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PROGRESS IN THE SYNTHESIS OF HIGH POLYMERS

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I. INTRODUCTION

The chemistry of high polymers is at the present time one of the most vigorously developing branches of chemical science. The most rapid progress is in the synthetic chemistry of high polymers, a field in which advances have been especially evident in recent times.

This rapid development is explained by the fact that advances in the synthetic chemistry of high polymers ensure the development of such important branches of technology as plastics, synthetic rubber, synthetic fibres, and synthetic film-forming materials. In its turn, the production of these materials plays an important part in the development of such branches of industry as aviation, automobile, electrical and radio engineering, machinery manufacture, building construction, etc. On the one hand, new synthetic polymers provide new materials with high thermal stability, strength, etc., and on the other, the production of synthetic materials enables a hugh quantity of

cheap materials to be obtained for industries producing consumer goods.

The first synthetic polymeric product was phenol–formaldehyde resin, obtained by Baekeland[1] at the beginning of the present century. Since then a great industry of synthetic high polymers has grown up, and is developing rapidly.

The rapid growth in the production of polymeric materials can be seen from Table 1, which gives figures for their world production (apart from the USSR and the People's Democracies). It is interesting that this rapid growth in production is due mainly to the development of the manufacture of various synthetic polymeric materials, as can be seen from Table 2, which gives comparative figures for the increase in the production of various natural and synthetic polymers, starting from 1940. Table 2 shows that the total production of synthetic polymers in 1957 had increased 5.38 times, whereas the production of the natural materials had remained almost at the 1940 level (an increase of only 16%).

The scale of production of various polymeric materials is nowadays quite large: for example, Table 3 gives comparative data for the production of non-ferrous metals and plastics. In comparing metals and plastics it is necessary to introduce a correction for the density of the material, as is done in Table 3. Comparison by volume instead of weight then shows that the production of plastics had by 1956 already exceeded the total production of non-ferrous metals.

From the rates of increase in the production of polymers and ferrous metals, Semenov[6] estimates that within 15–20 years the scale of production of polymers will have reached that of the smelting of ferrous metals. The rapid growth in production is paralleled by a similarly rapid growth in the volume of scientific research on the synthesis of high polymers.

The object of the present review is to appraise advances which are occurring in the development of synthetic methods for preparing high polymers.

Recently more than a thousand papers and patents on synthetic high polymers have been published annually[6]. It is evidently impossible to review the whole of this copious material within the limits of the present paper. The review is therefore confined to the publications of the past two or three years. Even here, however, the superabundance of published results has made it necessary to select only those that appeared to be of practical interest.

TABLE 1. Growth of world production of various polymeric materials[2-5] (in thousands of tons).

Material	Year		
	1950	1955	1957
Fibres (natural and artificial)	8648	12343	12419
Plastics	1500	3100	4000
Rubbers (natural and synthetic)	2434	3045	3280
Paints and varnishes	—	—	4562
Total			24261

TABLE 2. Growth in the production of various forms of polymeric materials[2] (in thousands of tons).

Material	Year					1957 production as a percentage of	
	1940	1946	1950	1956	1957	1940	1950
Synthetic polymeric materials							
Synthetic rubber	43	844	583	1303	1350	3134	232
Artificial and synthetic fibres	1106	760	1624	2560	2700	244	166
Plastics	350	720	1530	3600	4000	1140	261
Total	1499	2324	3737	7463	8050	538	216
Natural polymeric materials							
Natural rubber	1437	851	1890	1915	1930	135	102
Cotton	6100	4300	5400	7200	6700	110	124
Wool	1130	940	1050	1140	1180	104	112
Total	8667	6091	8340	10255	9810	116	113

TABLE 3. Production of non-ferrous metals and of plastics[2].

Material	Year			1956 production as a percentage	
	1940	1950	1956	1940	1950
Aluminium	710	1310	2894	408	221
Copper	2330	2290	3016	129	132
Zinc	1540	1860	2488	162	134
Lead	1640	1560	1861	113	119
Tin	232	177	180	77	102
Total, 10^3 tons	6452	7197	10430	162	145
$10^3 m^3$	919	1166	1951	215	167
Plastics, 10^3 tons	350	1530	3600	1028	236
$10^3 m^3$	259	1133	2667		
Ratio of plastics to non-ferrous metals wt.%	5.4	21.3	34.5		
vol.%	28.2	97.2	137.0		

II. NEW METHODS FOR THE SYNTHESIS OF HIGH POLYMERS

The growth in the production of polymers is based on scientific research which is developing equally rapidly. As a result, many new synthetic methods for polymers have been discovered, and many thousands of new high polymers have been prepared.

We shall point out only the main advances in the field of new methods for the synthesis of polymers. Among them are the discovery by Ziegler and Natta of new catalysts for the polymerisation of olefinic hydrocarbons, which have enabled stereoregular polymers to be prepared; the discovery of methods of preparing graft and block copolymers; the discovery of the cyclopolymerisation of diene monomers; the application of dehydrogenation polymerisation; the discovery of the polyrecombination of various compounds; the use of polycondensation at the interface between two immiscible liquids; the development of the hydrolytic polymerisation of cyclic compounds; and the preparation of co-ordinated-chain polymers. Each of these cases will be considered briefly.

A. Stereospecific Polymerisation

We shall consider first the work of Ziegler, who discovered a new method of synthesising polyethylene. The

catalysts which he found[7], consisting of a trialkylaluminium and titanium tetrachloride, enabled the polymerisation of ethylene to be carried out at ordinary pressures[8,9].

1. Mechanism of the reaction. Polymerisation occurs as an ionic process. An ethylene molecule adds on to a C–Al bond in the original catalyst or in the growing chain according to the scheme $Al-R + C_2H_4 \rightarrow Al-[CH_2]_2-R$, etc. This reaction is characterised by the absence of free-radical processes, which would lead to branching of the polymers being formed. Low-pressure polyethylene therefore contains no branched macromolecules, in contrast to high-pressure polyethylene, which has an extremely branched macromolecule, as is shown in Fig. 17.

Use of $TiCl_3$ and trialkylaluminium compounds enabled Natta to prepare stereoregular polymers of propene and other α-olefins[10,11]. The reaction mechanism for the formation of stereoregular polymers is as follows. The start of chain growth occurs by addition of a monomer molecule to a metal atom in the catalyst and one of the radicals according to the equation

$$[X_nMR \rightleftarrows X_nM + R-] + CH_2=CHR_1 \rightarrow$$

$$\rightarrow [X_nMCH_2CH(R_1)R \rightleftarrows X_nM\overset{+}{C}H_2CH(R_1)R].$$

The reaction occurs in this case as an anionic polymerisation, in which the growing molecule is combined with aluminium and not with titanium. Chain propagation and termination occur according to the scheme shown in Fig. 1.

D'Alelio and Miranda[12] consider that the catalyst system consisting of a trialkylaluminium and titanium tetrachloride can act by a cationic mechanism in the presence of an excess of the latter component, and by an anionic mechanism with excess of the trialkylaluminium.

Natta[13] suggests the following scheme of individual stages in the process of polymerisation. The first stage in the reaction, initiation, occurs as follows:

$$[cat]^{(+)}-R^{(-)} + CH_2=CH-CH_3 \rightarrow [cat]^{(+)}-{}^{(-)}CH_2\underset{\underset{CH_3}{|}}{CH}-R.$$

Chain propagation then continues according to the scheme

$$[cat]^{(+)}-CH_2\underset{\underset{CH_3}{|}}{CH}(CH_2-CHCH_3)_{n-1}R + CH_2=CHCH_3 \rightarrow$$

$$\rightarrow [cat]^{(+)}-{}^{(-)}CH_2\underset{\underset{CH_3}{|}}{CH}(CH_2CHCH_3)_nR.$$

Chain termination can occur in several ways: (*a*) unimolecular termination; (*b*) first-order termination with respect to monomer; and (*c*) termination by the aluminium alkyl.

(*a*) Unimolecular termination, which consists in the splitting off of catalyst:

$$[cat]^{(+)}-{}^{(-)}CH_2\underset{\underset{CH_3}{|}}{CH}(CH_2CHCH_3)_nR \rightarrow [cat]^{(+)}-{}^{(-)}H + CH_2=\underset{\underset{CH_3}{|}}{C}(CH_2CHCH_3)_nR.$$

(*b*) First-order termination with respect to monomer, consisting in chain transfer via the monomer:

$$[cat]^{(+)}-{}^{(-)}CH_2\underset{\underset{CH_3}{|}}{CH}(CH_2CHCH_3)_nR + CH_2=CHCH_3 \rightarrow$$

$$\rightarrow [cat.]^{(+)}-{}^{(-)}CH_2CH_2CH_3 + CH_2=\underset{\underset{CH_3}{|}}{C}(CH_2CHCH_3)_nR$$

(*c*) Termination by the aluminium alkyl, consisting of the exchange of alkyl groups between the growing chain and the aluminium alkyl:

$$[cat]^{(+)}-{}^{(-)}CH_2\underset{\underset{CH_3}{|}}{CH}(CH_2CHCH_3)_nR + R'AlR_2' \rightarrow$$

$$\rightarrow [cat.]^{(+)}-{}^{(-)}R' + R_2AlCH_2\underset{\underset{CH_3}{|}}{CH}(CH_2CHCH_3)_nR$$

or

$$TiCl_nAlY_2P + AlR_3 \rightarrow TiCl_nAlR_3 + AlY_2P,$$

where Y is the alkyl and P the polymer chain.

Cooper and Rose[14] give the following reaction scheme, in which the first stage is adsorption of ethylene on the surface of titanium:

$$Ti^{2+} + \overset{CH_2}{\underset{CH_2}{\|}} + ClAlR_3 \rightarrow Ti^+CH_2CH_2R + AlR_2Cl.$$

Polymerisation then proceeds by a monomer molecule breaking into the Ti–C bond:

$$Ti^+CH_2CH_2R + nC_2H_4 \rightarrow Ti^+(CH_2CH_2)_nCH_2CH_2R.$$

Chain transfer is then possible via ethylene:

$$Ti^+CH_2CH_2(CH_2CH_2)_nR + CH_2=CH_2 \rightarrow Ti^+CH_2CH_3 + CH_2=CH(CH_2CH_2)_nR.$$

In this case the polymer will contain the same end-groups as in Natta's scheme.

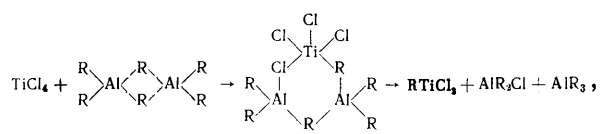
Another mechanism is possible, with formation of a hydride ion:

$$Ti^{2+} + CH_2=CH_2 \rightarrow Ti^{3+}CH=CH_2 + H^-,$$

$$Ti^{3+}CH=CH_2 + nC_2H_4 \rightarrow Ti^{3+}(CH_2CH_2)_nCH=CH_2,$$

$$Al-R_2Cl + Ti^{3+}(CH_2CH_2)_nCH=CH_2 \rightarrow Ti^{2+} + R(CH_2CH_2)_nCH=CH_2 + AlR_2Cl.$$

There exist other views on the reaction mechanism. Thus Badin[15] suggests the following mechanism:



$$RTiCl_3 \rightarrow R + TiCl_3.$$

He considers that the radical which is formed is able to initiate the polymerisation reaction. Further, the resulting $TiCl_3$ also can activate the double bond of the olefin.

The following mechanism is possible for the polymerisation with a catalyst consisting of titanium tetrachloride and phenyllithium:

$$TiCl_4 + LiC_6H_5 \rightarrow C_6H_5TiCl_3 + LiCl,$$

$$C_6H_5TiCl_3 \rightarrow C_6H_5 + TiCl_3.$$

The presence of phenyl groups in the resulting polymer was actually detected by infra-red spectroscopy[15]. Study of the infra-red spectra of the $TiCl_4 + (CH_3)_2AlCl$ system has shown that the two components react to form CH_3TiCl_3:[18]

$$2TiCl_4 + Al_2(CH_3)_4Cl_2 \rightleftarrows 2CH_3TiCl_3 + Al_2(CH_3)_2Cl_4.$$

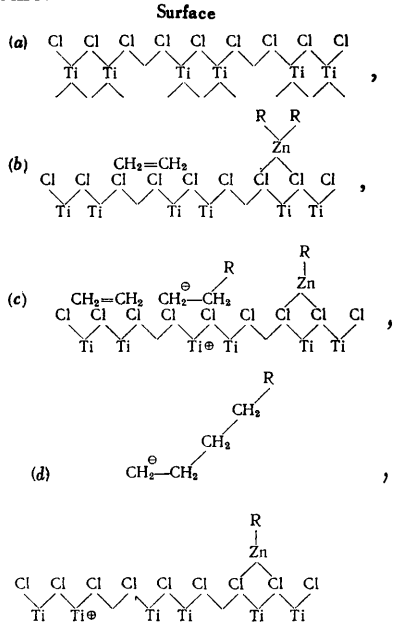
Beerman[17] isolated CH_3TiCl_3 (dark-violet crystals, m.p. 28.5°) by the action of $(CH_3)_3Al$ on $TiCl_4$, and showed that in

the presence of $TiCl_3$ it is more active than the $AlR_3 + TiCl_4$ system in catalysing the polymerisation of ethylene.

Gilchrist[19] gives a different scheme for the action of a Ziegler catalyst. He considers that polymerisation occurs at the surface of $TiCl_3$ crystals formed by the reduction of $TiCl_4$ by the reaction

$$TiCl_4 + Zn(C_4H_9)_2 \rightarrow TiCl_3 + Zn(C_4H_9)Cl + C_4H_9-$$

$TiCl_3$ separates in the form of particles the surface layer of which consists of chlorine atoms. Ethylene and $Zn(C_4H_9)_2$ undergo equilibrium adsorption on these particles, and a slow initiation reaction occurs. Chain growth occurs at a rate which is proportional to the amount of ethylene adsorbed on the surface, the positive charge travelling along the surface behind the negative charge, as is shown in the following scheme:



In this mechanism chain growth occurs along the surface, and not from a single centre represented by the organometallic compound. Gilchrist[19] finds support for his scheme in the fact that products of the radiolysis of $TiCl_4$ bring about the polymerisation of ethylene in the absence of other substances, just as a mixture of ethylene and $TiCl_4$ vapour yields low-pressure polyethylene on ultra-violet irradiation.

We see that there is at present no single viewpoint on the mechanism of stereospecific polymerisation: this is due to the complexity of this process and the difficulty of investigating it, as has been indicated in other reviews[16,20,22].

Apart from catalysts belonging to the $TiCl_4 + AlR_3$ system, a number of others have been proposed, e.g. $CH_3TiCl_3 + TiCl_3$,[17] $TiCl_4 + C_6H_5Li$,[15] $TiCl_4 + C_5H_{11}Na$,[21] $TiCl_4 + RLi$,[22,23] $TiCl_3 + AlR_3$,[11] $TiCl_4 + Zn(C_4H_9)_2$,[19] and $HLi + AlCl_3 + TiCl_4$.[24]

A common defect of these catalysts is their insolubility in the reaction mixture and the difficulties associated with their removal from the resulting polymer. Therefore soluble catalysts are of great interest. The first of them consists of tetraphenyltin, aluminium chloride, and vanadium trichloride, $(C_6H_5)_4Sn + AlCl_3 + VCl_3$,[25] and the second of dicyclopentadienyltitanium dichloride and diethylaluminium chloride, $(C_5H_5)_2TiCl_2 + (C_2H_5)_2AlCl$.[26] Bawn and Symcox[27] prepared a soluble catalyst for the polymerisation of ethylene from tetrabutyl orthotitanate and triethylaluminium, $Ti(OC_4H_9)_4 + Al(C_2H_5)_3$.

The use of soluble catalysts enables the reaction to be carried out in a homogeneous system with a lower consumption of catalyst and yields an unbranched polyethylene with a narrow molecular-weight distribution. Boldyrev et al.[28] have shown that titanium tetrachloride is reduced by a trialkylaluminium to Ti^{3+}, Ti^{2+}, and even metallic titanium. The extent of reduction depends on the nature of the alkylaluminium: $Al(C_2H_5)_3$ is the most vigorous reducing agent. Natta[29] was able to control the molecular weight of the polymer by adding various substances, $Zn(C_2H_5)_2$, HCl, $CH(C_6H_5)_3$, and C_2H_5Br. The use of hydrogen (under pressure) lowers, and that of oxygen-containing catalysts raises, the molecular weight of the polymers.

