after a time they lead to the formation of different products depending on the duration of the reaction.

Fig.9 shows which intermediates are formed in an exchange reaction between two polymers[127]. Evidently in the initial stage of the process there is a mixture of the two initial polyamides with an increasing admixture of a block copolymer. After 2 h, the final product is the block copolymer and then its content decreases and, when 12 h have elapsed, the only product becomes a statistical copolymer of the two initial diamine salts. Thus, by interrupting the process for any period at any stage, it is possible to obtain a large set of polymers of different structure and with different properties.

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In conclusion we must consider the problem of the prospects for the development of polymer modification processes. We may note in the first place that the number of reactions used to modify polymers is increasing and that the relevant research is being presented on a rapidly widening front. Our knowledge of this field has now become much deeper and fairly clear ideas have been developed concerning the characteristics of the polymer modification processes and their specific features, due to the polymeric nature of the starting materials, have been established. The fundamental characteristics of these reactions, which determine the results of the substitution reaction, have been discovered. It has been established that the polymers obtained in modification reactions contain in their macromolecules anomalous units and are therefore of the heterounit type. A definite relation between the properties of heterounit polymers obtained by modification methods and their structure has been demonstrated.

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