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THE MAIN LINES OF RESEARCH ON THE CHEMICAL REACTIONS OF MACROMOLECULES

A. A. Berlin

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INTRODUCTION

The development of synthetic chemistry has led to the production of an immense variety of polymeric substances, differing in chemical and spatial structure. As experimental knowledge of the conversion of monomers into high polymers has accumulated, investigators have been faced with the ever more urgent problem of studying the effect of various chemical, physical, and mechanical factors on the structure and chemical reactions of macromolecules. Work on these lines has been stimulated by the requirements of industry, which has been interested in modifying the properties of polymers and in obtaining comprehensive information about their operating characteristics. Solution of the problems of modifying the properties of polymers made it necessary to develop methods of carrying out chemical changes in macromolecules in order to obtain materials having specified properties.

The search for methods of modifying the properties of polymers has led, especially during the past 10–15 years, to new synthetic processes for converting one class of polymer into another, for introducing different atoms and groups into macromolecules, "hybridising" macromolecules by chemical grafting and linking together different blocks, and producing marked changes in the properties of polymers by intramolecular cyclisation, partial degradation, and the introduction of appropriate atoms and groups.

The voluminous experimental results which have accumulated on the chemical reactions of macromolecules[1] call for a rational classification which will facilitate systematisation and also the planning of new methods for modifying the properties of polymers. It is convenient to base this classification on the process producing the change in composition, struc-

ture, and properties of the macromolecules. In this way the whole range of reactions in which polymers participate can be combined into four main groups:

I. Intramolecular reactions in macromolecules.

II. Reactions of atoms, functional groups, and active centres in macromolecules unaccompanied by growth of the polymer chains.

III. Chain growth due to interaction between terminal atoms, groups, and active centres* of the macromolecules (block copolymerisation).

IV. Chain growth due to chemical reactions of groups and active centres within the macromolecules.

Group I includes dehydrogenation, dehydrochlorination, dehydration, and other elimination processes, as well as intramolecular cyclisation. As a result of these reactions, the structure and configuration of the main chain are changed without appreciable change in the degree of polymerisation.

Group II incorporates the chemical reactions of macromolecules which involve reactive atoms and functional groups of the main chain and substances of low molecular weight. Among them must be included addition reactions to double bonds in macromolecules (hydrochlorination, halogenation, hydrogenation, hydration, etc.), substitution reactions of atoms in the main chains or side groups of macromolecules (sulphonation, halogenation, alkylation, chloromethylation, etc.), and numerous chemical reactions of functional and other reactive groups.

Group III includes reactions between terminal groups or active centres of polymer molecules and monomeric or polymeric substances leading to the formation of high-polymer chains consisting of repeating sections or blocks having a definite size, composition, and structure.

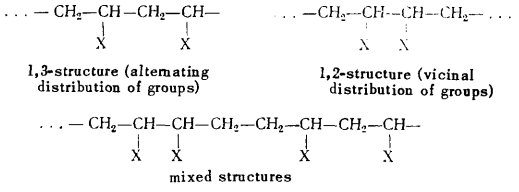
Group IV comprises reactions between polymers containing active centres along the chain with polymerisable monomers or reactive polymers.

In such processes branched or three-dimensional compounds of high molecular weight are formed, known as graft copolymers. This group includes also the "cross-linking" reactions, involving active centres, double bonds, and functional groups of the macromolecules. The suggested classification is to a considerable extent arbitrary, since many chemical reactions of polymers occur by a complex mechanism involving processes of different types at the individual stages.

Chemical changes in macromolecules may occur both by molecular and by ionic or radical mechanism. The magnitude of the activation energy necessary for reactions of different functional groups and atoms in polymer chains is practically the same as that required for the same reactions to occur with monomeric substances similar in structure to the units in the polymer chain[1]. Nevertheless, in most cases functional groups and the macromolecules themselves react considerably more slowly than do analogous substances of low molecular weight. This is explained by the fact that reactions involving polymer chains are more complicated, since the reaction velocity is affected by intermolecular forces, the shape and flexibility of the macromolecules, and other factors affecting the pre-exponential term in the Arrhenius equation.

* Active centres in macromolecules are atoms having electrons with unpaired spins or groups which can form free radicals.

The polymerisation of unsaturated monomers leads to the formation of isomers in which different arrangements of functional groups are theoretically possible:



Determination of the factors that influence the formation of a particular structure in the polymer chain is of fundamental importance in elucidating the relation between the structure and the reactivity of macromolecules. In order to understand this as yet unstudied question it must be remembered that mutual repulsion forces must be overcome in order to form 1, 2-structures, involving greater consumption of energy than the formation of 1,3-structures.

Hence it follows that raising the temperature of polymerisation must affect not only the mean degree of polymerisation but also the structural isomerism of the high polymers. Harsher conditions of polymerisation increase the probability of the vicinal distribution of substituents, which must increase the internal energy and the reactivity of the polymer.

Available experimental data support these theoretical ideas. Thus it has recently been shown that the relative proportions of 1,2- and 1,3-structures in polyvinyl alcohol and polyvinyl chloride) depend on the conditions of polymerisation, and that the presence of even a comparatively small amount of the 1,2-structures exerts a great influence on the chemical properties of compounds of high molecular weight[1]. Investigation of the structure of polyvinyl alcohol prepared by saponification of polyvinyl acetate synthesised at 35° and 50° showed that the ratio of 1,2- and 1,3-structures in the former product did not exceed 1 : 110, whereas in the latter case it reaches 1 : 50. Polyvinyl alcohol enriched with the vicinal structure contains the 1,2-glycol group and readily undergoes oxidative degradation under the influence of air or HIO_4.

Vicinal polyvinyl chloride synthesised by chlorination of polybuta-1,4-diene is characterised by diminished thermal stability, splitting off HCl to form an insoluble product on slight heating or even on repeated dissolution[2]. Partly dehydrochlorinated polydichlorobutadiene contains isolated and conjugated double bonds.

The reactivity of macromolecules and the types of chemical changes they undergo should be influenced by stereoisomerism as well as by structural isomerism. Unfortunately, this important question still remains uninvestigated, although it has no less scientific and practical interest than the investigation of the physical and mechanical properties of stereoregular polymers.

I. INTRAMOLECULAR REACTIONS IN MACROMOLECULES

Intramolecular reactions occur in polymer chains by the elimination of reactive atoms and groups or by intramolecular cyclisation under the influence of heat, light, or radiation, as well as by the action of acids, bases, complex-forming salts, and some other reagents.

1. Intramolecular Elimination Reactions

Intramolecular elimination has great scientific and practical interest, since such reactions can be used to prepare polymers having a system of conjugated double bonds (polyvinylenes). These polymers should exhibit the features of the so-called "metallic covalent" bond[2], which endows the polymer with high thermal stability, increased electrical conductivity and magnetic properties[2-6].

A soluble polyvinylene is most readily obtained by eliminating HBr from polyvinyl bromide by the action of alcoholic alkali or organic bases[5]. A similar change may also be brought about by the thermal dehydration of polyvinyl alcohol. The conversion of polyvinyl bromide and polyvinyl alcohol into polyvinylenes is achieved by thermal or chemical treatment of these polymers in the form of fibres and films. The dark brownish polyvinylenes formed by these reactions possess well defined dichroism and semiconductor properties in the oriented state; the electrical resistivity of films of these materials is diminished by a factor of ten on heating to 60°–70°.[5]

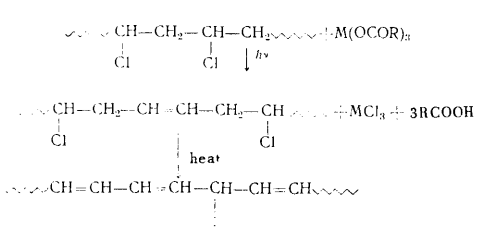
Work was carried out not long ago on the conversion of polyvinylidene chloride, and its copolymers into polyvinylenes[6]. Elimination of HCl was achieved by boiling with morpholine or heating with alcoholic alkali in nitrogen under reduced pressure. Such treatment yielded insoluble dark-coloured polymers containing 7.3–17.5% of combined chlorine and having a magnetic susceptibility of $+1.56 \times 10^6$, wich corresponds to a magnetic moment of 1.19 Bohr magnetons or one free electron for every 18 carbon atoms along the conjugated chain. Analysis for the elements and infra-red spectroscopy indicated the presence of CH_2 and CCl_2 groups, which suggested that conjugation had broken down in some sections of the chains. The dependence of electrical resistivity on temperature for the product of the dehydrochlorination of polyvinylidene chloride is shown in Fig.1, from which it is seen that these substances exhibit semiconductor properties, evidently due to delocalisation of π electrons in the conjugated chain.

Halogenated polymers may also be converted into brownish polyvinylenes by ultra-violet irradiation[7].

The formation of chromophoric polyene groups on irradiating polyvinyl or polyvinylidene chloride is markedly accelerated by the introduction of Al or Fe stearate into the polymer. The catalytic action of these salts is explained by the fact that the HCl which is split off under the action of light reacts with Al and Fe to form the corresponding halides, which are active dehydrochlorination catalysts.