Kargin et al.[31] have shown that when the catalysts are very finely divided, which is achieved by the molecular-beam method, polymerisation of styrene, α-methylstyrene, methyl methacrylate, and other monomers occurs in the presence of beryllium chloride, lithium chloride, or metallic magnesium at the temperature of liquid nitrogen.

2. Formation of stereoregular polymers. An interesting feature of the polymers formed under these conditions is their regular spatial structure, in contrast to polymers obtained by radical polymerisation. Natta[11] explains this by the entry of monomer molecules between the catalyst surface and the end of the growing polymer chain, which grows like a tree, obtaining its supply analogously to roots from the soil, as shown in Fig. 1. Every monomer molecule which enters therefore arranges itself in the same way as all those which have entered previously, and the resulting polymer chain is made up solely of *dextro* or *laevo* units. Since at no instant during this process will the growing tip of the macromolecule be absolutely free, no racemisation will occur.

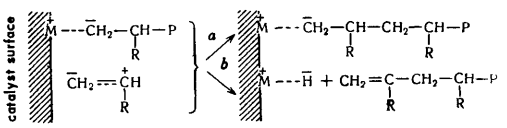


Fig. 1. Chain growth (a) and chain termination (b) during the formation of stereoregular polymers by ionic polymerisation.

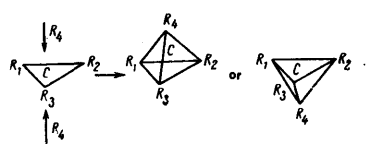


Fig. 2. Addition to a free radical.

In contrast to this, during radical polymerisation each of the similar carbon atoms remains for a short period of time in the state of a free radical. Addition of this free radical to the next olefin molecule can occur in two ways, as shown in Fig. 2. Since there are usually no reasons making one or other mode of addition more difficult, the

polymer formed has a random arrangement of atoms and atactic[32]. In some cases, however, formation of stereoregular polymers is possible even with radical polymerisation, if conditions are created which ensure that the monomer molecules shall be oriented, and which diminish their mobility (see below).

Every carbon atom in a polymer obtained by stereoregular polymerisation has a definite, recurring configuration. If all the asymmetric carbon atoms have the same configuration, an isotactic polymer is formed. If there is strict alternation of atoms having the *dextro* and the *laevo* configuration, a syndiotactic polymer is formed. Finally, if the distribution is random, as occurs with inactive catalysts, as well as during radical polymerisation, an atactic polymer will be obtained (see Fig. 21).

An interesting feature of isotactic polymers which has attracted attention to them is the fact that, because of the regular structure of the polymer chains, they are easily packed in the solid state and form crystalline products possessing high melting points and great strength (see Table 6). Natta[13] considers the presence of a solid catalyst surface to be an essential condition for the formation of isotactic polymers. No isotactic polypropylene is formed in the presence of the hydrocarbon-soluble catalyst system $Ti(OC_3H_7)_4 + Al(C_2H_5)_3$. When this catalyst is deposited on aluminium silicate ($SiO_2 + Al_2O_3$) 10% of isotactic polypropylene is obtained, and when it is deposited on $CoCl_2$, 35–45% results. This shows the necessity for the presence of a solid catalyst[13]. Three crystalline forms of $TiCl_3$ have been discovered, the α- (violet), β- (brown), and γ-forms[13]. The structure of the first two is shown in Fig. 3. The α-form gives the purest stereopolymers. With dienes the α- and γ-forms give *trans*-1,4- and the β-form yields *cis*-1,4-polymers.

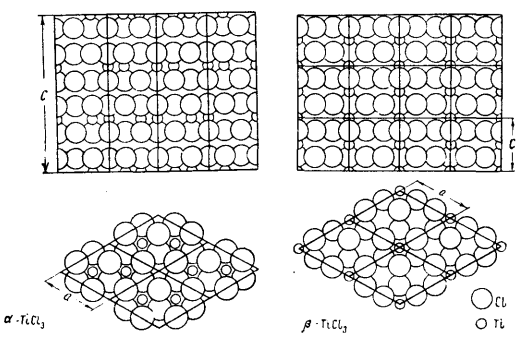


Fig. 3. Crystal structure of the α (violet) and β (brown) modifications of titanium trichloride.

Natta[13] has shown that the stereospecificity of a catalytic system depends also on the ionic radius of the metal in the metal alkyl: in the polymerisation of propene with $TiCl_3$ and a metal alkyl, the amount of isotactic polymer decreases with increase in the ionic radius: Be (r = 0.35 Å), 94–97%; Al (0.51 Å), 80–90%; Mg (0.66 Å), 78–85%; and Zn (0.74 Å), 30–40%.

Danusso and Sianesi[33] have shown that the stereospecificity of the $TiCl_4 + AlR_3$ catalyst system depends on the proportions of the components and is a maximum when $TiCl_4 : AlR_3 = 1 : 2.5$.

Very similar properties to those of polyethylene obtained with Ziegler catalysts are possessed also by polyethylene obtained at medium pressures (~ 50 atm) in the presence of a heterogeneous catalyst consisting of CrO_3 deposited on an aluminium silicate carrier ($SiO_2 + Al_2O_3$) (Phillips method)[34,35]. A continuous method for polymerising ethylene and propene at moderate pressures has now been worked out[36]. This process is particularly interesting when polyethylene is employed as solvent[37].

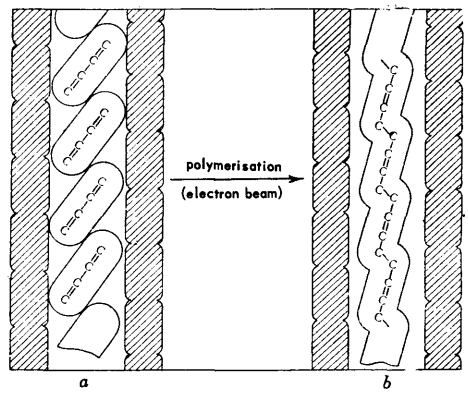


Fig. 4. Stereoregular polymerisation of butadiene in clathrate compounds under the influence of fast electrons: *a*) position of butadiene molecules before polymerisation; *b*) position after polymerisation.

Topchiev et al.[38] have investigated the structure and properties of molybdenum and chromium oxide catalysts, and have shown that with their aid polyethylene and polypropylene of a high degree of crystallinity can be prepared.

Recently stereoregular polymers have been successfully prepared with other catalysts. Thus Fridlander and Thomas[39] obtained crystalline polymers of α-methylstyrene and α,p-dimethylstyrene in the presence of boron fluoride, stannic chloride, etc. By polymerisation in the presence of a Grignard reagent, Muller et al.[40] obtained isotactic and syndiotactic polymers of methyl methacrylate, and Garrett et al. those of isopropyl acrylate[41]. Fox et al.[42] showed that at low temperatures (0°–75°) methyl methacrylate forms crystalline polymers even by radical polymerisation.

Browne and White[43] found that formation of crystalline polymers can occur as a result of the radical polymerisation of butadiene, acrylonitrile, vinyl chloride, vinylidene chloride, and cyclohexadiene by the action of a beam of electrons. The main condition for success is the use of clathrate compounds (inclusion compounds) of these monomers with urea. After completion of polymerisation the urea is removed. The monomer molecules occur in a definite position relative to one another, and this leads to the formation of stereoregular polymers. Butadiene under these conditions forms a crystalline *trans*-1,4-polybutadiene.

The clathrate compounds are crystalline solids containing channels filled with the monomer, the arrangement of the molecules being strictly fixed. On exposure to fast

electrons (1 MeV), therefore, addition of monomer molecules to one another occurs in a fixed position. For the same reason no branching occurs, since the chain can grow only by combination of the monomer head to tail, as shown in Fig. 4. The result is solid *trans*-1,4-polybutadiene. This process resembles stereospecific syntheses in living organisms.

Sakurada and Nambu[44] obtained a syndiotactic polymer of vinyl chloride by exposing the complex compound of the latter with urea to γ-rays (from Co^{60} of intensity 1000 c at 75° for 50–70 h).

3. Polymerisation by means of lithium alkyls. Organolithium compounds used with dienes enable the process to be carried out in such a way that the polymer formed contains up to 90% of structural units combined in the *cis*-1,4-position.

Korotkov et al.[45] investigated the polymerisation of isoprene, methyl methacrylate, and other monomers in the presence of butyllithium, and suggested the following mechanism for the process:

chain initiation:

$$RLi + M \rightarrow MRLi,$$

chain propagation:

$$M_iRLi + M \rightarrow M_{i+1}RLi,$$

chain termination by interaction of two growing chains:

$$M_iRLi + M_jR'Li \rightarrow R'M_iLi + RM_jLi,$$

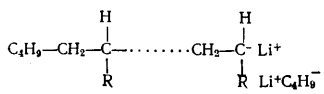
or by reaction with a catalyst molecule:

$$M_jRLi + R'Li \rightarrow R'M_jLi + RLi,$$

chain transfer:

$$M_iRLi + M \rightarrow RM_iH + MLi.$$

The structure of the transition state in this reaction is as follows[30]:



At the end of the chain is a quadrupole, which controls the addition of monomer to the growing chain.

Lithium alkyls in the presence of titanium tetrachloride form isotactic and amorphous polymers of olefins[15,23].

Fox et al.[46] found that polymerisation of methyl methacrylate in the presence of fluorenonelithium leads to the formation of stereoregular high polymers.

B. Preparation of Graft and Block Copolymers

A second new type of polymer is represented by the block and graft polymers and copolymers, whose structure had not been recognised although they have existed earlier. All polymers which have already been obtained for a long time by radical polymerisation are, owing to the occurrence of chain transfer, branched polymers, in which "grafted" side chains are attached to the main chain of the macromolecule. Fig. 5 shows diagrammatically an "ideal" linear polymer and a real polymer obtained by radical polymerisation. The presence of side chains has a great effect on the properties of the polymer, as numerous examples have shown recently. Branching exerts a particularly great influence on the ability to crystallise.

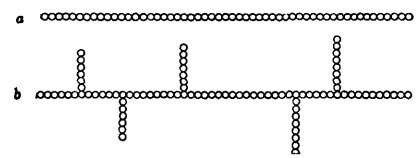


Fig. 5. Structure of (*a*) an "ideal" linear polymer and (*b*) a real polymer obtained by radical polymerisation.

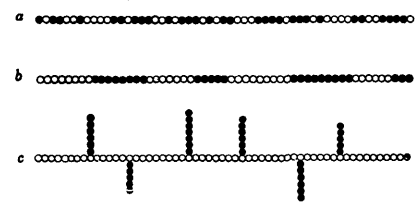


Fig. 6. Structure of "ideal" copolymers: *a*) normal, *b*) block, and *c*) graft copolymers.

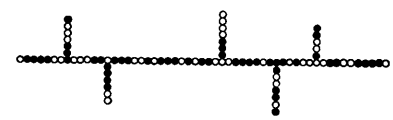


Fig. 7. Structure of a real copolymer obtained by a radical process.

The properties of the polymer are still more changed when the side chains in the graft copolymer are different in nature from the main chain. Such graft copolymers have been intensely investigated recently, and many methods are already known for obtaining them.

A block copolymer is a polymer whose macromolecule is made up of alternating fragments of polymers of different composition (blocks). The structure of graft and block copolymers is shown diagrammatically in Fig. 6. However, such a structure is possessed only by those copolymers, including block and graft copolymers, which are obtained by polycondensation or ionic polymerisation. Polymers obtained by radical processes have a different structure. They are characterised by the presence of a larger or smaller number of side branches of different size. This is shown diagrammatically in Fig. 7. In the same way, block copolymers obtained by a radical process possess a branched macromolecule, as shown diagrammatically in Fig. 8. This diagram shows quite clearly that the distinction between a block copolymer and a graft copolymer is extremely arbitrary. Graft copolymers are still more branched, as can be seen from Fig. 9.

A number of methods have been proposed for obtaining graft and block copolymers, based on processes of polycondensation and radical and ionic polymerisation, among

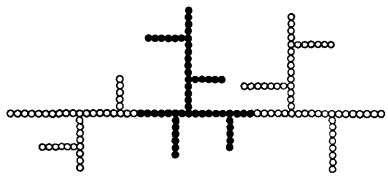


Fig. 8. Structure of a block copolymer obtained in a radical process.

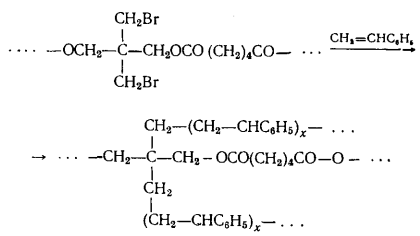
which are: (1) use of chain transfer; (2) method of active centres; (3) copolymerisation; (4) use of radiation; (5) preparation of block copolymers; and (6) a mechanical–chemical method. The results will be considered in the same order.

1. Use of chain transfer. Several procedures are available for preparing graft copolymers by this process: a polymer is added to a monomer undergoing polymerisation, and owing to chain transfer, fragments of the latter are grafted on to the polymer. Here formation of the graft copolymer is accompanied by that of a mixture of the two homopolymers[47,48].

Berlin was able to prepare graft copolymers by carrying out the polymerisation of vinyl chloride in a latex of a copolymer of butyl methacrylate with methacrylic acid[49], and also by the polymerisation of a mixture of butyl methacrylate and methacrylic acid in a latex of poly(vinyl chloride)[49]. He obtained a graft copolymer of butadiene–styrene rubber with polystyrene in this way[49].

The simplest case occurs when the reaction is carried out in a swollen polymer. Swift[50] observed that a monomer and an initiator within a swollen polymer form a graft copolymer (~ 25%) together with the homopolymer. Hartley[51] obtained a graft copolymer from vinyl acetate and polyvinyl alcohol by polymerising the former in a suspension stabilised with the latter.

In the polymerisation of styrene in the presence of the polyester of pentaerythritol dibromide and adipic acid Schonfeld and Waltcher obtained a graft copolymer[52]:



Here, more active points (bromine atoms) are produced, and this fixes the position of the grafts.

2. Copolymerisation. This is based on the use of polymers containing double bonds, at which the added monomer can enter into copolymerisation. This is usually accompanied by the formation of grafts by chain transfer. The relative proportions of these reactions depend on the structure of the polymer.

A widely used method for obtaining glass-like plastics reinforced with polyesters is based on the use as binders of polyesters of maleic, fumaric, or other unsaturated acid. These polyesters copolymerise with styrene or other monomers with formation of a graft copolymer. The formation of such copolymers has been studied in detail by Spasskii et al.[53] The introduction of groups having double bonds, e.g. by the formation of acrylic esters of cellulose followed by their copolymerisation with methacrylic esters, enables insoluble three-dimensional polymers to be obtained[49].

Merrett and Wood[48] modified natural rubber by forming graft copolymers with methyl methacrylate and styrene, and proved their formation by fractionation. Swift[50] impregnated rubber with the monomer and the initiator and then carried out the polymerisation, obtaining a graft copolymer together with a homopolymer.

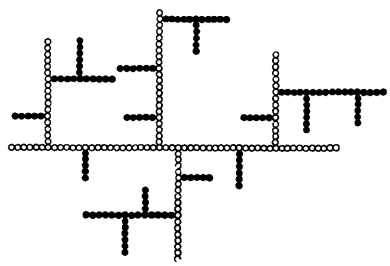
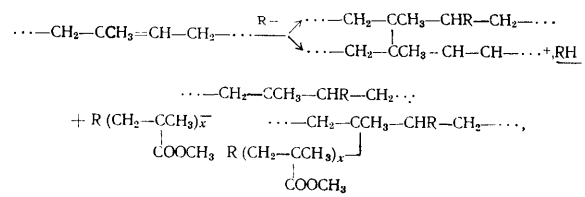


Fig. 9. Structure of a graft copolymer obtained in a radical process.

Kobryner and Banderet[54] investigated the reaction by which methyl methacrylate is grafted to natural rubber, and concluded that grafting is a result of combination of the growing poly(methyl methacrylate) chain with a free radical in the rubber chain:



where R = C_6H_5 or C_6H_5COO.

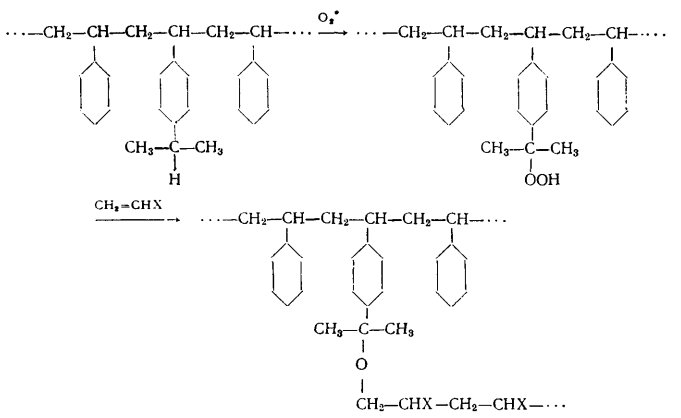
Thus grafting occurs partly by copolymerisation at the double bonds, and partly by chain transfer.

Abkin et al.[55] regard copolymerisation involving the double bond as unlikely, since from energy considerations chain grafting at a methylene group is more probable.

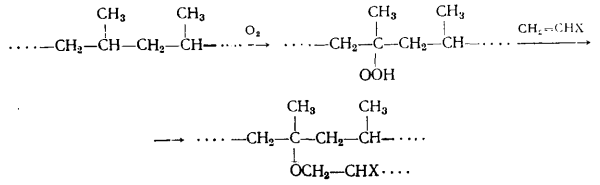
Banderet and Kobryner[56] broke down the graft copolymer of methyl methacrylate on natural rubber by the action of ozone, and isolated poly(methyl methacrylate) of molecular weight 350 000.

3. Method of active centres. A more reliable way of obtaining graft copolymers with a definite arrangement of the grafts is to form active centres in the original polymer, on to which monomer molecules are subsequently grafted. These active centres are formed in various ways.

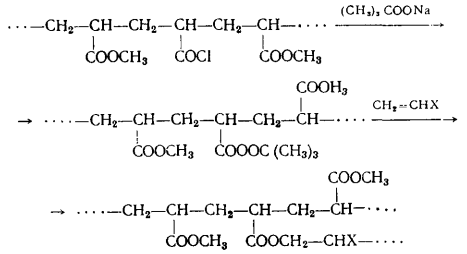
They can be obtained by oxidising such readily oxidisable groups as isopropyl, or by introducing peroxy groups by oxidation with ozone. In hydrolytic polymerisation other active groups are those containing reactive hydrogen atoms, etc. Mesrobian[57] introduced active groups by preliminary oxidation with atmospheric oxygen of a copolymer of styrene and *p*-isopropylstyrene. The resulting hydroperoxy groups form points at which monomer molecules are grafted on[57]:



Natta[58,59] used this method for grafting methyl methacrylate on to polypropylene and other isotactic polyolefins. When air is passed into a 15–20% solution of polypropylene, hydroperoxy groups are formed, on which monomer is then grafted:



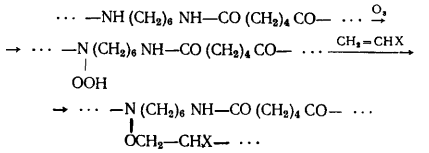
Smets et al.[59,60] prepared graft copolymers from a copolymer of methyl acrylate and acryloyl chloride by displacing the chlorine with t-butyl hydroperoxide:



Jones obtained a graft copolymer by ultra-violet irradiation of methyl methacrylate containing brominated styrene[61].

Manson and Cragg[62] employed oxidised polystyrene or a copolymer of styrene with 4-vinylcyclohexanone, copolymerising it with styrene.

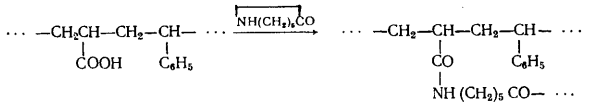
Korshak and Mozgova[63] found a way of obtaining graft copolymers by first subjecting the initial high polymers to the action of ozone to produce active hydroperoxy groups. The resulting polymer is then treated with a vinyl monomer, with the formation of grafts at the active groups. This method enables a graft to be made on any polymer. By means of it graft copolymers have been prepared of such polyamides as poly-ϵ-caprolactam (Capron, Perlon)[63,64], polyhexamethyleneadipamide (Anid, 6,6-nylon)[65], and the mixed polyamide Anid G-669[63,65,66], and also such polyesters as poly(ethylene terephthalate) (Lavsan, Terylene)[67], with monomers such as styrene, methyl methacrylate, acrylonitrile, and vinylidene chloride. The reaction probably occurs as follows:



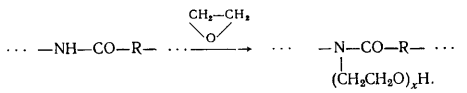
This method enables grafts to be made in the surface layer alone, making it possible to vary the surface properties of finished articles made of various high polymers. The ozonisation method proved to be suitable for other polymers as well, and was successfully employed by Kargin et al. for grafting styrene to starch[68] and also acrylonitrile or styrene to cellulose[69]. Kozlov et al.[70] prepared graft copolymers of polystyrene and acrylic acid in this way.

Wichterle and Gregor[71,72] suggested a method for grafting poly-ϵ-caprolactam on to the main chain of poly(methyl methacrylate). At first a copolymer of *N*-methacryloyl-ϵ-caprolactam with styrene is obtained, and then in ϵ-caprolactam medium, in the presence of alkali, side branches are grafted on, usually leading to the formation of a gel.

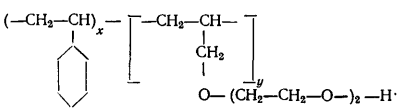
Chapman and Valentine[59,73] prepared graft copolymers of poly-ϵ-caprolactam on vinyl polymers containing COOH, $COOCH_3$, and NH_2 groups, e.g. the copolymer of styrene with methyl acrylate, acrylic acid, or maleic anhydride. The reaction is carried out in the presence of water:



Haas et al.[74] and Rafikov et al.[75] obtained graft copolymers by the action of ethylene oxide on polyamides:



Weiss et al.[76] synthesised graft copolymers of ethylene oxide on the copolymer of styrene with dimethyl maleate, and of styrene with allyl acetate, of the following structure:



4. Application of radiation. The use of high-energy or ultra-violet rays is an extremely promising method. The initial polymer, often containing halogen or similar atoms, is exposed to ultra-violet radiation or, better, to γ-rays from Co^{60}. Free radicals are formed at various points on the polymer by rupture of chains, splitting off of hydrogen, bromine atoms, etc., and grafting occurs at these points. Since the polymer is not changed uniformly by the action of the radiation, a complex product is formed, consisting of a mixture of graft and block copolymers together with a hybrid of them which is at the same time both a graft and a block copolymer. Fig. 10



Fig. 10. Structure of a graft block copolymer obtained by irradiation or by a mechanical method.

shows a diagram of such a graft block copolymer. The radiation method has been very widely employed by various investigators, in particular by Chapiro[77], Ballantine[78], and others[59].

Several methods are known for obtaining graft and block copolymers with the aid of ionising radiations[79]. The first consists in irradiating a mixture or a solution of two high polymers when the macroradicals which are formed combine to yield a block copolymer. However, the yield of the latter is small, since the formation of each macromolecule of graft copolymer is accompanied by two homopolymer molecules[79,80].

The second method consists in irradiation of a polymer in contact with a monomer, and also in solution or in emulsion[72]. A mixture of graft copolymer and homopolymer due to polymerisation of the monomer is formed[80-82]. Formation of homopolymer can be minimised by choice of appropriate starting materials or by reducing the amount of the original monomer taken. In the latter case some article made of the finished polymer is soaked in the monomer, and the swollen specimen exposed to the radiation[79,83,84].

In a third method the polymer alone is irradiated in air. The macroradicals formed react with atmospheric oxygen to form peroxy groups[83]. When the treated polymer is placed in the monomer, the peroxy groups form the active centres on which polymerisation of the monomer begins, leading to the formation of grafts[79,84]: any formation of homopolymer is insignificant. A given weight of the original polymer can have grafted on to it as much as 122 times its weight of a second polymer by this method.

Ballantine et al.[85] have shown that polymers can be irradiated in the absence of oxygen, and then the monomer added. The radicals which are formed initiate growth of the grafts.

Chapiro[86] grafted acrylonitrile on to polyethylene; above 135° a cross-linked copolymer is formed.

Cooper et al.[87] prepared graft copolymers of methyl methacrylate and natural rubber by exposing latex to visible light, ultra-violet radiation, and γ-rays.

5. Mechanical method. Mechanical processing of polymers (grinding, rolling, crushing, treatment with ultrasonic vibrations, freezing of a solution, etc.) is accompanied by destruction of the macromolecules with formation of macroradicals:

$$\cdots -CH_2-CHX-CH_2-CHX- \cdots \rightarrow \cdots -CH_2-CHX- + -CH_2\cdot -CHX- \cdots$$

If a mixture of several polymers is subjected to such treatment, recombination of the various macroradicals should yield block copolymers:

$$\cdots -CH_2-CHX- + -CH_2-CHY- \cdots \rightarrow \cdots -CH_2-CHX-CH_2-CHY- \cdots$$

block copolymer

The occurrence of chain transfer should, however, lead to the formation of branched graft copolymers and graft block copolymers (see section B. 4).

If mechanical destruction of a polymer is carried out in a monomer medium, the resulting macroradicals initiate polymerisation of the monomer, evidently with the formation mainly of a block copolymer together with a graft copolymer and a graft block copolymer (see section B. 4):

$$\cdots -CH_2-CHX- + CH_2=CHY \rightarrow \cdots -CH_2-CHX-CH_2-CHY- \cdots$$

$$\cdots -CH_2-CHX-CH_2-CHY- \cdots 2R \rightarrow \cdots -CH_2-\underset{|}{CX}-CH_2-\underset{|}{CY}- \cdots \xrightarrow{CH_2=CHY}$$

$$\rightarrow \cdots -CH_2-\underset{|}{\overset{|}{CX}}-CH_2-CY- \cdots$$

$$CH_2-CHY- \cdots \quad CH_2-CHY- \cdots$$

graft block copolymer

These two variants are employed in practice for the production of graft and block copolymers by mechanical means[88].

Angier and Watson[89] have shown that when natural rubber is cold-rolled together with chloroprene rubber, a graft copolymer is formed, the presence of which was proved by fractionating the product.

Dogadkin et al.[90], using a fractionation method, showed that when a mixture of natural and butadiene–styrene rubbers is masticated on microrollers, graft and block copolymers are formed.

Kargin[91] and other investigators used a mechanical method to obtain graft and block copolymers by plasticising a mixture of a phenol–formaldehyde resin with a copolymer of butadiene and acrylonitrile.

Berlin et al.[92] obtained a graft and a block copolymer by prolonged rolling of a mixture of poly(vinyl chloride) with phenol–formaldehyde resin.

Kovarskaya et al.[93] obtained graft and block copolymers of butadiene–acrylonitrile rubber with polystyrene and phenol–formaldehyde resin by a mechanical method from the finished polymers.

Slonimskii et al.[94] synthesised graft block copolymers of butadiene–styrene and sodium–butadiene rubbers with styrene or methyl methacrylate by subjecting the rubber mixed with the monomer to mechanical treatment. The resulting copolymers possessed better characteristics than the original rubbers.

Angier et al.[95] observed the formation of graft and block copolymers by the cold rolling of rubber with methyl methacrylate, methacrylic acid, chloroprene, and styrene, but vinyl chloride and vinyl acetate do not copolymerise with rubber under these conditions.

Angier et al.[96] prepared block copolymers by mechanical mixing of a polymer with a monomer, using twelve polymers and twelve monomers in different combinations. They investigated the reaction of such polymers as poly(methyl methacrylate), polystyrene, poly(vinyl acetate), poly(vinyl chloride), polyethylene, poly(vinylidene chloride), polyvinylpyrrolidone, a copolymer of styrene and butadiene (85 : 15), polyhexamethyleneadipamide (6,6-nylon), ethylcellulose, chlorinated rubber, and starch with the monomers methyl methacrylate, ethyl methacrylate, methacrylic acid, vinyl acetate, styrene, acrylonitrile, vinylpyrrolidone, vinylpyridine, vinylidene chloride, allyl acrylate, calcium acrylate, and divinylbenzene. It was found that copolymers were not formed in the case of vinyl acetate and polystyrene or poly(methyl methacrylate). In

the majority of the other cases formation of copolymer occurred after 20–30 min rolling.

Kargin and Plate[97] were able to graft monomers on to the surface of solid crystalline materials (quartz, common salt, and graphite) by grinding the latter in styrene or methyl methacrylate medium in a vibration mill.

Ultrasonic vibrations cause the destruction of polymers, so that exposure to them of a mixture of two polymers leads to the formation of block copolymers as a result of subsequent recombination, which has been shown in the case of a mixture of polystyrene and poly(methyl methacrylate)[98,99], as well as in other cases[100]. The action of ultrasonic vibrations on a solution of a polymer in a monomer leads to the formation of graft and block copolymers[101,102].

Berlin and his collaborators[103] have shown that disintegration of macromolecules with formation of macroradicals occurs when polymer solutions are frozen. If this is applied to starch in a vinyl-monomer medium, graft copolymers of starch with vinyl monomers are formed. A graft copolymer of starch with styrene has been obtained in this way.

6. Preparation of block copolymers. Both block and graft copolymers can be obtained by polycondensation as well as radical or ionic polymerisation. A block copolymer was obtained by Allen[104] by the polycondensation of dimethyl terephthalate with a mixture of ethylene glycol and poly(ethylene oxide). It contains blocks of poly(ethylene oxide) and poly(ethylene terephthalate), and can be represented as follows[105]:

$$\{[-O(CH_2CH_2O)_2COC_6H_4CO]_x(OCH_2CH_2)_y-\}_n.$$

An interesting method for obtaining block copolymers was proposed by Hicks and Melville[106]. They passed a monomer through a capillary tube illuminated with ultra-violet radiation. Polymerisation occurred, and the solution of the resulting polymer ran into a second polymer, which produced further growth in the active chains.

Orr and Williams[107] obtained a block copolymer of styrene with butadiene and other monomers. They first synthesised a block containing peroxy groups at the ends, by polymerisation of the appropriate monomer in the presence of *p*-diisopropylbenzene hydroperoxide. The resulting block was placed in styrene medium, when blocks of polystyrene grew on to its ends:

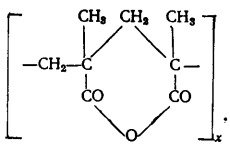
$$HOOROM_nOROOH \xrightarrow{CH_2=CHC_6H_5} (CH_2CHC_6H_5)_xOROM_nORO(CH_2CHC_6H_5)_y$$

Dunn et al.[108] employed for the production of block copolymers polystyrene prepared in the presence of carbon tetrabromide and containing CBr_3 groups at the ends of the macromolecules. This polystyrene was dissolved in methyl methacrylate and exposed to ultra-violet radiation, as a result of which the bromine atom was replaced by a growing chain, forming a block of methyl methacrylate units.