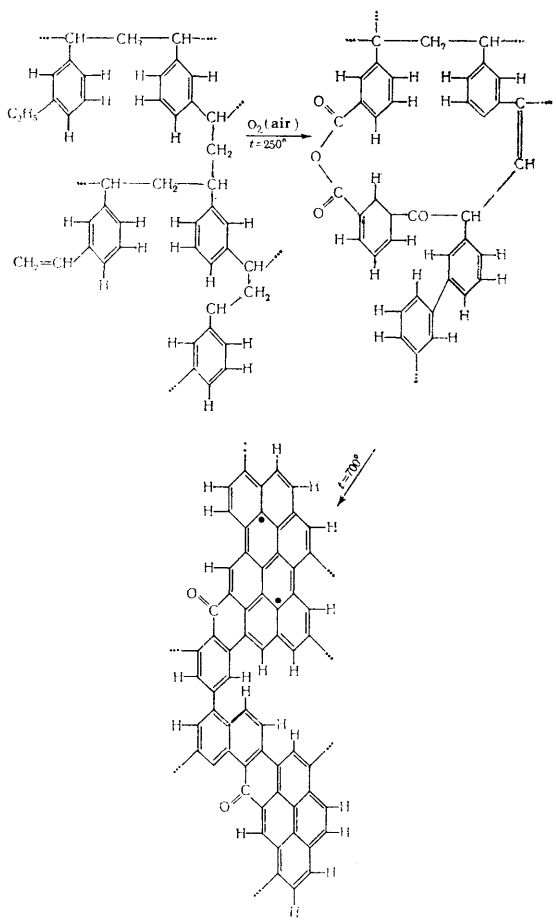
The ability of halogenated polymers to form coloured dehydrochlorination products has been successfully used to prepare light-sensitive plastics and coatings, enabling a photographic image to be obtained directly on the surface of articles[8].

The chemistry of photography on plastics can be represented by the following scheme:



When polyvinyl chloride containing Al or Fe stearate is irradiated with visible light, the bonds which are unstable to this type of radiation are weakened, leading to the elimination of HCl and the formation of Fe^{3+} or Al^{3+} chloride. Increasing the intensity of the radiation accelerates the dehydrochlorination, and thus increases the formation of chlorides which catalyses this process. Subsequent heating of the irradiated material leads to rapid dehydrochlorination, formation of chromophoric groups, and the development of colour.

Aromatisation processes occurring during the pyrolysis of certain three-dimensional polymers are of considerable theoretical and practical interest. Condensed aromatic systems were obtained in the pyrolysis of poly-*m*-divinylbenzene and of copolymers of *m*-divinylbenzene with *m*-ethylstyrene[9]:



The maximum increase in electrical conductivity is achieved in the pyrolysis of the polymer of *m*-divinylbenzene at 600°–700°, in which polyaromatic compounds containing a system of conjugated bonds[9] are formed (see Fig.2).

An extremely interesting intramolecular reaction occurs on prolonged heating of polyacrylonitrile at 200° (up to 500°). When polyacrylonitrile fibre is exposed to a temperature of 200° for many hours, the fabric becomes black and lustrous, and the polymer loses its solubility. Cloth treated in this way becomes more brittle and less strong, but is nevertheless suitable for certain practical applica-

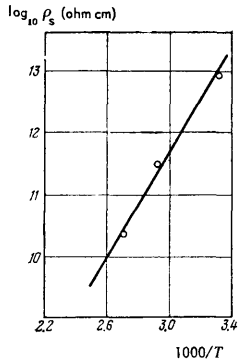


Fig. 1. Dependence of electrical resistivity on temperature for the product of the dehydrochlorination of polyvinylidene chloride.

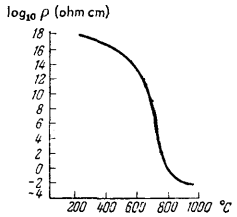
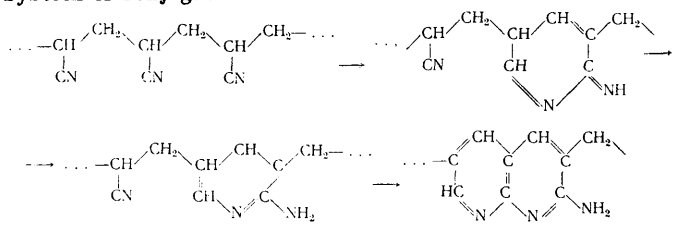


Fig. 2. Electrical resistivity of the product of oxidative pyrolysis of poly-*m*-divinylbenzene as a function of the temperature of pyrolysis.

tions. It is curious that such cloth is not damaged by a Bunsen flame, and can be used at 300°–400°.[10]

It is suggested that polyacrylonitrile undergoes oxidative dehydrogenation and intramolecular cyclisation during heating, leading to the production of polymers having a system of conjugated bonds[10]:



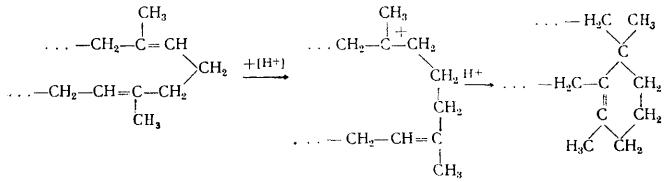
Products of the heat treatment of polyacrylonitrile contain unpaired delocalised electrons[11]. The electrical conductivity of such polymers rises sharply with rise in temperature above 300°. In this respect, products of the oxidative thermal degradation of polyacrylonitrile behave in an analogous manner to polyphenylenes[12] and polyarylvinylenes[12–14] as well as to the types of polymers with conjugated bonds described above.

Thus the development of systematic methods for converting saturated polymers into polyvinylenes or aromatic compounds opens up new possibilities for modifying the properties of polymers, especially for increasing their thermal stability, electrical conductivity, optical and electrical anisotropy, and some other special properties.

2. Intramolecular Cyclisation

This occurs when a macromolecule contains reactive groups situated at distances which are suitable for the formation of five- or six-membered rings when they react. Since cyclic structures are formed in such processes, the rigidity of the macromolecules is markedly increased, which entails a rise in the vitrification temperature and in the viscosity of the polymer. In several cases, intramolecular cyclisation enables the adhesive properties to be improved and other new properties to be conferred on the material.

An example of intramolecular cyclisation is the production of the so-called "cyclised rubber". When natural rubber is slowly heated or is treated with sulphuric acid, sulphonic acids, sulphuryl chloride, or hexachlorostannic acid, it is converted into a hard, brittle product, which is used in the production of adhesives and protective coatings[15]:

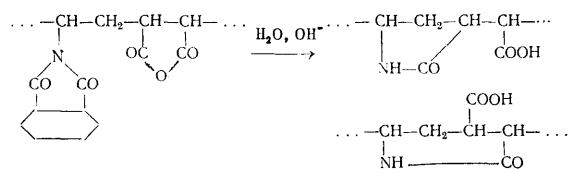


If a macromolecule contains hydroxyl and carboxyl groups, intramolecular lactonisation is possible. Thus the action of an alcoholic solution of a mineral acid on the copolymer of maleic anhydride and vinyl acetate leads to the formation of γ- and δ-lactones[16].

Increase in the rigidity of the chains due to intramolecular lactonisation entails an increase in the ultimate tensile strength and a decrease in the extension at break.

The formation of lactam rings in various polymers was achieved quite recently. Intramolecular lactamisation is possible with polymers containing NH_2 and COOH groups, or groups from which these are readily formed[17].

The simplest example of this type of change is the reaction of the copolymer of vinylphthalimide and maleic anhydride with aqueous solutions of quaternary ammonium bases:



The recently developed intramolecular lactamisation based on the use of the classical Curtius reaction is also of interest[18]. When this reaction is carried out, a large number of butyrolactam units are formed, but complete conversion is not observed and more than 10% of unchanged carboxyl or isocyano groups remain.

Lactamised polymers are beginning to attract the attention of technologists, since they resemble polymers of vinylpyrrolidone (vinylbutyrolactam)[19] in properties, and consequently may find application in medicine (as a substitute for

blood plasma) and in industry (textile finishes, thickeners, emulsifiers). Opening up the lactam rings yields polymers containing both acidic and basic groups, which find application as ion-exchange resins.

II. REACTIONS OF MACROMOLECULES WITH SUBSTANCES OF LOW MOLECULAR WEIGHT UNACCOMPANIED BY CHAIN GROWTH

Among the great variety of reactions of macromolecules which occur without substantial increase in length of the main (or side) chain, we shall confine ourselves to those which have been developed or have acquired importance during the past 8–10 years.

1. Substitution Reactions

An extremely promising method of modifying polymers is chlorosulphonation. Introduction of SO_2Cl groups into polyethylene and several other polymeric olefines yields various products which can be vulcanised to form thermally stable, strong, and chemically resistant polymeric materials[20]. Polyethylene can be chlorosulphonated by reaction of the polymer (M_{av} 20 000) with SO_2 and Cl_2. The main process is accompanied by chlorination of the polyethylene, as a result of which the product contains 1.3–1.75% of sulphur combined as SO_2Cl groups and 26–29% of chlorine.

Infra-red spectroscopy and chemical analysis of chlorosulphonylpolyethylene show that one chlorosulphonyl group is present for every 90 carbon atoms, and one Cl atom for every 7 carbon atoms.

The presence of SO_2Cl groups makes chlorosulphonylpolyethylene capable of numerous reactions, which are used to obtain various sulphonyl derivatives and vulcanisates[21]. Thus when alkylamines (e.g. butylamine) act on a 10% solution of chlorosulphonylpolyethylene in toluene at 25° for 24 h, a sulphonamide derivative is formed:

$$RSO_2Cl + 2R'NH_2 \rightarrow RSO_2NHR' + R'NH_2 \cdot HCl.$$

When this reaction is carried out in more concentrated solutions, the mass is observed to gel, owing to intermolecular association between the sulphamoyl groups. The resulting gel is soluble in toluene and butylamine.