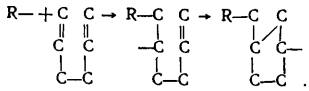
Bawn et al.[72,109] prepared block copolymers by the decomposition of aliphatic diazo compounds $RCHN_2$ under the influence of alkylborons. First of all one diazo compound was decomposed, and the first block was obtained with active end groups:

$$BX_2-(CH)_n-X;$$
$$\quad\quad\quad

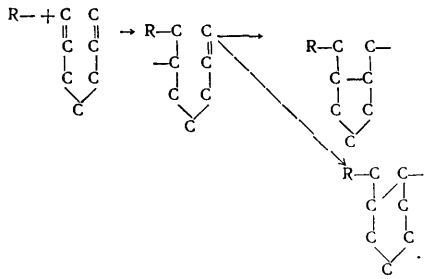
on radical polymerisation yields a polymer, which melts at about 200°, containing rings in the chain:



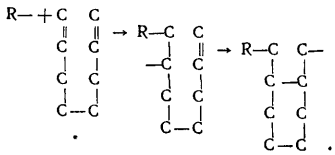
In general, cyclopolymerisation leads to the formation of five- or six-membered rings, the former being produced as follows:



Simultaneous formation of five- and six-membered rings can also occur:



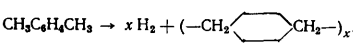
Six-membered rings are formed as follows:



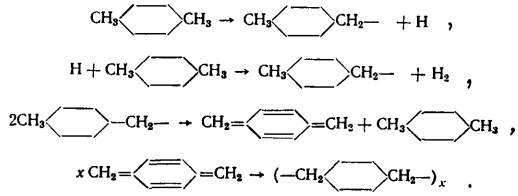
Thus the decisive factor is the number of atoms of carbon (or other elements) separating the double bonds. It varies between two and four. When the number of atoms is outside these limits, cyclopolymerisation obviously does not take place, and formation of linear or three-dimensional polymers will occur.

D. Dehydrogenation Polymerisation

Recently polymers containing aromatic nuclei in the chain have attracted a great deal of attention. Thus Szwarc[118] obtained a polymer of *p*-xylylene by pyrolysis of *p*-xylene vapour in a vacuum. The reaction leading to the formation of poly-*p*-xylylene is represented as follows:



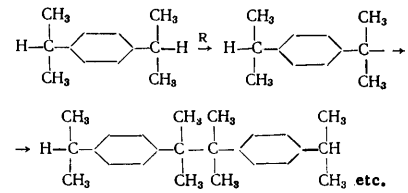
Errede and Landrum[119] showed that this reaction involves the intermediate formation of free radicals:



Rapid cooling and freezing of the products of the pyrolysis to -78° gave a solution of diradicals: these are evidently stabilised by the formation of a quinonoid structure. With iodine they form *p*-xylylene iodide, and when the solution is heated to 20° they polymerise, forming poly-*p*-xylylene.

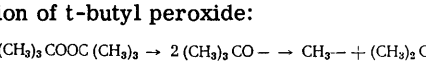
E. Polyrecombination

Korshak et al.[120-122] found a new way of obtaining compounds similar in structure to those described above, by polyrecombination. The initial hydrocarbon is treated with a peroxide. The secondary radicals formed combine with one another to form a polymer chain, as shown by the following equation:



Thus *p*-diisopropylbenzene yields a polymer by stepwise polyrecombination.

The initial primary radicals can be obtained by the decomposition of t-butyl peroxide:



This is usually accompanied by the formation of both butoxy and methyl radicals, their proportions depending on the temperature and the properties of the solvent. The molecular weight of the polymer depends on the amount of peroxide taken, as shown in Fig. 11. During the reaction there is a gradual conversion of monomer to polymer by a stepwise mechanism. Fig. 12 shows the variation in the composition of the reaction mixture as a function of the amount of peroxide taken.

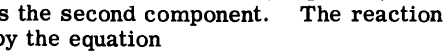
F. Radical Polymerisation

At the present time radical polymerisation is the main method of preparing the most important polymers. The great scientific and practical achievements of this branch of the chemistry of high polymers have been described in a number of monographs[123,124] and reviews[125,126], and therefore they will not be discussed here.

G. Polycondensation

The results of numerous investigations on polycondensation have been reviewed in monographs[127,128]. Together with the broad development of research on classical lines, aimed at studying the mechanism and the kinetics of polycondensation, a new approach consists in carrying out the reaction at the boundary separating two phases[129-132].

The starting materials are an acid chloride of a dicarboxylic acid dissolved in benzene, carbon tetrachloride, chloroform, etc. and a diamine, diphenol, etc. dissolved in water as the second component. The reaction is represented by the equation



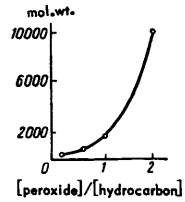


Fig. 11. Variation of molecular weight of polymer of *p*-diisopropylbenzene with molar ratio of peroxide to *p*-diisopropylbenzene.

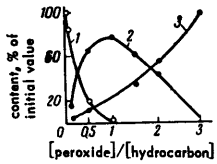


Fig. 12. Composition of reaction products of polyrecombination as a function of the amount of peroxide added: 1) diisopropylbenzene; 2) polymers of low molecular weight; 3) polymers of high molecular weight.

Alkali is added to the aqueous layer to neutralise the acid which is formed. A film of polyamide is produced at the boundary between the two phases. If the initial solutions are mixed rapidly, a fine powder is obtained. The reaction product can also be obtained in the form of a fibre.

Morgan[129] points out that polymer formation occurs in the organic phase, to which the diamine diffuses. The role of the aqueous phase is a solvent for the diamine or the diphenol, an acid acceptor, and a medium which serves to remove the acid formed. The laws governing polycondensation at the boundary between two phases differ from those for ordinary polycondensation in that the process is non-equilibrium in character, excess of the starting materials has no effect on the molecular weight of the resulting polymer, etc.[130]

Korshak et al.[130] have found that the molecular weight of the polyamide does depend on the concentration of the reactants, as shown in Fig. 13. It is not affected by the relative proportions of the starting materials (see Fig. 14). For comparison this diagram shows also a curve demonstrating the variation in molecular weight with the relative proportions of the starting materials for equilibrium polycondensation. In addition, the molecular weight is strongly affected by the presence of such monofunctional substances as monoamines and chlorides of monocarboxylic acids, as shown in Figs. 15 and 16.

Korshak et al.[133] have investigated the reaction of dichlorides of aromatic dicarboxylic acids with diphenols, and have shown that in this case there is an optimum concentration of the reactants at which the resulting "polyarenate" has the maximum molecular weight.

In a two-phase system polycondensation is carried out at comparatively low temperatures, and can yield products of very high molecular weight with a non-equilibrium distribution[30]. Polyamides and polyurethanes can be obtained with very high melting points: such polymers are impossible to obtain in the usual way owing to their decomposition at the high temperatures required by normal polycondensation.

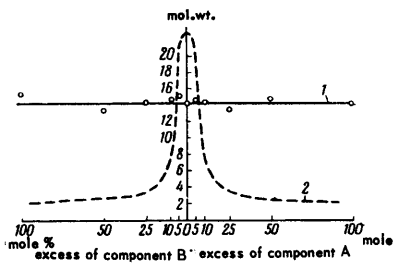


Fig. 14. Dependence of molecular weight of polyamide on the presence of an excess of starting materials: 1) during two-phase (non-equilibrium) polycondensation with excess of hexamethylenediamine (A) and of adipoyl chloride (B); 2) as above, during equilibrium polycondensation.

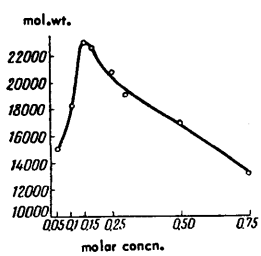


Fig. 13. Variation of molecular weight of polyamide with initial concentrations of reactants.

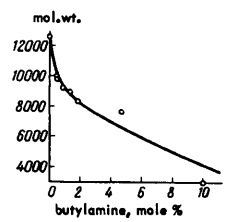


Fig. 15. Change in molecular weight of polyamide with amount of butylamine added.

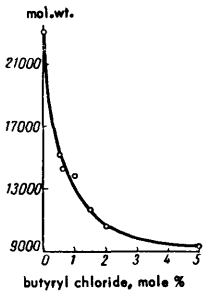


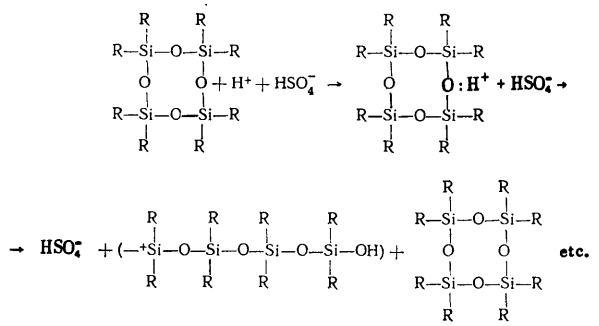
Fig. 16. Variation of molecular weight of polyamide with amount of butyryl chloride added.

H. Polymerisation of Cyclic Compounds

Great advances have been made in the polymerisation of cyclic compounds. A great deal of research has been devoted especially to the polymerisation of ϵ-caprolactam[134]. Wichterle[135] developed a method for the rapid polymerisation of ϵ-caprolactam in the presence of alkaline reagents, which enables this process to be carried out in a few minutes instead of the many hours required for polymerisation in the presence of water.

Mention must be made of the reversible polymerisation of the six-membered carbonates of $\epsilon,\epsilon,\epsilon'$-disubstituted 1,3-propanediol, studied by Sarel and Pohoryles[136].

The polymerisation of cyclic siloxanes in the presence of sulphuric acid and other catalysts, leading to the formation of linear macromolecular polysiloxanes, has attracted a great deal of interest[137-140]. Andrianov and Yakushkina[137] suggest the following reaction mechanism:



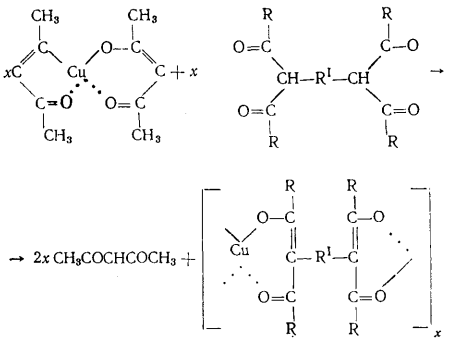
J. Preparation of Polymers by Complex Formation

A new way of preparing polymers of previously unknown type consists in using the reaction of complex formation to build up a polymer chain[133,140-143]. Reaction is carried out between a complex containing several complex-forming groups and metal ions or such relatively simple complexes as metal acetylacetonates. Chelate structures are formed, consisting of complex heterocycles with the central metal atom, which are far more stable than ordinary complexes. This effect of an increase in stability accompanying the formation of chelate compounds is explained by an increase in entropy of such complexes in comparison with the original substances.

In the preparation of complex polymers, the acceptors generally employed are cations of the transition metals — V^{3+}, Cr^{3+}, Fe^{2+}, Fe^{3+}, Co^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pd^{2+}, Ag^{+}, Pt^{2+}, etc. — or the ions Ga^{3+}, In^{3+}, Te^{3+}, Ce^{4+}, and Pb^{2+}, which follow them. The small sizes of these cations in combination with their high effective charge, as well as the presence in some cases of unfilled *d* orbitals, ensure a stable bond with donor groups. Ions of the alkaline-earth metals and the lanthanides are feeble acceptors, and alkali-metal ions form complexes only in rare cases.

Complexones which are to be used to obtain chelate polymers should contain in their molecule such donor groups as $-NH_2$, =NH, =N, =NOH, –OH, =CO, –COO–, $-PO(OH)O-$, $-SO_2O-$, –S–, =C=S, etc.

A typical example of the formation of a complex polymer is the reaction between tetraketones and a metal acetylacetonate[140,142,143]:



For individual representatives see part III, section B. 11.

III. NEW HIGH POLYMERS

Many new polymers have been obtained both by using new methods of synthesis and by applying those which are already known. In view of their immense number, any complete description of all these polymers within a short review is impossible, and we must confine ourselves to isolated examples, which will serve as an illustration of the most important achievements in synthesis and as an indication of the main trends in the development of this field.

We must first note the tendency during recent years to develop production and research work on polymers based on petroleum chemicals, coal, and natural gas, which represent the most readily available and cheapest forms of raw materials for the large-scale production of a great number of polymers. This trend is shown by the production of polyethylene, isotactic polypropylene and other stereoregular polymers of α-olefins, polyformaldehyde, polyacrylonitrile, polystyrene, polybutadiene, polyisoprene, and other polymers which form the starting materials for the production of plastics, synthetic fibres, and synthetic rubber. The bulk production of cheap polymers has the aim of satisfying the day-to-day needs of industry and the demands of the population for various types of consumer goods.

There is also a marked tendency to seek polymers of higher quality than those already known, which are required to satisfy the needs of modern technology, demanding high thermal stability, great chemical stability, and high mechanical strength, electrically insulating or semiconducting properties, etc.[144]

Nesmeyanov[145] points out that a solution of this problem is to use different elements for the synthesis of polymers and so to bring into this field all the remaining elements of the Periodic System. This trend is reflected in the

development of organosilicon polymers and analogous polymers containing other elements.

In addition to these lines of development, great progress has been made in the synthesis and processing of polymeric materials and in the search for new fields of application for already known substances. As a result, more and more new articles are appearing, based on polymers which have already been known for a long time.

An example is the use of monomers of very high purity, yielding high polymers which are very stable to the action of elevated temperatures, light, etc.[146] Application of this method to poly(vinyl chloride) give a polymer which can be worked without the use of plasticisers. Thus in this case, although we are dealing with a polymeric material which has long been familiar to us, improvement in the technology of its production has actually provided us with a completely new product.

The position is similar with block copolymers and graft copolymers, which include units of known monomers, but with a different arrangement from that in the usual, irregular copolymers. The properties also change, resembling those of a mixture of polymers rather than a normal copolymer.

Grafting a layer of one polymer on to the surface of another is a new method of modifying the surface properties of polymers, enabling such characteristics as adhesion, dyeing properties, and stability to light, chemical reagents, etc. to be varied, and providing us with a polymer having a different combination of properties.

Individual high polymers will now be considered, dividing them into separate groups in accordance with the previously suggested chemical classification of high polymers based on the structure of the main chain and the nature and number of the substituents[147].

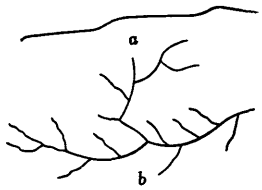


Fig. 17. Structure of the macromolecule of (*a*) low-pressure and (*b*) high-pressure polyethylene.

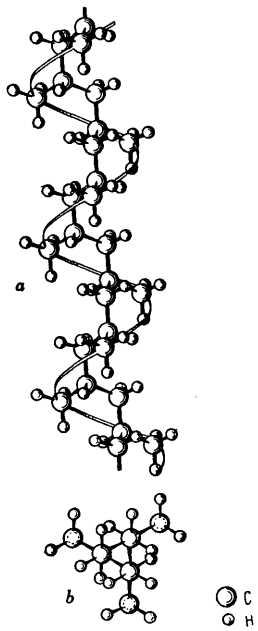


Fig. 18. Conformation of the macromolecule of isotactic polypropylene: *a*) side view; *b*) view from above.

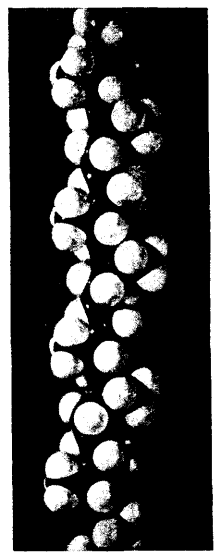


Fig. 19. External view of a model of the macromolecule of isotactic polypropylene.

A. Carbon-Chain Compounds

1. Saturated polyhydrocarbons (polyethylene and its homologues). Representatives of this first group of saturated carbon-chain high polymers which have been known for a long time are polyethylene, polyisobutylene, and polystyrene. Recently, after the work of Ziegler and Natta[7,10] in discovering new methods for polymerising olefins, this group has been expanded by a number of new compounds. Great advances have been made by the Soviet scientists Topchiev, Krentsel', and others in the development of methods for polymerising ethylene and other olefins[8,24,35].

The monomers are readily obtained from petroleum and these polymers are becoming increasingly important. Among them low-pressure polyethylene must be mentioned first. It is distinguished from the previously known high-pressure polyethylene by an almost complete absence of branching and a high molecular weight. Fig. 17 shows diagrammatically the molecules of the two types of polyethylene.

Low-pressure polyethylene has already acquired considerable importance. Its preparation by the Ziegler method[48] is based on the use of organoaluminium compounds containing added titanium tetrachloride as polymerisation catalysts. Polymers obtained with these catalysts have no chain branching, which affects their physical properties. Thus the usual branched, high-pressure polyethylene melts at 107°–120°, whereas the unbranched polymer obtained at low pressures by the Ziegler method melts at 130°–138°. Low-pressure polypropylene melts at 165°–175°, whereas propene yields only liquid polymers of low molecular weight on radical polymerisation.

Recently the production of polyethylene by the Phillips method based on the use of solid catalysts (Al_2O_3 + SiO_2 + + CrO_3) under moderate pressure[34,38,149] (50 atm) has successfully competed with the Ziegler method. We may note also a method based on the use of very high pressures (5000–20 000 atm)[150,151].

A new method for the polymerisation of ethylene by exposure to γ-rays[152,153] can yield a highly crystalline polyethylene resembling the product obtained at low pressures. Table 4 gives several properties of polyethylenes obtained in various ways. The applications of polyethylene are extremely varied, and are discussed in a number of papers and reviews[20,22,154].

A very promising new polymer among the polyolefins is isotactic polypropylene. Topchiev and Krentsel' et al.[155,156]

TABLE 4. Properties of polyethylene obtained by various processes.

Polythene specimen	M.p., °C	Density, g/cm³	Tensile strength, kg/cm²	Relative elongation at rupture, %	Amorphous content, %	Ratio of side chains to number of carbon atoms in main chain
High pressure	105	0.92	110—140	150—600	36—45	1 : 46
Low pressure	130	0.96	200—300	112—1000	7—13	1 : 333
Moderate pressure	127	0.97	200—400	400	7—10	1 : 667
Very high pressure	127	0.96	200—400	1200	10	1 : 200

have investigated the polymerisation of propene using an organometallic catalyst, and have shown that a good polymer can be obtained even from technical propene.

Polypropylene has a low specific gravity and a high melting point[157]. It melts at 160°–170° and has a specific gravity varying between 0.842 and 0.914, depending on its crystallinity. Isotactic polypropylene has a spiral arrangement of the side groups[158], as shown in Fig. 18.

Fig. 19 shows an external view of a model of a polypropylene macromolecule[158]. This polymer has been suggested as a starting material for a synthetic fibre. The polypropylene fibre is characterised by high strength, which is not inferior to that of other synthetic fibres[158], as is shown in Fig. 20.

Pipes can be made from polypropylene which can operate up to a temperature of 100°. Their strength is considerably greater than those of polyethylene[159]. Polypropylene is known in Italy under the name Moplen, in the USA as Pro-Fax, and in Western Germany as Hostalen.

The properties of polymers obtained from homologues of ethylene by polymerisation with Ziegler catalysts are set out in Table 5, which shows that the majority of the high polymers have high melting points and are crystalline materials of great mechanical strength, so that they will undoubtedly find wide application in industry.

Apart from isotactic polypropylene, other isotactic polymers have been prepared and are characterised by higher melting points than the corresponding atactic polymers[20]. At the present time isotactic polymers of

TABLE 6.

Polymer	M.p., °C	
	isotactic	atactic
Polypropylene	170	80
Polystyrene	220	80
Poly(methyl methacrylate)	200	115

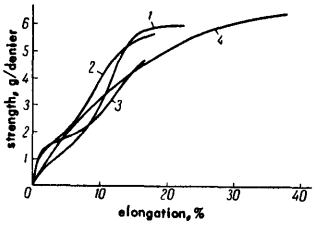


Fig. 20. Load — elongation curves for various synthetic fibres: 1) nylon; 2) Dacron; 3) Orlon; 4) polypropylene.

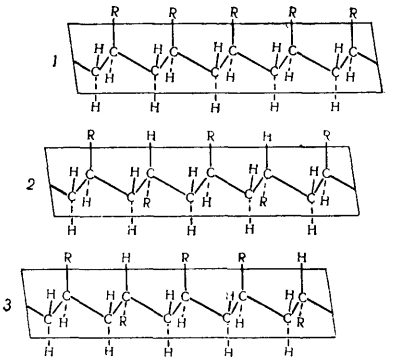


Fig. 21. Plane diagram of the chain structure of polymers of α-olefins: 1) isotactic; 2) syndiotactic; 3) atactic. The broken lines link atoms and groups situated below the plane.

TABLE 5. Properties of some polymeric hydrocarbons[8,160].

Polymer	Structural unit	M.p., °C	Density, g/cm³
Polypentylene	$-CH_2-CH_2-$	130—138	0.95—0.96
Polypropylene	$-CH_2-CH-$ $\quad\quad\quad

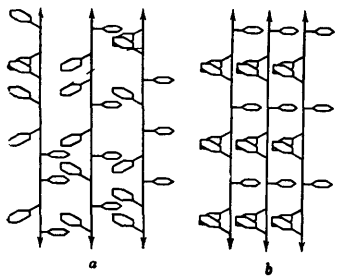


Fig. 22. Relative positions of side groups under conditions of close packing in (*a*) atactic (irregular) polystyrene and (*b*) isotactic polystyrene.

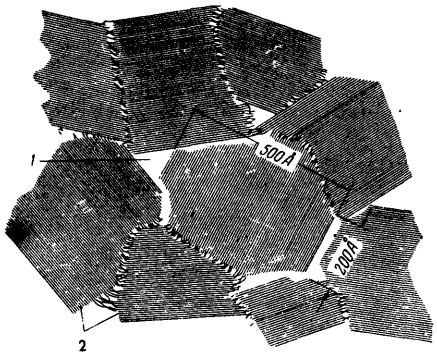


Fig. 23. Structure of a crystalline polymer: 1) amorphous regions; 2) crystalline regions.

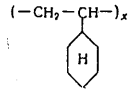
ment of side groups, in contrast to atactic polymers, in which the side groups prevent close packing of the macromolecules, as is shown in Fig. 22.

The regular structure of the chain facilitates crystallisation of the polymer, so that a large proportion of the macromolecules are contained in the crystalline phase, whereas the amorphous phase, filling the interstices between the crystals, is small. Fig. 23 shows the structure of the crystalline polymer.

Natta et al.[162,163] have reported the preparation of stereoblock polymers of propene, the molecules of which contain both isotactic and atactic blocks. Such polymers melt over a wider temperature range (100°–170°) and possess a greater elongation (100–200%) and a lower modulus of elasticity than isotactic polymers (Fig. 24). Mikhailov et al.[164] isolated stereoblock polymers of propene by extraction with heptane, and showed that such a structure is specific to polymers obtained by stereoregular polymerisation.

Copolymers of ethylene and propene obtained by Natta proved to be of great interest, since they possess elastic properties and yield very good and cheap rubbers, known as "C23" (Italy). They have the same elasticity as natural rubber, high tensile strength, and high relative elongation[165]. They are also very stable to the action of ozone and other oxidising agents.

A very interesting isotactic polymer is that of vinylcyclohexane (m.p. 300°):



A promising field for the application of isotactic polymers and polyethylene is the manufacture of synthetic fibres. These fibres are characterised by great strength in both wet and dry states[160].

Such a long familiar high polymer as polystyrene, which is manufactured in large quantities, is characterised by the desirable properties of transparency, good electrical insulation, etc., but has the great disadvantage of being inherently brittle owing to its low impact strength. This defect can be eliminated by copolymerising styrene with other monomers, and because of this, a number of copolymers of styrene are in practical use. Among them must be mentioned copolymers of styrene with acrylonitrile, methacrylonitrile, and methyl methacrylate containing 15–20% of one of these monomers, and also the ternary copolymer of styrene with acrylonitrile and butadiene.

The ternary copolymer, known as Kralastic[167], possesses good impact strength, increased hardness, high strength, and stability to the action of chemical reagents, and is used for the manufacture of pipes, fittings, etc.[166] Pipes made of Kralastic can be used to transport hot water and steam at moderate pressures[168].

The ternary acrylonitrile–butadiene–styrene copolymer was chosen to replace brass in the manufacture of shell cases. Its density is half that of brass and it showed good results at pressures of 420–2450 kg/cm² and with a flame lasting for a minute at a temperature exceeding 2200°.[160]

The copolymer of styrene with methyl methacrylate (Perlon 150) is a thermoplastic material possessing high

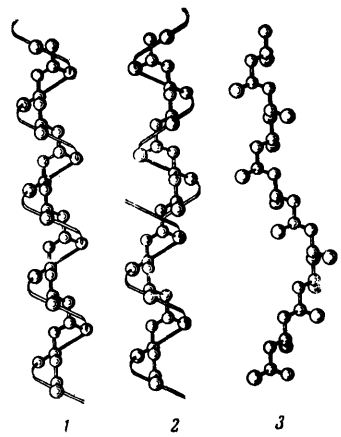


Fig. 24. Three-dimensional structure of the macromolecule of (1) isotactic polymer, (2) polymer with alternating isotactic and syndiotactic units, and (3) atactic polymer.

transparency, good strength, and resistance to heat and light[170]. The copolymer of styrene with acrylonitrile (polystyrene 51 or styrene 767) possesses greater hardness, impact strength, wear resistance, and stability to the action of solvents[171,172]. These copolymers are characterised by considerably greater strength and lower brittleness, and have an impact strength five times as great as that of ordinary polystyrene.

The polyhydrocarbon obtained by heating poly(vinyl acetate) or treating poly(vinyl alcohol) with concentrated sulphuric acid possesses interesting semiconducting properties. The product thus formed can be termed "polymethine" or "polyvinylene" in conformity with its structure[173]:

$$(-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-)_n \xrightarrow{-nH_2O} (-CH=CH-)_n$$

It is used for the manufacture of polarising sheets, and withstands heating to 600°.

2. Halogenated polyethylene derivatives. Apart from such widely and long familiar representatives of this group as poly(vinyl chloride), poly(vinylidene chloride), polytetrafluoroethylene, and polytrifluoroethylene, a number of new compounds of this type have recently been prepared, and the former compounds have found a number of new fields of application. New types of fibres have evolved, based on poly(vinyl chloride) — Teviron (Japan) — and on poly(vinylidene chloride) — Saran (USA).

Chlorinated poly(vinyl chloride), sometimes incorrectly termed "perchlorovinyl", has been used for the manufacture of the synthetic fibres Chlorin, Acetochlorin, and Vinitron[174,175]. Acetochlorin is obtained from a mixture of chlorinated poly(vinyl chloride) and cellulose acetate (15%), and Vinitron from a mixture with cellulose nitrate (30%)[174].

Among chloro derivatives of polyhydrocarbons must be mentioned also chlorinated polyethylene (sometimes incorrectly termed "perchloroethylene") and chlorosulphonated polyethylene. The former, depending on the method of chlorination, is a product melting at temperatures between 40° and 90°. Like poly(vinyl chloride), it is used for the manufacture of electrical insulating materials and other purposes. Chlorosulphonated polyethylene is obtained by treating polyethylene with a mixture of chlorine and sulphur dioxide. The best properties are displaced by a product containing 27% of chlorine and 1.5% of sulphur, in which one chlorosulphonyl group is present for every ninety carbon atoms, and one chlorine atom for every seven carbon atoms. This is a rubber-like material which can be vulcanised, and is termed Hypalon: it is used for the manufacture of rubber compositions, various coatings, etc.[8]

Krentsel' et al.[176] prepared chlorinated and chlorosulphonated polypropylene, which are of great interest as new polymeric materials.

Other representatives of this group of polymers are the fluoro derivatives, which represent the most thermostable group of organic polymers. The most important polymer of this type is polytetrafluoroethylene (Teflon), which has long been used as a heat-resistant material, very stable to chemical corrosion, owing to which it has gained the descriptive name of "the organic platinum". The production of polytetrafluoroethylene in the USA amounts to 2000 tons annually[177]. Recently it has acquired a new field of application in the textile industry for the manufacture of a synthetic fibre[178]. This fibre and cloth made from it are characterised by great chemical and thermal stability. Teflon (Fluoroplast) is used for the manufacture of films employed for the magnetic recording of sound and vision[179].

The new material Duroid is a ceramic fibre (50% silica and 50% alumina) which is coated with polytetrafluoroethylene and then formed into homogeneous sheets. This material has been used as packing where polytetrafluoroethylene itself cannot be used because of high pressures, e.g. in the flanges of pipelines[180].

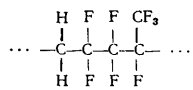
Rogovin has described a fibre, Ftorlon, which is characterised by high thermal stability. It is prepared from a copolymer of acrylonitrile and vinylidene fluoride[181,182].

A copolymer of tetrafluoroethylene and hexafluoropropylene (Teflon 100X) is more easily worked than polytetrafluoroethylene[183], can be pressed into sheets at 300°–350° without appreciable decomposition, has a high elasticity, and is transparent in relatively thick layers[184]. It is used to make tubes, films, vessels, and other articles. It softens at 285° and can be used at temperatures between -185° and +203°.

Polychlorotrifluoroethylene[177] is also widely employed.

Several new polymeric fluorides have appeared recently. Poly(vinyl fluoride) $[-CH_2-CHF-]_x$ (Polymer E) is a new polymer characterised by high thermal stability. It melts above 200° and, in view of its great strength and comparative accessibility, will obviously find wide application[177,182]. Poly(vinyl fluoride) film, which is distinguished by great resistance to the action of acids, alkalis, and solvents, is now made[185]. This film can be employed at temperatures between -100° and +200°. Its dielectric constant is 7.5. It is stronger than Mylar[182].

Fluoro rubbers based on copolymers of fluorinated ethylenes have been greatly developed. A very heat-resistant rubber is a copolymer of vinylidene fluoride and hexafluoropropylene (Viton A)[186,187]:

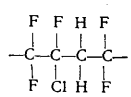


Its softening temperature is ~300°.[182]

A characteristic feature of Viton A is its high thermal stability[177]. Articles made of it withstand prolonged heating in dry air at 315°, and in oil and other solvents at 200°. Viton A can be worked on ordinary equipment[188]. Table 7 shows the temperature and time of ageing, in a thermostat with air circulation, during which the elastic properties of the vulcanised rubber are fully maintained (elongation not less than 100%)[188].

Viton A retains its elasticity down to -70°.[182] It is used for making diaphragms in pumps for gases, air conduits for the transfer of hot air, and hose for pumping hot liquids. Mixed with epoxy resins it is used for bonding ceramics to produce a material applicable at high temperatures. Viton A can be vulcanised with amines or peroxides, and also by means of high-energy radiation.

Another interesting copolymer is that of chlorotrifluoroethylene and vinylidene fluoride:



It is a rubber known as Kel-F. It is stable above 300°. It

has high strength and abrasion resistance, and is stable to the action of oils, fuels, and nitric acid; it is swollen by ethers[186].

A copolymer of vinyl fluoride and hexafluoropropylene also possesses the properties of an extremely heat-resistant rubber[189].

New polymers of perfluoroalkyl propenyl ketones[190], perfluoroalkylacrylamides[191], and pentafluorostyrene[192] have been described.

3. Oxygen derivatives of polyethylene. Poly(vinyl alcohol), which has been known for a long time, has found a new field of application in the manufacture of a synthetic fibre, known as Kuralon (Japan) or vinylon (USSR and USA). Ushakov developed a process for obtaining vinylon fibre from poly(vinyl alcohol)[193]. This fibre is distinguished by outstanding tensile strength and a markedly hydrophilic nature. Ushakov[194] has prepared copolymers of vinyl acetate with crotonamide and with hydroxymethylcrotonamide, which on heating readily give three-dimensional cross-links, of interest for the production of a synthetic fibre of increased strength and for other purposes.

Several new compounds have been obtained belonging to the group of acrylic polymers, among which the isotactic and syndiotactic acrylate polymers must be mentioned first. Fox et al.[46] prepared stereoregular polymers of methyl methacrylate in the presence of fluorenonelithium in the solution. Their glass and melting points are given in Table 8.

TABLE 7.

Temperature, °C	Time, h
200	2400
228	1000
255	250
282	72
310	24

TABLE 8. Melting points and glass points of stereoregular polymers of methyl methacrylate.

Type of polymer	Glass point, °C	Melting point, °C
Isotactic	115	200
Syndiotactic	45	160
Stereoblock	60—95	170

Isotactic poly(isopropyl acrylate)[41] is a crystalline substance melting at 162°.