Chlorosulphonylpolyethylene reacts with oxides of bi- and multi-valent metals in the presence of traces of water at 25°–150°, forming salt cross-links[22] to yield insoluble, thermally stable products:

$$RSO_2Cl + H_2O \rightarrow RSO_3H + HCl,$$

$$2RSO_3H + PbO \rightarrow RSO_2OPbOSO_2R.$$

Similar reactions occur when the dry polymer interacts with organic di- and poly-amines at room temperature or above[23].

At elevated temperatures amide derivatives of chlorosulphonylpolyethylene react vigorously with isocyanates, aldehydes, and also with chlorosulphonylpolyethylene itself[21].

$$2RSO_2NHR' + R''(NCO)_2 \rightarrow (RSO_2NR'CONH)_2R'',$$

$$2RSO_2NHR' + CH_2O \rightarrow (RSO_2NR')_2CH_2 + H_2O,$$

$$RSO_2Cl + RSO_2NHR' + MO \rightarrow RSO_2NR'SO_2R + M(OH)Cl.$$

Chlorosulphonylpolyethylene can be vulcanised by means of melamine, salts of multivalent metals, the usual accelerators (mercaptobenzothiazole, thiuram, etc.), quinones, and benzidine. However, these aromatic compounds can react with SO_2Cl groups only at comparatively high temperatures (125°–150°).

Chlorosulphonated polyethylene ("Hypalon") is soluble in aromatic and chlorinated hydrocarbons. Vulcanised Hypalon (containing 40 g of PbO or 20 g of MgO per 100 g of polymer) is very stable to oxidising agents (e.g. ozone), and are chemically stable to light and the atmosphere. The ultimate tensile strength of such compositions without a filler reaches 240–250 kg cm^{-2} at an extension of 200–600%. Heating Hypalon at 190°–200° for 5–10 h reduces the tensile strength to 100 kg cm^{-2}*. At 170° this decrease in strength is reached only after heat treatment for 10 days, and on heating to 120° after almost three months. These results show that Hypalon surpasses rubbers of many types in strength and heat resistance.

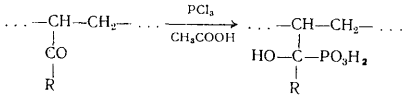
The electrical insulating properties of Hypalon are intermediate between those of natural rubber and Neoprene. Hypalon insulation can be successfully employed at temperatures up to 125°.

Vulcanised chlorosulphonated polyethylene is finding increasing application for the lining of chemical equipment, the manufacture of chemically and thermally stable packing, the electrical insulation of leads for low and medium voltages, and as floor-covering materials. Hypolon varnish coats are transparent and elastic, and possess good adhesion to metals, rubber, wood, and plastics[22,23].

Chlorosulphonation may be employed to modify the properties of polystyrene, polybutadiene, and stereoregular polymeric olefines.

2. Reactions of Functional Groups in Macromolecules

Recently developed methods for the phosphorylation of polymers are interesting, from both theoretical and practical aspects. For example, a mixture of phosphorus trichloride and glacial acetic acid acts on carbonyl-containing polymers in dioxan at 20°–25° to convert the carbonyl groups into hydroxy-phosphonic groups[24]:



Investigation of this reaction with poly(alkyl vinyl ketones) and copolymers of alkyl vinyl ketones with α,β-unsaturated aldehydes showed that increase in the size of the radical greatly increases the difficulty of reaction between the phosphorus trichloride and the keto groups of the polymer. The best results were obtained in the phosphorylation of polymers of methyl vinyl ketone and acrolein, as well as their copolymers with styrene and acrylonitrile.

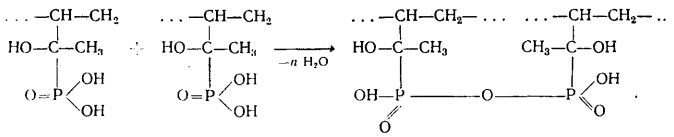
Several halogenated derivatives of tervalent phosphorus are also able to add on to the keto groups of a polymer, the best results being obtained with phenoxydicholorophosphine.

Copolymers containing hydroxy-phosphonic acid groups are readily converted on heating into infusible, insoluble

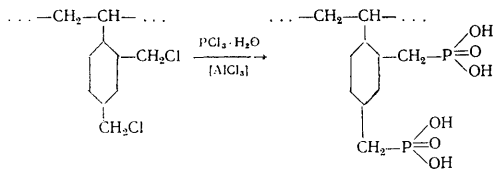
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* The original Russian has "reduces the extension at fracture to 100 kg cm^{-2}". The intended meaning may be "reduces the extension at fracture to 100%" (Ed. of Translation).

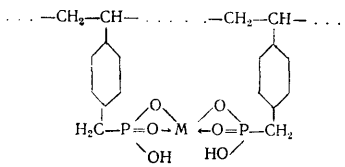
products:



In addition to the phosphorylation of polymeric ketones and aldehydes, methods of introducing hydroxy-phosphonic groups into chloromethylated polystyrene and copolymers of chloromethylstyrene with divinylbenzene, methyl methacrylate, and several other monomers[24] are also of interest. Reaction of these polymers with PCl_3 in the presence of $AlCl_3$ with subsequent oxidative hydrolysis yields the corresponding polymeric phosphonic acids:



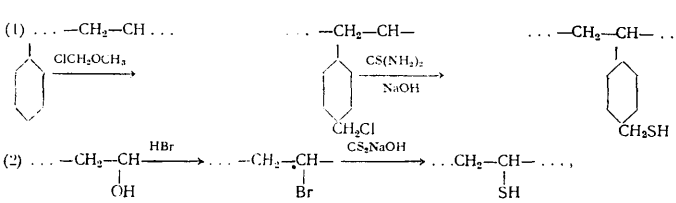
Polyvinyl chloride and phenol-formaldehyde resins have been phosphorylated by analogous methods. Phosphorylation enables the material to be made non-flammable. Further, the presence of phosphonic groups in a polymer makes it able to form chelate complexes with ions of transition metals (Fe^{2+}, Fe^{3+}, Co^{2+}, Cu^{2+}, etc.)[25,26]:

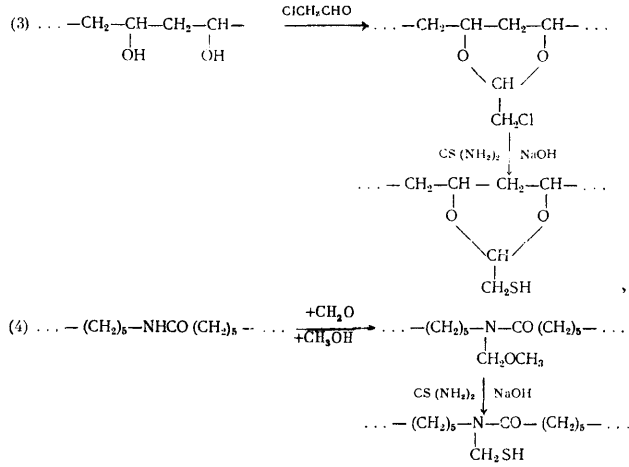


Phosphorylated copolymers of 2,4-bis(chloromethyl)-styrene are therefore used as selective adsorbents for ions. The possibility of cross-linking phosphorylated polymers by forming intermolecular chelate rings can be successfully employed to produce thermosetting plastics[26]. These materials may be expected to combine great strength and heat-resistance with an interesting set of physical properties.

Some recent papers deal with methods of introducing mercapto groups into macromolecules. The synthesis of polymeric thiols is of considerable interest, since thiols readily take part in oxidation-reduction processes and are able to initiate and control many radical-chain reactions. It is these properties of thiols which are responsible for their important role in biological processes.

Mercapto groups can be introduced into polymers by the following reactions[27]:

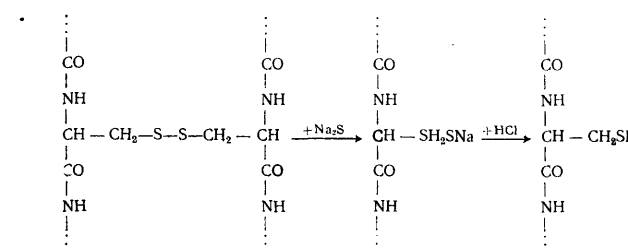




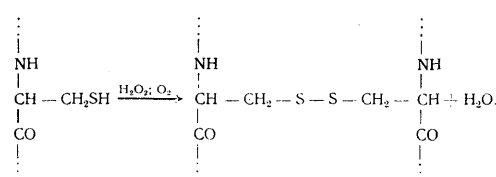
Polymeric thiols, in contrast to those of low molecular weight, have almost no unpleasant odour. They are readily oxidised to disulphides, forming partly insoluble compounds. The resulting disulphides can be reduced back to the thiols. The ability of polythiols to pass into disulphides and the reverse process open up great prospects for the application of HS-containing polymers as ion- and electron-exchange resins. For example, the polythiol obtained by reaction (1) adsorbs mercury ions in the presence of Mg^{2+}.

It has recently been shown experimentally that polymeric thiols can initiate the thermal decomposition of diazoaminobenzene and the dehydrogenation of hydrazo compounds.