Apart from the long familiar polymeric esters of acrylic and methacrylic acids, many new polymers and copolymers of this series have now appeared: e.g. such compounds as polymeric esters of acrylic and methacrylic acids and various fluorinated monohydric alcohols. These polymers possess elastic properties and great chemical stability, since the main polymer chain is surrounded by quite long fluorinated groups which protect it from external attack. One which has found practical application is poly(heptafluorobutyl acrylate) (Fluoro-rubber F4):

$$(-CH_2-CH-)_x$$
$$\quad\quad|$$
$$\quad COOCH_2(CF_2)_2CF_3.$$

It is stable up to 300° and possesses high strength, thermal stability, and resistance to benzene and oils[177].

Another interesting product is poly(trifluoromethoxyhexafluoropropyl acrylate) (Fluoro-rubber EF4)[177]:

$$(-CH_2-CH-)_x$$
$$\quad\quad|$$
$$\quad COOCH_2CF_2CF_2OCF_3.$$

It has better characteristics at low temperatures than the previous rubber[186].

4. Nitrogen derivatives of polyethylene. Interesting properties are possessed by polymeric esters of α-cyanoacrylic acid:

$$\left(\begin{array}{c} CN \\ | \\ -CH_2-C- \\ | \\ COOR \end{array}\right)_x.$$

They have found application as adhesives, which stick various materials very firmly together. The β-methoxyethyl and β-ethoxyethyl esters are recommended for this purpose. These glues contain no solvent, and set rapidly at ordinary temperatures directly in the glued joint[195]. Vinylidene cyanide $CH_2=C(CN)_2$ has been applied in the form of a copolymer with vinyl acetate for the manufacture of a synthetic fibre, Darvan[196].

Finally, polyacrylonitrile has increasing application in the manufacture of the synthetic fibres Orlon and Nitron or Zefran[197], which are valuable substitutes for wool. A fibre can be obtained also from polymethacrylonitrile[198].

Several copolymers of acrylic derivatives find application in the manufacture of synthetic fibres. Thus it is proposed to make a fibre from a copolymer of acrylonitrile and methyl acrylate (Creslan or Courtelle fibre)[199], from a copolymer of acrylonitrile and vinyl acetate (Verel fibre)[200], and from a copolymer of acrylonitrile with vinylidene chloride (Verel or Saniv fibre)[200,201]. A copolymer of acrylonitrile with methacrylamide (5–10%) gives a strong fibre with good dyeing properties[202].

Polymers of *N*-carboxyphenylmethacrylamides synthesised by Koton[203], are new derivatives of methacrylic acid, with high glass temperatures (~200°):

$$\left[\begin{array}{c} CH_3 \\ | \\ -CH_2-C- \\ | \\ CO \\ | \\ NH \\ | \\ \text{C}_6\text{H}_4 \\ | \\ COOH \end{array}\right]_x$$

5. Unsaturated polyhydrocarbons. Considerable progress has been made in the group of polymers of diene compounds, the majority of which are rubber-like materials. Apart from natural rubber, this group was previously represented by polybutadiene (sodium–butadiene rubber), polychloroprene, and also copolymers of butadiene with styrene or acrylonitrile.

Polymers of isoprene $[-CH_2-C(CH_3)=CH-CH_2-]_x$, obtained in the presence of organolithium compounds, have now been developed in the USSR by Korotkov et al.[204] These polymers are very similar to natural rubber not only in composition but also in their physical and mechanical properties, and thus represent a "synthetic natural rubber".

This rubber is known as SKI. In the USA it is termed Ameripol[205], Coral[206], or Natsin[207].

Polyisoprene prepared in the presence of alkyllithium catalysts contains 90% or more units linked in the 1,4-position and having a *cis*-configuration[15,23,45,204,206-208]. Similar products have been obtained in the presence of a Ziegler catalyst[205,207,209,210]. In this case, too, a polyisoprene is obtained which yields vulcanised rubbers with properties closely similar to those of products from natural rubber[209]. An interesting characteristic of this polyisoprene is the narrow molecular-weight distribution[211], which does not depend on the extent of conversion. This form of rubber is being greatly developed, and by 1965 some 25% of rubbers produced in the USSR will be polymers of isoprene[212]. They are used for the manufacture of car tyres and other articles previously made from natural rubber, which they are fully capable of replacing[209]. A road test of experimental car tyres containing SKI showed its high quality, little inferior to that of natural rubber[213].

A new rubber-like polymer, polydeuteroisoprene[214], has been obtained starting from deuteroacetone and deuteroacetylene:

$$(-CD_2-C(CD_3)=CD-CD_2-)_x.$$

The butadiene polymer prepared with Ziegler catalysts is of great interest. Natta[13] has shown that poly-*cis*-1,4-butadiene of extremely uniform structure is obtained. This polymer is characterised by highly elastic properties, surpassing in some respects even natural rubber[215]. It is known as "*cis*-1,4 rubber". Tests with tyres made of this rubber have shown that the wear resistance of the tread is 30–40% higher than when natural rubber is used. With tyres used by lorries there is a smaller production of heat[215].

Butadiene polymers can have different structures, depending on whether the units are combined in the 1,2- or 1,4-positions, and also on the presence of geometrical isomerism. Fig. 25 shows plane diagrams of four isomeric polymers of butadiene.

Among these, poly-*cis*-1,4-butadiene, whose chain conformation is depicted in Fig. 26, is of the greatest interest as a rubber. The other butadiene polymers, whose conformations are shown in Figs. 27–29, are of no interest as rubbers, but may be of interest from other points of view.

The carboxylate rubbers, an extremely interesting type of synthetic rubber, are copolymers of divinyl and other monomeric diolefins, and are obtainable in emulsion with monomers based on acrylic or methacrylic acid[216,217]. They can be obtained also by addition to a finished synthetic or natural rubber in solution or in a latex, or during processing on rollers such substances as thioglycollic acid, maleic anhydride, or acrylic acid[217]. Dolgoplosk and Tinyakova[218] prepared a carboxylate rubber by copolymerising methacrylic acid with butadiene or isoprene. Owing to the presence of free carboxy groups, carboxylate rubbers can be vulcanised not only with sulphur but also with metal oxides and diamines. Carboxylate rubbers surpass ordinary rubbers in mechanical properties, having a higher modulus and tensile strength and being more stable to ozone. They are employed for the manufacture of strong adhesives, and also for impregnating cord, fabrics, and paper.

Copolymers of butadiene and 2-methyl-5-vinylpyridine, or methylvinylpyridine rubbers, are characterised by high wear resistance. They have the name Philprene in the USA[219]. These rubbers have higher tensile strength and resistance to tearing and the widening of cuts than ordinary butadiene–styrene rubber[220]. The wear resistance of vulcanised methylvinylpyridine rubber is nearly twice that for divinylstyrene rubber: i.e. it approaches that for polyurethane rubber[221].

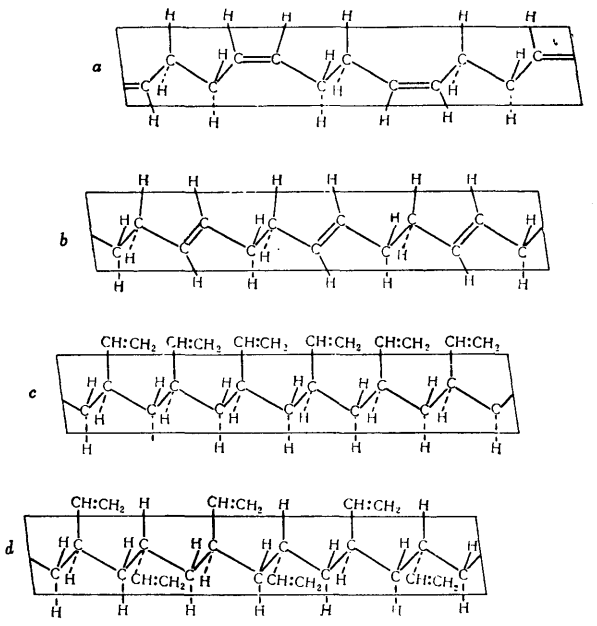


Fig. 25. Structure of isomeric polymers of butadiene: *a*) poly(*cis*-1,4-butadiene); *b*) poly(*trans*-1,4-butadiene; *c*) isotactic poly(1,2-butadiene); *d*) syndiotactic poly(1,2-butadiene).

Meyer, Gibbs, et al.[222] report a new class of elastomers with varied properties, obtained by treating latices of butadiene, chloroprene, butadiene–styrene, and other rubbers with alkanethiols in the presence of an initiator

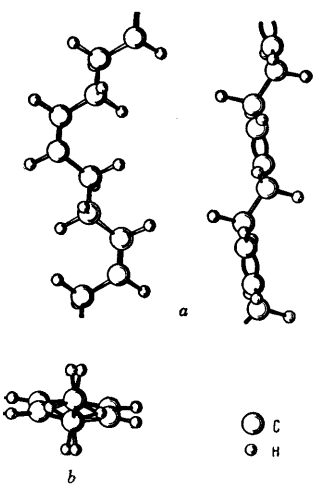


Fig. 26. Conformation of the chain of poly(*cis*-1,4-butadiene): *a*) side view; *b*) view from above.

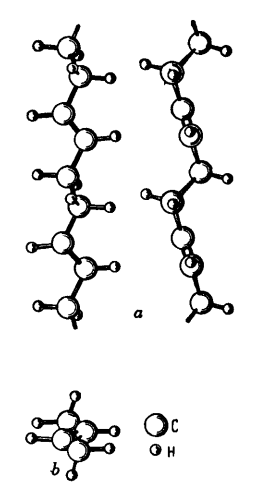


Fig. 27. Conformation of the chain of poly(*trans*-1,4-butadiene): *a*) side view; *b*) view from above.

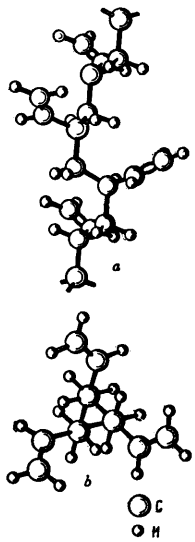


Fig. 28. Conformation of the chain of isotactic poly-(1,2-butadiene): *a*) side view; *b*) view from above.

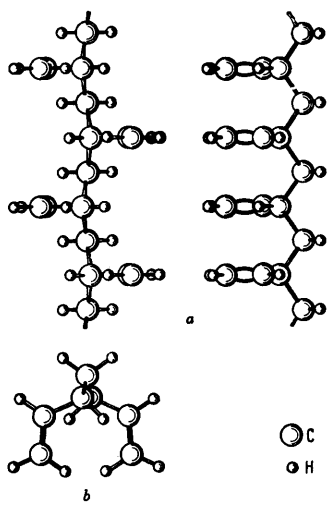


Fig. 29. Conformation of the chain of syndiotactic poly(1,2-butadiene): *a*) side view; *b*) view from above.

(usually azodiisobutyronitrile). In this process molecules of the thiol add on to the double bonds:

$$\cdots -CH_2-CH=CH-CH_2- \cdots \xrightarrow{CH_3SH} \cdots -CH_2-\underset{\displaystyle S\\ \displaystyle CH_3}{CH}-CH_2-CH_2- \cdots$$

The resulting products are characterised by increased saturation, are more stable to the action of ozone, and have increased resistance to heat, frost, solvents, and ageing.

Polyfluoroprene $[-CH_2-CF=CH-CH_2-]_x$ is a new polymer[223], which, in contrast to polychloroprene, possesses no rubber-like properties.

The liquid copolymer of butadiene and styrene linked in the 1,2-position has been suggested as a basis, instead of polyesters, for the production of glass-like plastics which are stable to hydrolysis[224].

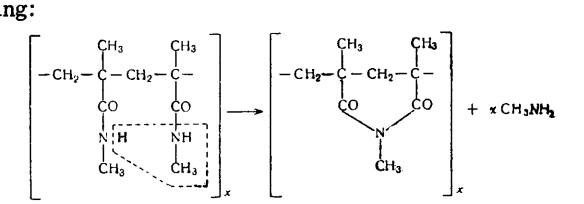
6. Polymers containing rings in the chain. The classical example of these polymers is phenol–formaldehyde resin. It has been suggested that, to eliminate its inherent defect of brittleness, it can be modified by mixing with such polymers as rubber[91-93] and polyamide[225], epoxy[226], and other resins. Various materials for corrosion protection, based on phenol–formaldehyde resins, have been made[227].

Recently Burke and Ruetman[228] described the production of linear phenol–formaldehyde polymers by the polycondensation of *o*-chlorophenol with formaldehyde in the presence of *p*-toluenesulphonic acid in a solution of bis-β-ethoxyethyl ether in an autoclave at 150°. These polymers can form fibres.

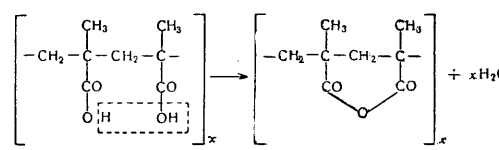
Great thermal stability and resistance to oxidation are characteristic of polymers containing benzene nuclei in the chain, such as polyphenylene $[-C_6H_4-]_x$[229], polyphenylene--ethyl or polyxylylene $[-CH_2-C_6H_4-CH_2-]_x$[118,119], polycarboxyphenylene $[-C_6H_3(COOH)-]_x$[229], polydiisopropylbenzene $[-C(CH_3)_2-C_6H_4-C(CH_3)_2-]_x$[120,121], polyperfluorophenylene $[-C_6F_4-]_x$[192], etc.

The introduction of rings into a chain generally results in an increase in the thermal stability of the polymers, as Bresler, Koton, et al.[117] have shown in the case of polymethylmethacrylamide and polymethacrylic acid.

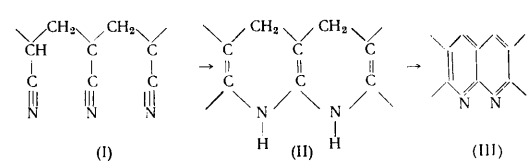
The former yields rings of the following structure on heating:



while the latter forms anhydride rings:



An interesting product is formed from polyacrylonitrile by heat treatment, the fibre being heated in air at 200°. The fibre blackens, becoming insoluble, and is not affected by the burner flame. Houtz[230] has shown that a polymer is obtained consisting of fused pyridine rings (III):



Topchiev et al.[231] studied the products formed by heating polyacrylonitrile and showed that they possess semiconducting properties. Fibres of this polymer are stable

at 400°. They are used for filtering concentrated sulphuric and hydrochloric acids, solutions of caustic soda, etc.

Recently great interest has been aroused by resins obtained from furfural and acetone. They are characterised by high thermal and chemical stability and have various uses, especially for "cementless" concrete[232].

Recently, flexible fibres and fabrics containing 99.9% graphite have been obtained[233]. They are prepared by carbonisation in a quite complex manner of such carbon-containing materials as cotton, viscose, rayon, etc., which are then converted into graphite by heating to 2980°. It is thus possible to convert any textile material into graphite form. These materials are suitable for reinforcing plastics to be used at high temperatures, for the manufacture of filter hose for hot non-oxidising gases, equipment for transporting corrosive liquids, high-temperature thermal insulation, etc.

B. Heterochain Polymers

1. Polyethers. Previously only one representative of this group, poly(ethylene oxide), was widely known, but now we are acquainted with several polymers of this type.

Polyformaldehyde $[-CH_2-O-]_x$, although it has been known for a long time, could not be obtained with a sufficiently high molecular weight, in spite of the fact that Staudinger[234] as early as 1929 reported the preparation of fibre-forming polymers of formaldehyde. Recently, formaldehyde polymers of high molecular weight, with extremely interesting properties, have been prepared[235-238]. Polyformaldehyde has m.p. 185°, sp. gr. 1.25, and high mechanical strength[236]. It readily crystallises. A peculiarity of polyformaldehyde is its high impact strength, which is of great practical interest. Because of the availability of the starting materials and the excellent mechanical properties, polyformaldehyde will undoubtedly have an immense field of application in the near future[236]. At present it is used in the manufacture of a synthetic fibre known as Delrin, which has a strength of 4 g/denier at an elongation of 11%. The comparatively low strength of the synthetic fibres is explained by the fact that only a fraction of the macromolecules in the fibre effectively resist rupture, as can be seen from Fig. 30.