The soluble derivative of keratin — keratein — evidently possesses analogous properties. Keratein is obtained by the action of a 7–10% solution of sodium sulphide or hydrosulphide on finely ground keratinous waste from the wool, leather, and meat-processing industries[28]. The reaction between keratin and sulphides at 20° leads to complete dissolution of the protein:



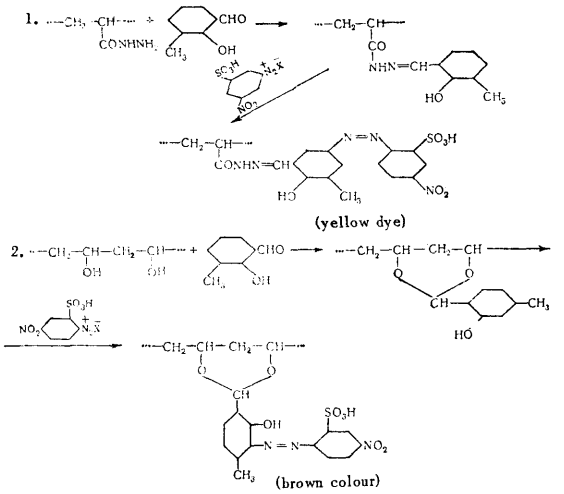
Keratein is readily soluble in water, dilute alkalis, and cuprammonium solutions, from which it can be obtained as films and fibres. Dilute (0.1–0.5%) solutions of H_2O_2 convert keratein into "pseudokeratin":

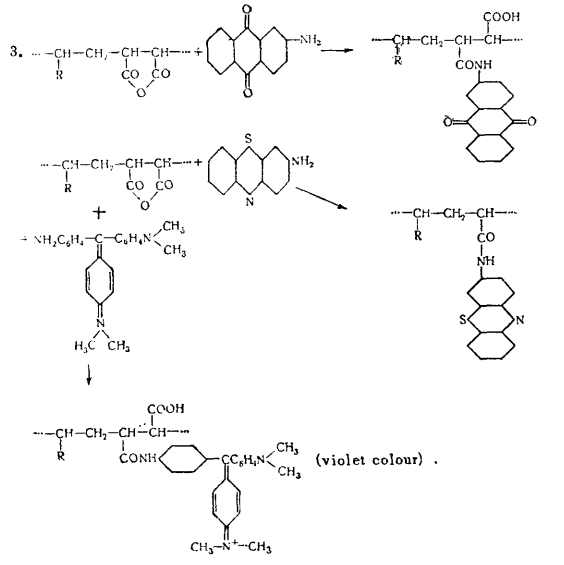


Keratein is of technical interest as an extremely effective and cheap stabiliser for emulsions, a detergent, a casein substitute in latex-protein impregnating compositions, and as a raw material for the production of films, plastics,

and fibrous materials[28,29]. In conformity with the properties of polymeric thiols noted above, it may be assumed that keratein will possess selective ion-exchange properties.

Other reactions of functional groups in macromolecules can be used to give polymers the properties of dyestuffs. Derivatives of carboxyl- and hydroxyl-containing polymers can be converted into polymeric dyes by the following methods[30]:

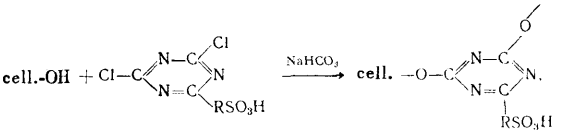




Since these compounds contain phenolic hydroxyl and a sulpho group, they are soluble in water. But their solubility can be adjusted by changing the proportions of polar, chromophoric, and hydrophobic groups in copolymers. Development on these lines will evidently lead to the production of a large range of chemically coloured polymeric fibres, films, and plastics.

Some polymeric dyes [e.g. those obtained by reactions (3)] possess oxidation-reduction properties, which suggests their possible use as electron-exchange resins.

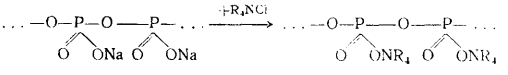
The presence of reactive OH groups in the cellulose molecule makes it possible to solve the problem of obtaining fast colours by using dyes which combine chemically with the fibre. Water-soluble dyes containing groups which can react with cellulose at pH > 7 may be used. Among these are the Procion (ICI) reactive dyes containing reactive cyanuric chloride groups in the molecule[31,32]. When cellulose fibres are treated with aqueous solutions of Procion dyes at pH > 7, the following reaction occurs[31]:



where R is the dye radical.

The chemical modification of cellulose has been discussed in detail in several exhaustive reviews[32,33].

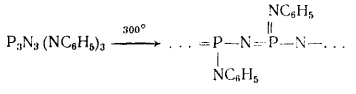
Little works has been published on the reactions of inorganic polymers, but it is worth mentioning results on the polymer-like changes that salts of polyphosphoric acid undergo[34]. Replacement of alkali cations in the polyphosphates by organic ions (trimethylammonium, benzyldimethylammonium) yields water-insoluble, heat-resistant, flexible polymers. The synthesis of such polyphosphates can be represented as



Polymeric phosphates are now under investigation as film-forming materials.

Interesting possibilities are opened up by the development of the chemistry of organic derivatives of polyphosphonitrilic chloride[30]. The phosphonitrilic chloride, formed by the interaction of ammonium chloride and PCl_5, is a mixture of cyclic trimers and tetramers of general formula $[Cl_2P:N]_{n=3,4}$. On heating to 300° phosphonitrilic chloride is polymerised, the ring opening to form a rubber-like product which crystallises at room temperature.

In order to obtain heat-resistant products not containing labile chlorine and remaining in an amorphous state over a wide range of temperatures, the synthesis of organic derivatives of polyphosphonitrilic chloride has been investigated[35]. Alcohols, phenoxides, organic acids, amines, and amides have been tested as reagents. The reaction of phosphonitrilic chloride with substituted anilides yields products which form thermoplastic polymers on heating:



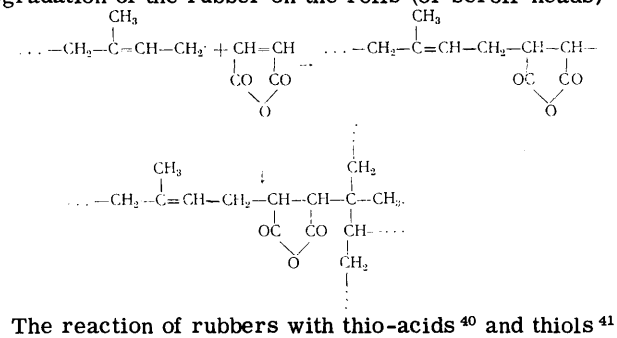
These derivatives of polyphosphonitrilic chloride melt above 300° and can be worked into films and plastics. Their impact strength can be improved by combining them with more elastic organic or organometallic polymers.

3. Addition to Double Bonds in Macromolecules

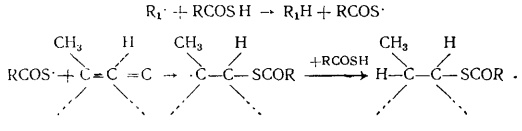
The presence of reactive double bonds in natural and synthetic rubber offers great opportunities for the chemical modification of these polymers. Hydrochlorinated rubber is widely used in industry for the production of film-forming materials; halogenation products of rubbers are employed in varnishes, adhesives, and plastics[15].

As long ago as 1938 it was shown that when toluene solutions of rubber containing a small amount of benzoyl peroxide and maleic anhydride are heated, the latter reacts with the rubber with the formation of rubber-like or rigid polymers[36]. This process was later carried out in the absence of solvents by masticating a mixture of rubber and maleic anhydride, acrolein, or acetylenedicarboxylic acid in the presence of benzoyl peroxide. The product obtained by treating the unvulcanised or vulcanised rubber[37,38] contained only 3–4% of maleic anhydride but differed markedly in properties from the original rubber; it was insoluble in benzene, formed strong vulcanisates with the oxides of lead, zinc, and several other metals, and was less permeable to gases.

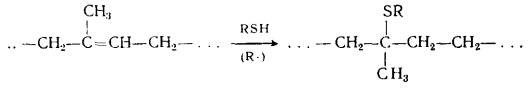
The mechanism by which rubber is modified when it is masticated with maleic anhydride has been little investigated as yet. It has recently been shown that the process is not to be regarded as a simple addition at the double bonds of the rubber and the monomer. It is more likely to be initiated by polymer radicals formed by mechanical degradation of the rubber on the rolls (or scroll-heads)[39]:



The reaction of rubbers with thio-acids[40] and thiols[41] is also of interest. For example, masticating natural rubber with 0.5–2 moles of thiobenzoic or trichlorothioacetic acid and an initiator yields a material of less regular structure, containing different types of units distributed in three dimensions[42]:



Rubbers modified with thio-acids are beginning to acquire practical importance for the production of a vulcanised rubber having increased resistance to frost and to oils and petrol[40]. A new type of elastomer developed not long ago also shows promise of practical application; it is obtained by treating latices of polybutadiene and other synthetic rubbers with thiols of low molecular weight (e.g. methanethiol) in the presence of azodiisobutyronitrile:



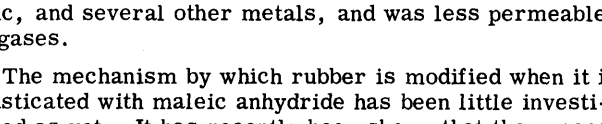
By varying the type of rubber, the thiol, and the degree of unsaturation, it is possible to obtain elastomers with various physical and mechanical properties[41].

When the quantity of thiol reacting is increased (raising the saturation to 85%), stronger and fairly elastic modified rubbers are obtained, having lower gas permeability, increased resistance to ageing, and greater stability to ozone, heat, solvents, and γ-radiation.

III. CHAIN GROWTH BY THE INTERACTION OF TERMINAL GROUPS OF MACROMOLECULES (BLOCK POLYMERISATION)

Reaction of terminal groups and active centres of macromolecules with polymerisable monomers, polymeric radicals, or terminal functional groups of oligomers yields linear or three-dimensional products of higher molecular weight.