A peculiarity of the polymerisation of formaldehyde is the necessity for using very pure monomer, since the presence of even minute amounts of impurity prevents the production of polymers of sufficiently high molecular weight[235], the presence of moisture being especially harmful. Concentrated sulphuric acid is used for the dehydration and purification of the monomer. The polymerisation catalysts are boron fluoride, triethylamine, sulphur trioxide, and also the carbonyls of iron, nickel, and cobalt, and such organometallic compounds as diphenyltin, triphenylbismuth, and phenylmagnesium bromide, calcium hydride, etc. The formaldehyde enters the solvent (benzene), to which the catalyst has been added, at the same rate at which polymerisation occurs. The polymer formed separates as a precipitate and is filtered off[235]. Polyformaldehyde is characterised by great strength. Table 9 gives the fundamental physical properties of Delrin.

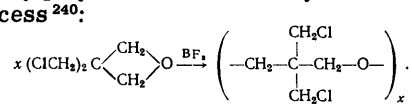
Polyacetaldehyde, suitable for the manufacture of articles, has recently been synthesised in Japan. It is obtained by polymerising acetaldehyde in the presence of an aluminium oxide catalyst[239]. Polyacetaldehyde is an

TABLE 9. Physical properties of Delrin[236].

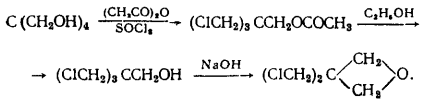
Property	Value
Elongation, %	
at 23°	16
at 70°	330
Specific impact strength, kg/cm	
at 4.5°	6.55
at 23°	7.63
Tensile strength, kg/cm²	
at 23°	700
at 70°	525
Modulus of elasticity under static bending, kg/cm²	
at 23°	28 700
Static-bending strength, kg/cm²	
at 23°	990
Fatigue limit at 23° and 100% relative humidity, kg/cm²	350
Shear strength, kg/cm²	666
Heat resistance, °C	
at 18.5 kg/cm²	100
at 4.62 kg/cm²	170
Deformation under load, % (140 kg/cm² at 50°)	0.5
Compressive stress at 1% deformation, kg/cm²	364
Moisture absorption, %	
on immersion in water for 24 h	0.4
at 50% relative humidity	0.2
Specific gravity	1.425
Rockwell hardness, M94	120
Flammability, cm/min	2.8
Softening point of crystalline polymer, °C	175
Yield point, °C	184
Coefficient of linear expansion	0.000081
Thermal conductivity, kcal/m²deg h cm	3 08
Specific heat, cal/g	0.35

elastomer, surpassing butadiene–styrene rubber in heat resistance. It is vulcanised under the influence of radiation.

An interesting new polymer is that of 3,3-bischloromethyloxacyclobutane, bearing the trade name Penton. It is obtained by polymerisation of the cyclic ether by the following process[240]:



The original monomer is synthesised from pentaerythritol via a series of intermediate stages:



The polymerisation is carried out in a solvent (methyl chloride, chloroform) in the presence of boron trifluoride at 0° and below[241]. Penton melts at 180°. Its glass temperature is 7.5°. It can be made into films, fibres, and

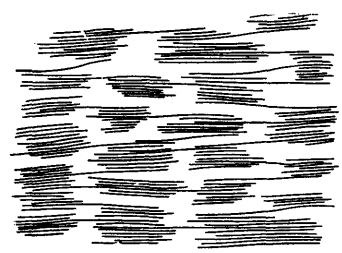
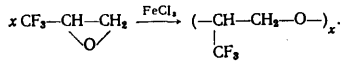


Fig. 30. Arrangement of macromolecules in a fibre.

plastics by extrusion[242,243]. Penton is a similar material to poly(vinyl chloride), but is more stable to heat and the action of chemical reagents.

Among other polymeric ethers must be mentioned the polymer of 1,1,1-trifluoro-2,3-epoxypropane, obtained in the presence of ferric chloride:



It is characterised by high thermal stability, is insoluble in hydrocarbons and halogenated derivatives[244], and is soluble in acetone.

Epoxy resins form a large group of substances obtained by reaction of various diphenols with epichlorohydrin and analogous alkylene oxides[245]. Thus dicyclopentadiene dioxide yields resins which are stable up to 300°. The ease of preparation of these polymers, their strong adhesion to various materials, and the great strength of articles made from them have led to the wide employment of epoxy resins in various fields[246].

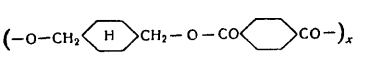
Great interest attaches to epoxy resins modified with polyamides[247,248]. They are used as film-forming materials or adhesives. Mixtures of epoxy resins with phenol–formaldehyde resins are also of interest[226]. Recently copolymers have appeared of epoxy resins with organosilicon resins, which retain their mechanical and electrical strength up to 200°–250°.[249,250]

2. Polyesters. These have long been widely employed in the paint and varnish industry, where in the form of alkyd resins they constitute ~ 50% of all film-forming materials used[251]. A huge number of different polyesters are now known[252].

Comparatively recently poly(ethylene terephthalate) $[-CH_2CH_2OCOC_6H_4COO-]_x$ has been obtained, and under such names as Lavsan, Terylene, Dacron, Mylar, Melinex, etc. has been widely employed for the production of synthetic fibres and films which are distinguished by outstanding strength and heat resistance. Films of Lavsan have exceptional strength, and are used as a basis for cinematograph films, for electrical insulating purposes, and also in various branches of technology[253].

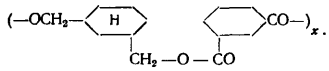
Several copolymers have been suggested for fibre production — mixed polyesters containing together with terephthalic acid and ethylene glycol also sebacic acid (10%)[254] or isophthalic acid (10–15%)[255]. The latter copolymer is termed Videne.

Recently production has begun of a new type of fibre (Kodel) based on a polyester of terephthalic acid with hydrogenated *p*-xylylene glycol:



The polyester melts at 270° and withstands heating up to 218°; it is used mixed with other fibres[256], and articles made from it do not crease and do not acquire an electrostatic charge.

The polyester of isophthalic acid and hydrogenated *m*-xylylene glycol (m.p. 200°) has been proposed for the manufacture of films:



Rubber-like properties are possessed by polyesters of fluorinated glycols and dicarboxylic acids[186]. Poly(hexafluoropentamethylene adipate) $[-OCH_2[CF_2]_3CH_2OCO[CH_2]_4 . CO-]_x$ has a working temperature range from -72° to +150°. It is closest in properties to natural rubber compared with other fluorinated elastomers. It is resistant to benzene[177], and can be vulcanised with peroxides in the presence of carbon black.

An interesting form of rubber is represented by the polyester–urethanes, obtained by the reaction of 2,4-tolylene diisocyanate with a branched polyester of an aliphatic dicarboxylic acid (adipic, etc.) and an aliphatic glycol or mixture of glycols (butylene glycol, ethylene glycol, trishydroxymethylpropane, etc.) or even with a polyether of sufficiently high molecular weight[257].

Polyester–urethanes are produced on an industrial scale under the names Adiprene (USA), Vulkollan (Western Germany), Chemigum (USA). A distinctive feature of rubbers of the Adiprene type is their exceptionally high abrasion resistance, in which they surpass all other rubbers; therefore the main application of polyester–urethanes is the manufacture of tyre treads and other parts which are subject to friction[258,259]. Losev and Datskevich[260] prepared a series of polyester–urethanes, and determined how their properties varied with the nature of the starting materials.

Great interest attaches to polyesters of carbonic acid and various diphenols, the polycarbonates, which represent a new type of polymer, distinguished by great strength, heat stability, and especially outstanding impact strength[261]. The most widely used among these products is the polymer prepared from carbonyl chloride and 2,2-bis(4-hydroxyphenyl) propane:

$$x\,COCl_2 + x\,HOC_6H_4C(CH_3)_2C_6H_4OH \rightarrow 2x\,HCl + (-OC_6H_4C(CH_3)_2C_6H_4O-CO-)_x .$$

Phosphoric esters are added during the reaction to obtain a colourless product. This polymer is known under the trade name Lexan[262]. It melts at 268°, softens at 140°, and is characterised by high impact strength, forty times as great as that of polystyrene. It is used for the manufacture of film, especially photographic film, bulky goods, electrical insulation, etc.

The "polyarylates" are very interesting, comprising polyesters of various dicarboxylic acids and dihydric phenols[263–265]. They are distinguished by high thermal stability, which may reach up to 500°, and possess great mechanical strength. They are prepared by the reaction of chlorides of dicarboxylic acids with dihydric phenols:

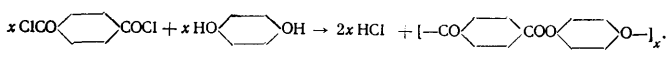


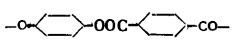
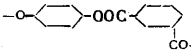
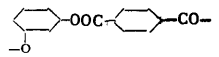
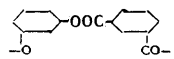
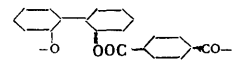
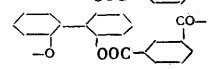
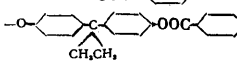
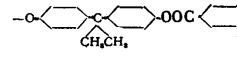
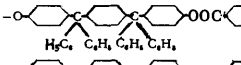
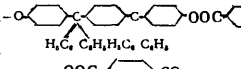
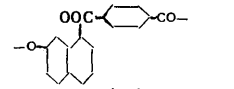
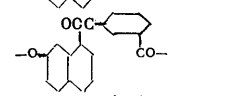
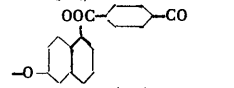
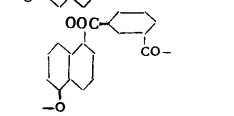
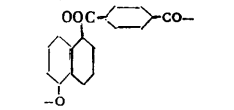
Table 10 gives the melting points of several representatives of the polyarylates.

Polyarylates dissolve appreciably only in tetrachloroethane, being insoluble in water and in other organic solvents. A series of mixed polyarylates have been prepared, whose properties can thus be varied over a wide range[264,265]. Polyarylates have also been obtained from various phosphinic acids[266], and are distinguished by their non-inflammability.

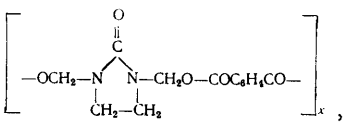
Conix[267] has described a large number of polyesters obtained from bisphenols, having the structure $HOC_6H_4RC_6H_4OH$, and dicarboxylic acids, and also polyesters of the general formula $[-COC_6H_4RC_6H_4COOC_6H_4RC_6H_4O-]_x$ with various radicals.

Some of the polyesters are of interest because of their

TABLE 10. Melting points of polyarylates [263].

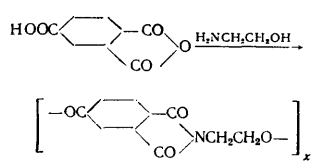
Acid	Dihydric phenol	Structural unit	M.p., °C
Terephthalic	Quinol		above 500
Isophthalic	Quinol		320
Terephthalic	Resorcinol		270
Isophthalic	Resorcinol		230
Terephthalic	o,o'-Dihydroxybiphenyl		172
Isophthalic	o,o'-Dihydroxybiphenyl		158
Terephthalic	p,p'-Dihydroxydiphenylpropane		350
Isophthalic	p,p'-Dihydroxydiphenylpropane		275
Terephthalic	1,4-bis(4'-hydroxyphenyldiphenylmethyl)benzene		220
Isophthalic	1,4-bis(4'-hydroxyphenyldiphenylmethyl)benzene		157
Terephthalic	1,7-Dihydroxynaphthalene		230
Isophthalic	1,7-Dihydroxynaphthalene		188
Terephthalic	1,6-Dihydroxynaphthalene		above 500
Isophthalic	1,5-Dihydroxynaphthalene		above 500
Terephthalic	1,5-Dihydroxynaphthalene		above 500

high melting points, among them being the polyester of terephthalic acid:

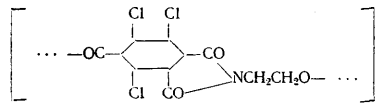


melting at 340°.

The polyester of trimellitic acid and monoethanolamine [268] melts at 350°. It is prepared by the following reaction scheme:



Still more thermostable is the analogous polyester of chlorinated trimellitic acid:



A large number of di- and tri-allyl esters of various polycarboxylic acids have been prepared. These polyesters are used together with those of unsaturated acids in the production of glass textolites [53,269].

A copolymer of the polyester of 1,3-butylene glycol and maleic acid with styrene is of considerable interest as electrical insulating material distinguished by high resistance to arcing [270].

Great interest attaches to alkyd resins based on isophthalic acid. They yield a stronger and more lustrous film than alkyds based on phthalic acid [271].

3. Polysulphones. Noether [272] prepared a series of polysulphones by means of the reaction

$$x\,\mathrm{NaS(CH_2)_m SNa} + x\,\mathrm{Br(CH_2)_n Br} \rightarrow 2x\,\mathrm{NaBr} + [\mathrm{-S(CH_2)_m S(CH_2)_n-}]_x \quad ,$$

$$[\mathrm{-S(CH_2)_k-}]_x + \mathrm{H_2O_2} \rightarrow [\mathrm{-SO_2(CH_2)_k-}]_x .$$

Poly(hexamethylene sulphone) melts at 220°. Fibres which are not inferior to polyamides in strength are made from polysulphones. They are readily dyed with Cellon dyes.

4. Polyanhydrides. Conix [273] prepared polyanhydrides of aromatic dicarboxylic acids of the type $HOOCC_6H_4O[CH_2]_xOC_6H_4COOH$. Polyanhydrides have proved to be good film- and fibre-forming substances, stable in the molten state to the action of oxygen and resistant to moisture and aqueous alkalis. A fibre can be made from them.

5. Polyamides. There is a general relation, established by Korshak and Frunze [274], between the melting points of heterochain polyamides and their chain structure. Korshak and Frunze found that the melting point is related to the number of methylene groups in a chain unit by the equation $y = ax + b$, where y is the melting point of the polyamide, x is a heterochain characteristic representing the ratio of the number of groups containing hetero atoms to the number of methylene groups expressed as a percentage, and a and b are constants characteristic of each series of polyamides (b = 110). Fig.31 shows plots for series of polyamides, polyesters, and polyanhydrides, showing the relation between the melting point and the heterochain characteristic [275]. Table 11 gives values of the constants and the equations for various groups of polymers.

Previously known representatives of heterochain polyamides are polyhexamethyleneadipamide, known as Anid or 6,6-nylon, and poly-ε-caprolactam, termed Capron, Perlon, or 6-nylon. Many new representatives of this group have now appeared, applicable as starting materials for synthetic fibres, and also as film-forming materials, and for the production of plastics [276]. It is interesting that laminated plastics based on phenolic resins reinforced with polyamide fibre have considerably better heat resistance than analogous glass-like plastics [277].

Strepikheev, Nesmeyanov, Freidlina, and other investigators developed Enant, a new form of synthetic fibre made

TABLE 11. Equations for various types of polymers[275].