When blocks differing in composition, structure, or spatial arrangement react, block copolymers are formed:



Block copolymers are thus isomers of the corresponding irregular copolymers. The presence in block copolymers of comparatively large (10–1000 Å) sections built up from units of the same type results in a kind of summation of the properties of the polymers involved in the copolymerisation.

The term "block copolymerisation" does not indicate the mechanism by which high polymers composed of segments of different types, or blocks, are formed. Both polyaddition and polycondensation processes, participating in chain growth by reaction of the end groups or active centres of macromolecules, are to be included among reactions of this type. It would be more correct to distinguish block copolymerisation and block co-condensation. These processes should be regarded as covering a far greater range of reactions than hitherto accepted. Indeed, it is now considered that such reactions occur in the synthesis of linear polymer[43,44]. Analysis of available experimental results shows, however, that, when end groups or active centres of macromolecules react either with themselves or with substances of low molecular weight, the formation of three-dimensional as well as linear structures is possible.

The extremely limited results so far available on the properties of three-dimensional block copolymers show that these substances possess several extremely important properties, determined by their spatial structure and the nature of the polymeric blocks involved in the reaction. We therefore consider it appropriate to examine separately synthetic methods, properties, and fields of application of linear and three-dimensional block copolymers. Such a classification is, of course, arbitrary in character, since in several cases synthesis of block copolymers may yield polymers both of linear and of three-dimensional structure.

1. Synthesis of Linear Block Copolymers

A. Mechanochemical methods. The formation of polymeric radicals by the mechanical degradation of high polymers was assumed in several papers published between 1930 and 1940[42-44]. But the possibility of using such macroradicals for the controlled synthesis of block copolymers has been investigated only since 1955[45-47]. The development of mechanochemical methods of synthesising block copolymers has enabled some important questions relating to the modification of polymeric materials to be solved; the general theory of the results obtained has been discussed, and they have been summarised in several reviews[49-51].

The mechanism and kinetics of chemical processes induced in polymers by mechanical means are undoubtedly of

fundamental significance in the mechanochemistry of compounds of high molecular weight, but at the present time investigation of this important problem is only in its initial stages.

Until recently a radical mechanism for the degradation of macromolecules by ultrasonic vibrations, by roller milling, masticating, mechanical grinding, and by repeated freezing has been demonstrated only by indirect methods (effect of acceptors on rate of degradation, initiation of polymerisation, formation of block copolymers); such methods cannot definitely confirm the formation of macroradicals, and give no idea of their life or chemical reactivity. In this connection great interest attaches to an investigation of the electron-paramagnetic-resonance spectra of the products formed by comminuting vitrified carbon- and hetero-chain polymers in an inert atmosphere over a wide range of temperatures (from -196° to +20°)[52].

When vitreous polyethylene, polystyrene, and several other carbon-chain polymers are ground in an eccentric mill for 15–20 min, a sharp drop (by a factor of 8–10) is observed in the value of $\bar{p}_{av}$ for the polymer, and paramagnetic-resonance spectra characteristic of radicals are produced. Radicals are also detected when fused quartz is ground, which points to a radical mechanism for the degradation of vitrified polysiloxanes. The concentration of paramagnetic species is in all cases of the order of 10^{17} per gram. After ground specimens of polyethylene (or polystyrene) have been thawed out and kept at room temperature, the intensity of the paramagnetic-resonance signal has almost vanished after 5–7 min. This important fact indicates that, in the case of linear polymers, recombination can occur even at temperatures below the vitrification temperature.

The intensity of the signal from ground fused quartz remains practically unchanged when specimens are maintained at 20°, and heating the degradation product of quartz to 40° leads to only a slow decrease in intensity, which points to the long life of three-dimensional macroradicals.

The electron-paramagnetic-resonance spectra of breakdown products of polymers obtained with a conical milling cutter also showed considerable concentrations of macroradical in the particles of the ground material. These investigations showed that macroradicals formed by milling polycaprolactam recombined rapidly even at 77°K.[53]

The most widely used mechanochemical method of modifying polymers is to work mixtures of polymers or polymer–monomer compositions on rolls, and ordinary and scroll-head masticators[54,55].

On mastication of polymers and polymer–monomer mixtures on rolls and in mixers of the Banbury type at temperatures as low as possible in an inert gas atmosphere, and sometimes even in the presence of air, block copolymers are formed which combine the properties of the polymers involved in the reaction.

The mastication of block and emulsion polystyrene mixed with polyisobutylene, butyl rubber, Butvar, polychloroprene, polybutadiene, and butadiene-styrene (SKS-30) and butadiene-acrylonitrile (SKN-18, SKN-30) rubbers has been investigated. By masticating mixtures of polystyrene with SKS-30 or SKN-18, a material is obtained having an impact strength greater than that of polystyrene by a factor of 4–5. The proportions of the rubber cannot conveniently be increased above 20–25%, since a great part of the elastomer would then remain uncombined with the polystyrene, which would diminish the strength characteristics and lower the vitrification temperature of the material[49].

The formation of block copolymers by the simultaneous mastication of polystyrene and a rubber is confirmed by results on the thermomechanical properties, solubility, and turbidimetric titration of a product containing combined rubber, and also by the fall in strength of the material observed on adding on to the rolls a radical acceptor (I_2) and certain dyes (pigment yellow, Bordeaux lake, etc.)[49]. Since some dyes contain reactive hydrogen or halogen atoms in the molecule, they can evidently act as fairly strong acceptors for macroradicals, and thus hinder the formation of a block copolymer.

High-strength plastics based on polystyrene or styrene–acrylonitrile copolymers modified with butadiene-styrene or butadiene-acrylonitrile rubber are used in the manufacture of refrigerator bodies, facing tiles, components of sanitary equipment, and other articles for a wide range of uses.

Treatment of mixtures of polymers and polymer–monomer compositions in a scroll-head masticator has been successfully used to obtain block copolymers of natural and synthetic rubbers[55,56], and also for the copolymerisation of rubbers with monomers (methyl methacrylate, acrylonitrile, acrylic acid, *p*-divinylbenzene, etc.[57]).

Raising the temperature of mastication was found to lower the rate of degradation of the polymer and hence the yield of macroradicals and block-graft copolymers formed with their aid. In spite of the relatively low activation energy of mechanochemical block copolymerisation, the activities of the macroradical and the monomer play a significant part in controlling the process[57].

Thanks to the work of Soviet investigators[58], the design of the scroll-head type of masticator has recently undergone considerable changes. By the simultaneous processing of mixtures of polymers and polymer–monomer compositions on the improved design of masticator, methods have been worked out for obtaining block copolymers of acrylonitrile rubber with phenol-formaldehyde and epoxy resins, coal-tar pitch, etc. The resulting block copolymers differ from the initial polymers in thermomechanical properties and solubility, and possess a combination of important physicomechanical properties (e.g. increased strength and adhesion, chemical stability, etc.)[59].

It was reported not long ago that several types of industrial scroll-head masticators are suitable for making block-graft copolymers by mechanical mastication of polymers[49]. Methods of modifying polymers during grinding, mastication, and extrusion are all included in the production cycle adopted for the processing of polymers. Owing to this circumstance, the introduction of such methods of modifying polymeric materials has great prospects in industry.

Apart from the study of mechanochemical changes in polymers and the synthesis of block copolymers in the condensed phase, work on methods of block copolymerisation by the action of ultrasonic vibrations on polymer solutions[49,60], by forcing the solutions through capillaries, and by vigorous stirring[61] also has much interest.

A new principle appears in the synthesis of block copolymers by cryolysis (freezing and unfreezing) of aqueous dispersions and solutions of polymers[45,62]. In this case degradation of macromolecules and formation of macroradicals are due to localisation of the internal pressure due to the phase transition at individual links in the polymer

chains. The cryolysis method has yielded block copolymers of starch and polystyrene with good emulsifying properties.

The mechanism of mechanochemical block copolymerisation is not yet finally established. The currently accepted view that formation of mechanochemical block copolymers is due solely to combination of polymer radicals does not, in the author's opinion, explain many experimental facts. Indeed, it has been noted above that the concentration of macroradicals formed by the ultrasonic degradation or mastication of polymers is of the order of 10^{-6}–10^{-7} mole g^{-1}. Yet the yields of block copolymers may reach 80–90% of the weight of degradable polymers. Such a disparity between the concentration of active molecules and the yield of block copolymer points to a chain mechanism for mechanochemical copolymerisation and cannot possibly be explained solely by radical combination or the possibility of graft copolymerisation by chain transfer from a polymer radical to macromolecules. It seems more probable that mechanochemical block copolymerisation involves degradation of polymer chains initiated by macroradicals. Mechanical degradation of polymers provides extremely favourable conditions for this reaction.

1. In view of the comparatively small number of macroradicals and the relatively large quantity of "non-radical" chains, the probability of interaction between polymer radicals and macromolecules is considerable.
2. During mechanical degradation macromolecules containing no unpaired electrons are activated by the distortion of valency angles due to the intense mechanical action on the polymer.
3. The rate of initiated degradation must be proportional to the concentration of macroradicals [R·] and "non-radical" macromolecules [P]: $v = k[R\cdot][P]$. As a result, even with small values of [R·] but large values of [P], initiated degradation may be quite intense. Block copolymers are formed, and new macroradicals arise, which further extend this chain process.

According to our suggested mechanism, mechanochemical block copolymerisation occurs as follows.