Polymer group	Equation
Polyureas with an even number of methylene groups in the unit	$y=8.4x+110$
Polyamides with an even number of methylene groups in the unit	$=7x+110$
As above (from other data)	$y=7x+125$
Polyamides from dicarboxylic acids with an odd number and diamines with an even number of methylene groups	$y=6.2x+110$
Polyamides from dicarboxylic acids with an even number and diamines with an odd number of methylene groups	$y=5.6x+110$
Polyamides from dicarboxylic acids and diamines with odd numbers of methylene groups	$y=4.5x+110$
Polyurethanes with an even number of methylene groups in the unit	$y=3.5x+110$
Polyamides containing sulphide sulphur in the chain	$y=3x+110$
Polyamides containing ether oxygen in the chain	$y=1.9x+110$
Polyanhydrides with an even number of methylene groups in the unit	$y=2.5x+110$
Polyesters with an even number of methylene groups in the unit	$y=3x+110$
Polyesters with an odd number of methylene groups in the unit	$y=3.6x+110$
Polyanhydrides with an odd number of methylene groups in the unit	$y=3.6x+110$

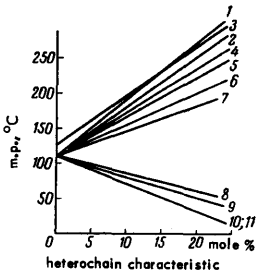


Fig. 31. Variation in melting points in the series: 1) polyureas; 2) polyamides with an even number of methylene groups in the diamine and in the acid; 3) as above, according to more accurate data; 4) polyamides formed from a diamine with an even number and an acid with an odd number of methylene groups; 5) polyamides from diamines with an odd number and acids with an even number of methylene groups; 6) polyamides from diamines and acids with odd numbers of methylene groups; 7) polyurethanes; 8) polyanhydrides with an even number of methylene groups in the structural unit; 9) polyesters from glycols and acids with even numbers of methylene groups; 10) as above, with an odd number of methylene groups in the acid; 11) polyanhydrides with an odd number of methylene groups in the structural unit.

from poly-ω-heptanamide $[-NH[CH_2]_6CO-]_x$. Enant fibre is characterised by high tensile strength and is especially resistant to double flexing[278].

Nesmeyanov and Freidlina[279] prepared ω-aminoheptanoic acid, starting from ethylene, by telomerisation with carbon tetrachloride:

$$R\cdot + CCl_4 \longrightarrow RCl + \cdot CCl_3,$$

$$\cdot CCl_3 + CH_2{=}CH_2 \longrightarrow Cl_3C-CH_2-CH_2\cdot \xrightarrow{+2CH_2=CH_2} Cl_3C(CH_2CH_2)_3\cdot,$$

$$Cl_3C(CH_2CH_2)_3 + CCl_4 \longrightarrow Cl_3C(CH_2)Cl + \cdot CCl_3,$$

$$Cl(CH_2)_6CCl_3 \xrightarrow[H_2SO_4]{H_2O} Cl(CH_2)_6COOH \xrightarrow{NH_3} H_2N(CH_2)_6COOH.$$

The formation of ω-aminoheptanoic acid in this reaction is accompanied by that of ω-aminononanoic and ω-aminoundecanoic acids, which are used to prepare two new types of synthetic fibres, Pelargon $[-NH[CH_2]_8CO-]_x$ and Undekan $[-NH[CH_2]_{10}CO-]_x$ (Rilsan)[278].

Among the large number of polyamides containing sulphur in the chain, that from thiodivaleric acid and hexamethylenediamine (m.p. 180°) has proved suitable for fibre production[280]. The fibre from this polyamide possesses increased elasticity and is of great interest for the production of staple fibre[281] since thiodivaleric acid, obtained from ethylene and carbon tetrachloride, is readily available[282].

A fibre from polypyrrolidone[283] known as 4-nylon absorbs water more strongly and is more easily dyed than 6- or 6,6-nylon.

A series of polyamides containing siloxane groups in the chain have been synthesised from acids of the structure:

$$HOOC-(CH_2)_2Si(R)_2-O-Si(R)_2-(CH_2)_2-COOH,$$

where R = CH_3, C_2H_5. These polyamides are characterised by rubber-like properties[284].

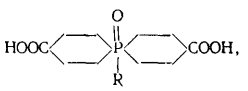
A series of polyamides, distinguished by their high melting points, have been synthesised from *p*-xylylenediamine and dicarboxylic acids[285]. If *trans*-isomers of hydrogenated diamines are employed, very high-melting polyamides can be obtained[286], whereas *cis*-isomers yield amorphous polyamides melting at lower temperatures.

A series of high-melting polyamides have been obtained from terephthalic and isophthalic acids with aliphatic and hydroaromatic diamines[287].

A large number of copolymers have been prepared and used as starting materials for the production of a synthetic fibre (Trelon)[288] and as film-forming materials (Anid G-669[289], etc.). A good solvent for polyamides has recently been found in trifluoroethyl alcohol[290].

Fedotova et al.[291] have prepared a number of polyureas $[-CONHRNHCOR'-]_x$ by the interaction of diamines with diisocyanates; these are strong materials with excellent dielectric properties.

Interesting organophosphorus polyamides are obtained by the polycondensation of diamines with carboxylated phosphine oxides, e.g.:



where R = CH_3 or C_6H_5. These polymers are capable of fibre formation and are completely non-inflammable[292-294].

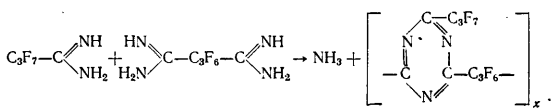
Combinations of polyamides with epoxy[247,248], phenol–formaldehyde[225], and urea– or melamine–formaldehyde resins, chlorosulphonated polyethylene, etc. have been widely used as coating materials, adhesives, etc.[247,295]

The application of polyamides to the production of laminated asbestos sheets, which withstand a temperature of above 1000° for 5 min, has been described[296].

Synthetic polypeptides are being increasingly studied; they are obtained by the decomposition of anhydrides of α-amino-acids and other compounds. These researches approach more and more closely to the synthesis of proteins, on which are based the vital processes of living beings. However, the preparation of proteins similar to those occurring in organisms is undoubtedly a very complicated problem, since the twenty amino-acids encountered in natural proteins with a molecular weight of 100 000 (which corresponds roughly to a degree of polymerisation of 1000) can yield 10^{1200} differently constructed molecules. To give

an idea of what this figure means, we may mention that the total number of atoms in the Earth is only 10^{50}.

A very interesting polymer, characterised by elasticity and great thermal stability, was obtained by Braun[186] by the pyrolysis of a perfluoromonoamidine with a perfluorodiamidine:



This polymer chain obviously contains triazine rings linked by perfluorotrimethylene groups. The polymer withstands heating up to 540°.

A polymeric triazine, obtained by the condensation of pentafluorobenzamidine with perfluorophthaloyldiamidine, has been described[192].

6. Organometallic and analogous polymers ("organo-elemental" polymers). These substances have been attracting increasing attention from investigators looking for materials of high thermal stability and with other qualities. Nesmeyanov[145,297] has made a detailed examination of various elements of the Periodic System from the point of view of the possibility of combining them with organic radicals to form polymers.

During the past few years various polymeric systems containing inorganic molecular chains have been studied[298]. Special attention has been paid to polymers containing the following structural units[186]:

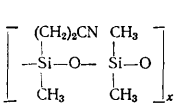
—B—N—B—N—	—Si—O—Al—
—B—P—B—P—	—P—N—P—N—
—Al—P—Al—P—	—C—N—C—N—
—P—O—P—O—	—S—N—P—
—Si—O—B—	—Sn—O—Sn—
—Si—O—Sn—	—Sn—S—Sn—
—Si—O—P—	R_f—X—R_f(X=O, N, P, S, metal)

coordination (chelate) polymers

The purpose of these investigations was to obtain polymers of great thermal stability (to 500° and above).

7. Polysiloxanes. Among organometallic and analogous polymers the most important are the organosilicon compounds, research on the synthesis and application of which has been intensively developed[299]. These compounds have been widely used in the form of silicone oils, rubbers, and varnishes[300].

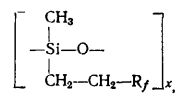
Recently new types of organosilicon polymers have appeared, in which great strength has been achieved by the introduction of nitrile groups. These are the nitrilosilicone rubbers[301,302], containing the nitrile groups in the alkyl radical attached to silicon, and may be represented by the general formula



They constitute copolymers of dimethylsilicone and methylcyanoethylsilicone rubbers. Other combinations are also possible. These rubbers are extremely resistant to oils and boiling hydrocarbons, their swelling is only 10% of that of ordinary methyl silicone rubber, and they are very strong over the temperature range from -70° to +260°.

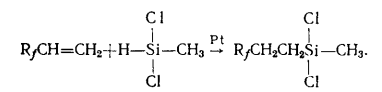
A very interesting group of organosilicon polymers is formed by the fluorosilicones, containing fluorinated alkyl groups attached to the silicon atoms. Their heat resistance is considerably greater than that of the alkylsilicon compounds.

Fluorosilicone rubbers have the structure[186]:



where R_f = CF_3, C_2F_5, C_3F_7.

The original monomers are obtained by addition of methyldichlorosilane to an olefin:

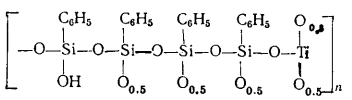


On the basis of these monomers, fluorosilicone rubber, poly(methyl-3,3,3-trifluoropropylsiloxane) (Silastic, LS-53), possessing good characteristics[177,303], has been evolved. Its brittle point is -68°, its operating temperature is 200°, and it has great resistance to oils. However, vulcanised fluorosilicone rubbers have low strength, and are therefore employed for making packing washers, sleeves, diaphragms, airtight seals, etc.

Polymers obtained from silanols, containing such unsaturated groups as vinyl[304], are of considerable interest. They are readily vulcanised and yield stronger rubbers.

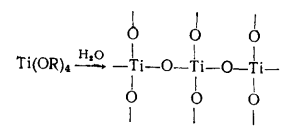
Andrianov has prepared polymers containing a chain of silicon, oxygen, and metal atoms[305], e.g. —Si—O—Al—O—, which are termed "aluminosiloxanes"; they are characterised by great thermal stability[306].

A still stronger bond is —Si—O—Ti—, which occurs in polytitano-organosiloxanes:



They have still greater heat resistance and hydrolytic stability than the polyaluminosiloxanes[307].

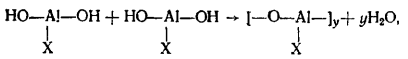
8. Polytitanoxanes. Among high polymers of other elements, practical use has been found for polymers of titanium oxide, prepared by hydrolysis of orthotitanic esters:



They form very strong films and are employed in the optical industry[308].

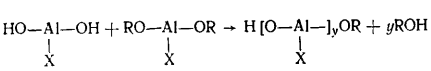
Mixed products have been obtained, containing silicon and titanium, by combination of a silicone polymer with esters of orthotitanic acid[307,308]. A Ti—O—Si bond is obviously formed in these compounds; they can be cold-hardened and yield strong films, which are suitable as coatings for ceramic electrical insulators and for imparting water-repellent properties to the walls of buildings[309].

9. Polyaluminoxanes. The preparation has been described of polymeric basic aluminium salts of organic acids[301], obtained by elimination of water from the basic salt

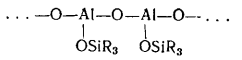


where X is a radical of stearic or other organic acid.

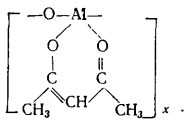
The starting materials can be the basic salt and a dialkoxyaluminium salt[311]:



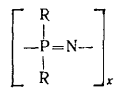
A new variety of compounds of this type is represented by the polyorganosiloxanoaluminoxanes prepared by Andrianov and Zhdanov[312]:



Interesting complex polymers have been obtained by Kugler[313] by the hydrolysis of a dialkoxyaluminium acetylacetonate, the macromolecule of which is made up of the following units:

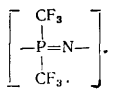


10. Organophosphorus polymers. Among phosphorus-containing polymers great attention has been paid to the group of substances based on a chain of phosphorus and nitrogen atoms[314]:



The first member of this group, which has been known for a long time, poly(phosphoronitrile chloride) $[-PCl_2=N-]_x$, possesses great thermal stability (~300°) and is a rubber-like material.

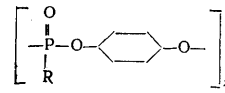
An interesting product is poly(phosphoronitrile fluoride), which is distinguished by great thermal stability[315]. A series of compounds have been obtained in which the phosphorus bears alkyl, aryl, alkoxy, aroxy, alkylamino, and arylamino groups. Many of them have high melting points[316]. An interesting derivative is the trifluoromethyl polymer which is an elastomer:



The use of phosphoronitrile polymers as additives to increase the thermal stability of phenolic and other resins has been suggested. Introduction of such additives enables these resins to be employed for the manufacture of brake shoes, various frictional materials, abrasives, etc.[314]

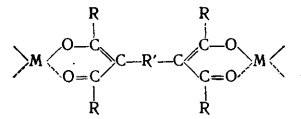
Linear phosphinoborines, containing a chain of phosphorus and boron atoms $[-P-B-]_x$, form a very heat-resistant plastic, with a molecular weight of 12 500, which withstands a temperature of up to 400°.[317]

In addition, a large number of organophosphorus polymers belonging to the polyester and polyamide groups have been prepared. Thus, a series of polyesters have been obtained from alkyl- and arylphosphinic acids with various glycols and diphenols[318]:



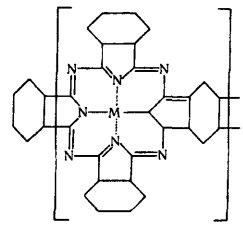
These compounds do not burn and can be used as coatings.

11. Coordination polymers. Examples of these interesting polymers are the complexes of tetraketones with copper, cadmium, zinc, and other metals, which have chains of the following structure[139,142]:

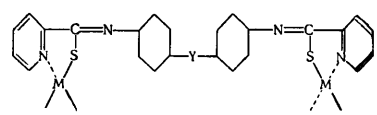


These compounds have different colours and high melting points (300° and above).

The phthalocyanine complexes of copper and other metals, described by Marvel and his collaborators[287,319] are still more heat-resistant. From pyromellitic acid, phthalic anhydride, and urea or from 3,3',4,4'-tetracyanodiphenyl ether and the latter two compounds they prepared a series of polymers of the type



Martin[279,322] prepared a series of complex polymers from bis(thio-α-picolinamide) compounds of the type



12. Inorganic polymers. Many substances belonging to this last group of polymers[320] are widely used in industry, but they are all natural products. Recently a number of synthetic inorganic polymers have been obtained and have already found several fields of application. Among them must be mentioned synthetic diamond, sapphire, alexandrite, ruby, mica, asbestos, and similar materials.

Borazon[321] can be cited as an interesting example. Ordinary boron nitride is softer than diamond and has a hexagonal structure. If it is subjected to a pressure of 70 000 kg/cm², its crystal structure becomes cubic. The Borazon thus obtained is harder than diamond and will scratch the latter. It withstands a temperature up to 1800°, whereas diamond burns at 870°.

An interesting product is Pyroceram, a vitreous material characterised by great heat-resistance and mechanical strength[323].

IV. CONCLUSION

In conclusion it must be remarked that even a cursory review of new polymers such as this shows that the large number of new high polymers now existing provide extensive opportunities for a fuller satisfaction of the needs of modern technology. The problem consists in utilising these new materials for the production of various goods.

Our survey of the achievements of synthetic polymer science also shows that the further development of synthetic methods undoubtedly promises to yield still more new polymeric compounds with new properties; their development is a most important task of macromolecular chemistry.

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ANIONIC POLYMERISATION IN THE PRESENCE OF ALKALI METALS AND THEIR COMPOUNDS

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INTRODUCTION

Anionic polymerisation processes are of considerable interest, since they enable us to synthesise polymers with valuable properties, e.g. polymers of regular structure, such as *cis*- and *trans*-polyisoprene, isotactic polystyrene, isotactic and syndiotactic methyl methacrylate, etc., and also block copolymers.

The catalysts for anionic polymerisation are substances of basic, electron-donor character — alkali metals and their amides, various organometallic compounds, complex organometallic compounds, organomagnesium compounds, etc. Anionic polymerisation of very reactive monomers is also brought about by water, alkalis, amines, and alkali-metal carbonates and bicarbonates.

The present review is concerned mainly with polymerisation in the presence of alkali metals and their derivatives.

The monomers most active in anionic polymerisation are compounds containing electronegative substituents attached to a double-bonded carbon atom — vinylidene cyanide, nitroethylene, acrylonitrile, methyl acrylate, methacrylonitrile, methyl methacrylate, etc. The polymerisation takes place by an ionic mechanism of the acid—base type[1], the catalysts or active centres acting as electron donors, and the monomers as electron acceptors.

Under the influence of an anionic catalyst BX an active