1. Production of active chains:

$$R{-}R + m{-}m \rightarrow R\cdot + m\cdot .$$

2. Chain growth:

$$R\cdot + m{-}m \rightarrow Rm + m\cdot \text{ etc.},$$
$$m\cdot + R{-}R \rightarrow Rm + R\cdot .$$

3. Chain termination:

(*a*) by recombination:

$$R\cdot + m\cdot \rightarrow Rm,$$
$$m\cdot + m\cdot \rightarrow m{-}m,$$
$$R\cdot + R\cdot \rightarrow R{-}R;$$

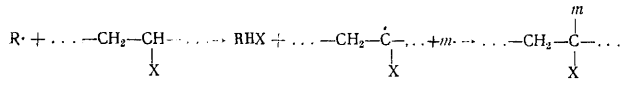
(*b*) by disproportionation:

$$R\cdot + R\cdot \rightarrow RH + \text{olefine},$$
$$R\cdot + m\cdot \rightarrow RH \text{ (or } mH) + \text{olefine};$$

(*c*) by reaction with the medium, the walls of the vessel, or impurities:

$$R\cdot + AX \rightarrow RX + A\cdot,\quad A\cdot + A\cdot \rightarrow A{-}A.$$

If the macromolecules contain bonds which can interact with macroradicals, the initiated degradation may be accompanied by a chain-transfer process, leading to the formation of branched macromolecules:



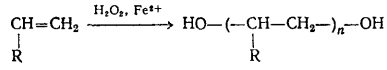
The probability of such a process is governed by the activity of the macroradical, the chemical nature of the polymer, and the conditions of mechanical degradation.

When a polymer undergoes mechanical degradation in the presence of a sufficiently active monomer, block copolymerisation occurs also by a radical-chain mechanism. However, the role of initiated degradation is then reduced to a minimum, since the dominant reaction is the macroradical-initiated polymerisation of the monomer.

The suggested mechanism for mechanochemical block copolymerisation explains the apparent discrepancy between the concentration of macroradicals and the yield of copolymers; it also accounts for the well-known fact that not all pairs of polymers can form block copolymers under conditions of mechanical degradation. It also readily explains the inhibiting effect of active acceptors of free radicals, and several other experimental facts.

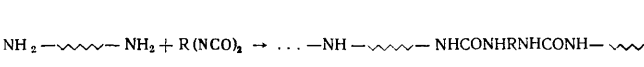
B. Chemical methods. General information on the synthesys of linear block copolymers by chemical methods, their properties, and their fields of application has been given in several reviews [18,43,65]. Chemical methods of obtaining block copolymers generally involve two stages; firstly the synthesis of polymeric blocks, which are macromolecules containing reactive functional groups at the ends of the chain, followed by reaction of the resulting products either with chemically different polymeric blocks or with monomers. For example, reaction of the terminal hydroxyls of polyoxypropylene (degree of polymerisation 20–80) with ethylene oxide yields a block copolymer of the composition $HO{-}[C_2H_4O]_n{-}[C_3H_6O]_m{-}[C_2H_4O]_n{-}OH$. At the present time block copolymers of propene and ethylene oxides are acquiring industrial importance as emulsifiers and cross-linking additives ("Pluronics").

The starting blocks may be synthesised by either polyaddition or polycondensation. In the former case, oxidation-reduction polymerisation of unsaturated monomers in aqueous medium yields carbon-chain polymers with OH end groups:



The synthesis of blocks by polycondensation of an excess of a glycol or an amine with a dicarboxylic acid yields polymers having either OH or NH_2 end groups. Appropriate proportions of a diisocyanate (in the preparation of polyurethanes) or of epichlorohydrin (in the synthesis of polyepoxides) give macromolecules with terminal isocyanate or ethylene oxide groups.

The polymeric blocks obtained by one of these methods are used to prepare various block copolymers with diisocyanates (hexamethylene diisocyanate, *m*-tolylene diisocyanate, etc.), diepoxides, diketens, tetrafunctional acrylates, etc. The principle underlying such block copolymerisation is illustrated by the following schemes [18]:



Block copolymerisation leads to vitreous or elastic products with average molecular weights exceeding those of the original blocks by a factor of 10–15. Linear block copolymers are of particular interest for the synthetic-fibres industry, since the degree of crystallinity of the polymer can be controlled by appropriate combination of crystalline and amorphous blocks. In this connection, block copolymers of poly(ethylene glycol terephthalate) (Terylene, Dacron) with poly(ethylene oxide) (Carbowax) are worthy of serious attention. This type of block copolymer contains both polyester blocks with the structure



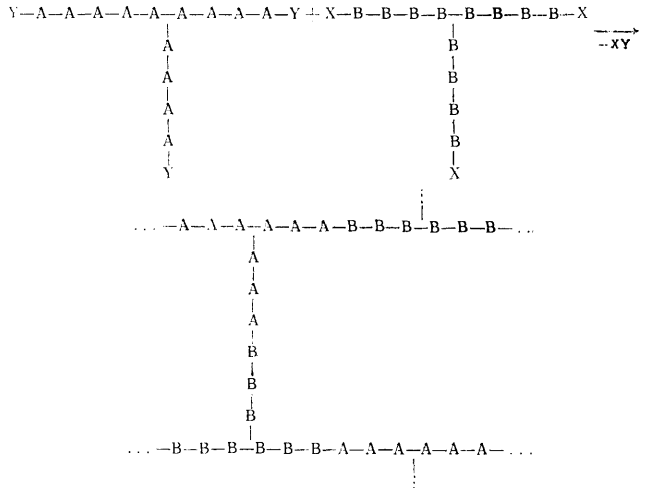
and also flexible and hydrophilic portions of poly(ethylene oxide) chains. The combination of such contrasting segments confers on the polymer considerable strength, extensibility, elasticity, and increased ability to absorb water.

2. Three-Dimensional Block Copolymers

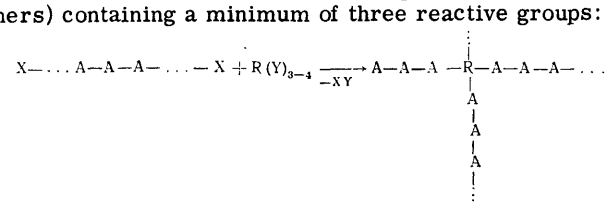
Three-dimensional block copolymers are of great theoretical and practical interest. They may be expected to combine the resistance to heat and solvents peculiar to three-dimensional structures with a wide range of other properties (e.g. elasticity, chemical stability, adhesion, etc.) contributed by the polymeric blocks involved in the reaction.

On the basis of the above definition of block copolymerisation as a method of synthesising substances of high molecular weight by reaction between the terminal groups of polymeric blocks, the following principles may be set out for the synthesis of three-dimensional block copolymers.

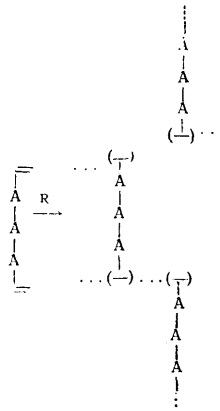
Type 1. Polymerisation or copolymerisation of branched blocks containing more than two terminal active centres or reactive groups:



Type 2. Reaction between linear (or branched) blocks and substances of low molecular weight (in the limit, monomers) containing a minimum of three reactive groups:



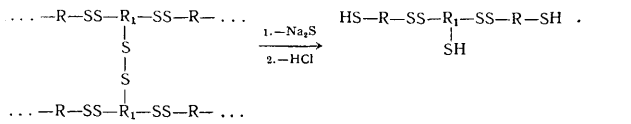
Type 3. Polymerisation of blocks having bifunctional groups capable of either chain or stepwise polymerisation at the ends of the chains:



Reactions of type 1. Blocks of branched structure may be prepared by mechanical or chemical degradation of three-dimensional polymers. Thus when vulcanisates of natural rubber (light crepe, smoked sheet) or synthetic rubber (butadiene-styrene, butadiene-acrylonitrile, butyl) are masticated in a laboratory mixer with a spiral rotor, mechanical degradation occurs and strongly branched, partly cross-linked macromolecular fragments are formed[66]. Such products swell in monomers (methyl methacrylate, methacrylic acid, styrene).

When vulcanisates which have been swollen in monomers are masticated in an atmosphere of nitrogen, incompletely soluble or insoluble copolymers are produced; these can be moulded as plastics and are more or less strong and elastic according to the quantity of combined polymer[46,66].

The use of degraded vulcanisates to obtain modified rubbers and high-strength plastics is practically important, since it enables reclaimed rubber to be used in making economically practicable polymers. The synthesis of branched blocks by the chemical degradation of network structures is no less promising. Thus, when a suspension of Thiokol, obtained by co-condensation of dichlorodiethyl formal, small amounts of trichloropropane, and sodium disulphide, is treated with sodium sulphide or hydrosulphide, liquid mercapto-polysulphides are obtained, which under appropriate conditions can form rubber-like materials[67].



The liquid mercapto-polysulphides obtained, have viscosities of 0.5–450 poises and mean molecular weights of 3000–4000, depending on the concentration of sodium disulphide and the composition of the bath. The action of organic or inorganic peroxides (cumenyl peroxide, acetyl peroxide, PbO_2, NO_2, etc.), alone or mixed with amides (diphenylguanidine), and also of atmospheric oxygen in the presence of driers, converts the liquid mercapto-polysulphides at 20° into rubber-like substances[67].

The hardening of the mercapto-sulphides evidently occurs by a radical mechanism, and can be represented to

a first approximation by the scheme

$$R(SH)_2 + R_i \rightarrow HSRS\cdot + R_iH$$

$$2HSRS\cdot \rightarrow HSRSSRH \xrightarrow{+R_i} HSR(SSRSSR)_nSH,$$

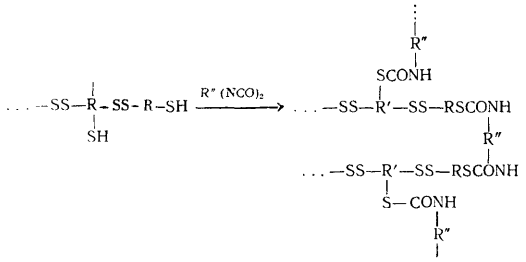
where R is the poly(alkyl sulphide) chain of liquid Thiokol.

Activation of the terminal mercapto groups of the branched chains and their interaction results in the observed transition from viscous liquid products to vulcanised rubbers. The rubber-like materials possess high resistance to petrol and oils, and are suitable for use over quite a wide range of temperatures (from -54° to +150°).

The ultimate tensile strength of filled vulcanisates (containing carbon black, PbO, TiO_2) is 80–90 kg cm^{-2} at an extension of 200–300%. Compositions based on liquid Thiokols have been successfully employed for the production of moisture- and gas-impermeable films and coatings resistant to weathering, the internal linings of petrol tanks, etc.

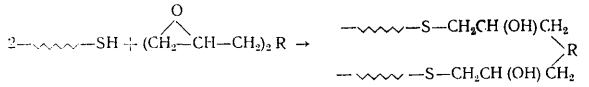
Liquid polysulphides can be used to plasticise polyvinyl chloride and also in compositions with phenol-formaldehyde resins[1,67].

The synthesis of three-dimensional block polymers by the interaction of branched and linear blocks with monomers opens up great opportunities for modifying the properties of polymers. In this connection the copolymers of liquid Thiokols with diisocyanates must be mentioned:



Diisocyanate-polysulphide copolymers possess high adhesion to metals, elasticity, frost-resistance, and resistance to oils and solvents.

The epoxy-polysulphide copolymers formed by reaction between polymeric epoxy compounds[68] and polysulphides in the presence of polyamines (triethylenetetramine, tris(dimethylaminomethyl)phenol, etc.) are becoming important. According to the relative proportions of the initial components and the quantity of hardener, these compositions can be hardened at 20°–100°. The chemistry of the reactions can be represented by the scheme

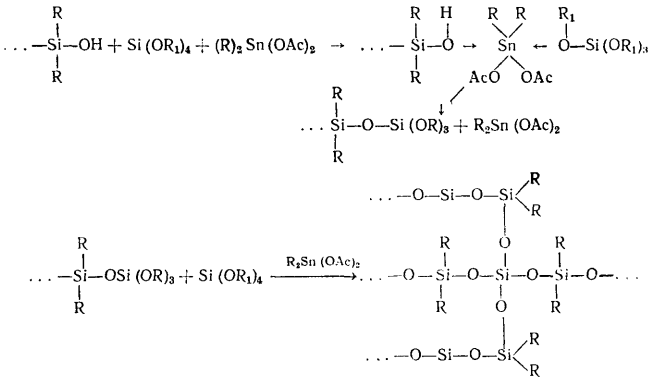


Before hardening, epoxy-polysulphide compositions are less viscous than the original polysulphide, but after hardening they form elastic products possessing high adhesion, and resistance to water, solvent, and ageing. The strength of such materials depends on the type of epoxy and polysulphide resin and the relative proportions of the components in the resin composition.

Epoxy-polyester resins are conveniently used in the preparation of adhesives, sealing compounds, protective coatings, binders, etc.

Reactions of type 2. Three-dimensional block copolymerisation of linear blocks with multifunctional monomers was recently used to convert viscous liquid polydimethylsiloxanes (M_{av} = 10 000–50 000) into rubber-like products, and also to vulcanise organosilicon rubbers at room temperature[61,69-71]. The principle of the method is the reaction of the terminal hydroxyl groups of the polydimethylsiloxane with tetraethyl orthosilicate in the presence of organotin catalysts of the type R_2SnOAc, where R is an alkyl or an aryl group, and Ac is an acyl group.

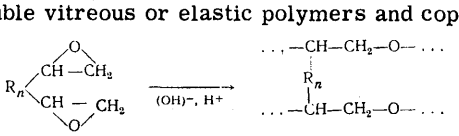
The mechanism of the reaction can be represented by the scheme[69]



It is evident from this scheme that the new method of polycondensation opens up a prospect of modifying polysiloxanes. Indeed, with the aid of this principle, various block copolymers differing in chemical nature from polysiloxanes, as well as other classes of oligomeric substances containing hydroxyl or carboxyl groups at the ends of the chains, can be obtained. The preparation of linear, three-dimensional, or branched block copolymers by interaction of polymeric blocks with tri- and multi-functional monomers is an extremely promising general method for the synthesis of such compounds.

This interesting reaction could appropriately be called a "multiplication reaction". The recently described method of "doubling"[72] is evidently merely a particular case of the general principle of block copolymerisation. However, the method of doubling, in the form proposed by Kern and his coworkers, can have only a limited application for decreasing the polydispersity of certain types of polymers.

Reactions of type 3. Let us consider the three-dimensional polymerisation of blocks containing, at the ends of the chain, groups which can undergo chain or stepwise polymerisation. Among such oligomers are epoxy-polyethers, obtained by the action of epichlorohydrin on dihydric phenols, glycols, or diamines[73,74]. In the presence of bases at room or slightly elevated temperatures (60°–110°), epoxy-polyethers are converted into infusible and insoluble vitreous or elastic polymers and copolymers:



The physical and mechanical properties of polyepoxides are largely determined by the chemical nature and the mean degree of polymerisation of the blocks used.

The ability of epoxy-polyethers to copolymerise with various hydroxyl-, amino-, and carboxyl-containing polymers (phenol-aldehyde resins, polyamides, polyesters, etc.) has enabled far-reaching modifications to be made in the properties of various polymeric materials. The large

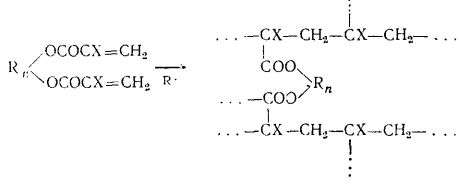
variety of materials obtained from epoxy-polyethers have found widespread application as binders for reinforced plastics, casting resins, plastic foams, coatings, sealing compounds, adhesives, etc.[74] The polyester-acrylates, a new type of oligomeric substances able to undergo three-dimensional polymerisation, which have been developed in the USSR, offer equal possibilities[75]. Polyester-acrylates are synthesised by controlling chain growth during polyesterification by adding monobasic methacrylic or acrylic acid to the reaction mixture. By analogy with a reaction known to occur by a radical-chain mechanism, we have termed this reaction "condensation telomerisation".

The course of the reaction can be represented by the general scheme

$$R(OH)_2 + R_1(COOH)_2 + CH_2=\underset{\displaystyle X}{\overset{\displaystyle |}{C}}-COOH \rightleftarrows$$
$$\rightleftarrows CH_2=\underset{\displaystyle X}{\overset{\displaystyle |}{C}}-CO(OROCOR_1COO)_nROCOC=\underset{\displaystyle X}{\overset{\displaystyle |}{C}}=CH_2,$$

where R and R_1 are alkyl or aryl radicals, and X = H, CH_3, Hal. When the proportion of methacrylic acid is reduced from 2.2 moles to 0.1 mole per mole of dibasic acid, polyester-acrylates are obtained with $\bar{n}$ = 1–20 and mean molecular weights reaching 4000–5000[76]. When the reaction of the monomers involves more than two functional groups, branched oligomeric polyester-acrylates are formed.

Investigations of the three-dimensional polymerisation of polyester-acrylates have shown that, in the presence of initiators, these viscous liquid products can be converted into infusible vitreous or ebonite-like polymers both at room temperature and above[77]:



where R_n is a polyester radical. The various polyester-acrylates can form block copolymers both among themselves and with bi- and multi-functional monomers (styrene, methyl methacrylate, acrylonitrile, etc.).

Increase in the distance between the acrylate groups in polyester-acrylates produces a sharp decrease in the contraction accompanying polymerisation (when $\bar{n}$ = 4 the volume contraction is 0.3–0.5), an increase in the impact strength and in the hardness of the three-dimensional polymer, and also an improvement in the adhesive properties; this opens up a prospect for their use as binders, adhesives, coatings, sealing compounds and pastes, etc.[76]

IV. REACTIONS OF GROUPS AND ACTIVE CENTRES WITHIN MACROMOLECULES ACCOMPANIED BY CHAIN GROWTH

Reaction of active centres or functional groups, distributed along the chains of macromolecules, with substances of low molecular weight, monomers, macroradicals, or polymers can give rise to branched or three-dimensional structures, differing in the chemical character and in the structure of the main chain and the side branches. If these processes result in growth of the side branches, they are to be regarded as graft polymerisation and to be distinguished from the conversion of macromolecules into spatial structures by the action of substances of low molecular weight which are incapable of homopolymerisation. Chemical reactions of macromolecules of the latter type are conveniently included among "cross-linking" reactions.

1. Graft Polymerisation

The fundamental principles of radical-chain graft copolymerisation were first worked out in the USSR in 1946[78] and somewhat later in France[79].

By graft copolymerisation a very extensive modification of the properties of polymers can be made in desired directions, since the introduction of polymeric blocks of 50–100 Å in the form of side branches or cross-linking chains, similarly to block copolymerisation, results in a summation of the properties of the substances involved in the reaction.

The growth of side chains can occur both by radical or ion-chain polymerisation and by direct stepwise (migration) polyaddition or polycondensation[43,65]. Synthesis of graft copolymers by radical-chain methods can be accomplished by chain transfer during polymerisation of a monomer in the presence of a polymer, by copolymerisation of branched polymers containing double bonds in the side chains, and also by the so-called "two-stage method", based on the introduction into the polymer of peroxide, perester, diazonium, and other groups which can break down to form active centres[43].

The use of polycondensation or stepwise polyaddition for the synthesis of graft copolymers is possible when the macromolecules of the polymer contain, in the main chain or in the side branches, reactive functional groups (OH, SH, NH_2, COOH, etc.) or groups which can add on a proton with formation of new covalent bonds (isocyano groups, three- and four-membered heterocycles, etc.). Graft copolymers are then formed by the reaction with the corresponding monomeric substances or with polymeric blocks containing reactive end groups.

2. Synthesis of Graft Copolymers by Chain Transfer

This is the easiest way to modify the properties of polymers. The separate stages in the formation of a graft copolymer by chain-transfer methods can be represented by the following scheme:

1. Formation of active centres:

   (*a*) by decomposition of the initiator:

   $$RR \rightarrow R\cdot + R\cdot;$$

   (*b*) by interaction of R· with R_nH macromolecules:

   $$R\cdot + R_nH \rightarrow RH + R'_n\cdot.$$

2. Chain growth:

   (*a*) by homopolymerisation of the monomer:

   $$R\cdot + M \rightarrow R-\sim\sim\sim\cdot;$$

   (*b*) by graft copolymerisation:

   $$R'_n\cdot + M \rightarrow R_n-M-M-M\cdot.$$

3. Chain termination:

   A.

   (*a*) by recombination of growing homopolymerisation chains:

   $$2R-M-M-M-M\cdot \rightarrow (R-M-M-M-M)_2;$$

(*b*) by recombination of dissimilar macroradicals:

$$R{-}M{-}M{-}M{-}M\cdot + R_n \cdot \rightarrow R{-}M{-}M{-}M{-}M{-}R_n \ ,$$
(branched graft copolymer)

$$2R_n{-}M{-}M{-}M{-}M\cdot \rightarrow (R_n{-}M{-}M{-}M{-}M)_2; \quad 2R_n \cdot \rightarrow (R_n)_2 \ ;$$
(three-dimensional graft copolymers)

B. by disproportionation:

$$R_n(M)_n + R_n(M)_m \rightarrow R_n(M)_n + R_n(M)_m .$$

In this case processes leading to the formation of graft copolymers are seen to be accompanied by homopolymerisation.

A chain-transfer reaction is characterised by a chain-transfer constant, representing the ratio of the velocity constant for transfer of the chains to that for their growth. When polymerisation is carried out in solution, the solvent takes part in chain transfer. Thus, with isopropylbenzene the chain-transfer constant is 0.8×10^{-4} at 60°, and 2×10^{-4} at 100°. The growth of the chains occurs 10 000 times as rapidly as their transfer, the activation energy for chain transfer being considerably greater than that for chain growth; in the case of isopropylbenzene the difference amounts to 5.5 kcal. A kinetic study of chain transfer shows that, in order to bring it about, a high temperature and a high concentration of polymer in the solution must be maintained. The high viscosity of a concentrated solution of a polymer considerably reduces the probability of chain termination, thus favouring the reactions of chain transfer and chain growth; numerous experiments have shown that high yields of graft copolymers are achieved under these conditions. Apart from the conditions under which transfer is carried out, the chemical nature of the polymer and the monomer, which determines their polarity and reactivity, and also the presence of steric hindrance, is an extremely important factor in graft polymerisation. Available data show that the intensity of graft copolymerisation decreases in the following sequence, according to the chemical nature of the monomer: vinyl chloride > vinyl acetate > styrene; and according to the chemical nature of the polymer: polyvinyl chloride > polyacrylonitrile > polyvinyl acetate > > polystyrene.

Although the method of chain transfer does not allow graft copolymers to be prepared free from admixture with homopolymers, it has been widely employed in practice. Thus, by the polymerisation of a series of monomers (acrylates, vinyl acetate, etc.) in a polyvinyl chloride latex, graft copolymers were obtained which combined the adhesion and atmospheric stability characteristic of acrylates and polyvinyl acetate with the increased resistance to abrasion, the action of chemicals, water, petrol, and oils of polyvinyl chloride. Such copolymers are used as protective coatings and film-forming materials[80].

Graft copolymers of rubbers and polystyrene or poly(methyl methacrylate) are widely used in industry. Such copolymers may be synthesised both by polymerising the monomers in a latex of synthetic or natural rubber in the presence of water-soluble initiators (e.g. potassium persulphate), and by polymerising the monomer with the rubber either dissolved or swollen in it. Either elastomers or strong plastics may be formed, according to the relative proportions of rubber and monomer.

Rubber-like graft copolymers are formed, when styrene, methyl methacrylate, or acrylonitrile are polymerised in latices of natural or synthetic rubbers in the presence of hydroperoxides and aliphatic amines with 20–50% of the monomer[81,82].

The vulcanisation of graft rubbers yields rubbers possessing increased strength and resistance to weathering and rubbing. Such materials are produced on an industrial scale in the USA and in England. The great strength of unfilled graft rubbers opens up new prospects in the technology of gas-filled elastomers; lighter and stronger foam rubbers can be obtained, and they will evidently be competitive with elastic polyurethane foams in future[83].

In preparing plastics based on graft copolymers of rubber, the proportion of elastomer relative to monomer must not exceed 10%. Otherwise, polymerisation of styrene in the latex gives very low yields of graft copolymer. Impact-resistant material is obtained by introducing even as much as 30% of rubber[84]. Such material, however, possesses diminished hardness and greater residual deformation than polystyrene on compression and extension.

It has recently been shown experimentally that graft copolymerisation of styrene with rubber in bulk at 80°–170° gives a high yield of graft copolymer with 5–10% additions of rubber. From such rubber-modified polystyrene quite hard and elastic materials are obtained, which withstand impact loads 3–5 times as great as in the case of plastics based on polystyrene or its copolymers with acrylonitrile[85]. Graft copolymers of styrene with butadiene-styrene rubber are not inferior to the so-called "latex polystyrene" in dielectric properties, and considerably surpass it in strength characteristics, so that these products can be used for sheet materials, films, and casting resins.

Great developments in the principle of grafting by chain transfer are made possible by methods of initiating graft copolymerisation with γ-rays and fast neutrons[86,87]. The velocity of radiation-induced graft polymerisation depends on the intensity of irradiation, the dose, the temperature, the medium, the presence of sensitisers or inhibitors, etc. When γ-rays (^{60}Co) are used, exposure is generally carried out at room temperature or somewhat above (40°–50°) with an intensity of the order of 200 000–300 000 rep/h.

Radiation grafting methods are very promising and allow graft copolymerisation to be carried out on the surfaces of film materials (so-called "surface grafting")[87-89]. In the future it should be possible to work out systematic procedures for modifying the properties of the finished articles. When graft polymerisation is carried out on the surfaces of films, a very important factor, in addition to those noted above, is the diffusion of the monomer into the polymer and the distribution of the former between the phases in contact (polymer and solution)[89].

Diffusion of monomer into the initial polymer plays a large part in determining the structure and properties of the product obtained. It depends on the coefficients of diffusion of the monomer in the solution D_l and in the polymer D_p, and also on the Nernst partition coefficient K (the ratio of the concentration of monomer in the polymer to its concentration in the solution), which determines the equilibrium distribution of the monomer between the two phases. During diffusion such an equilibrium is established directly at the film–solution interface. Surface and bulk graft polymerisation are possible in systems in which the resulting concentration gradient of monomer in the films is not too great. The lower K and the greater D_p (compared with D_l), the smaller is the concentration gradient during diffusion. This condition is satisfied in the polyvinylpyrrolidone–acrylonitrile and polymethacrylic ester–acrylonitrile systems. With a high partition coefficient K and a low diffusion coefficient D_p, the concentration of monomer directly at the film

surface is high, and a considerable concentration gradient appears in the course of diffusion. In this case the surface of the film swells, and changes its original shape. A surface graft without change in shape of the polymer is possible in such a system if swelling of the film is carried out with low concentrations of monomer in the solution and the period of diffusion is restricted. Bulk graft polymerisation does not then occur. An example is the polymethacrylic ester–vinylpyrrolidone system[89].

Complications arise from the fact that the diffusion of monomer into the polymer is affected by the graft polymer obtained from the initial monomer which had diffused during irradiation. Subsequently the graft polymer acts in the diffusion process as a third phase having its own coefficients of diffusion and of partition with the solution and with the polymer within the film which has not yet undergone graft polymerisation. If the graft polymer is more readily soluble in the monomer than is the original polymer, the partition coefficient for monomer between solution and film increases, and at the same time diffusion of monomer into the interior of the film (which has not undergone graft polymerisation) slows down. The polyisobutylene–styrene system is of this type.

When the resulting graft copolymer is more soluble than original polymer in the monomer, the velocity and completenes of grafting are substantially affected by osmosis. This may possibly explain the increase in the rate of graft copolymerisation with increase in film thickness observed in several cases[89].

Formation of homopolymers is not excluded during irradiation of polymer films in a monomer medium. Contamination with homopolymer can be diminished by using aqueous dispersions of monomers, and practically eliminated (or reduced to a minimum) by the two-stage method of graft copolymerisation. The principle of this interesting process for radiation grafting on films is based on the comparatively long life of macroradicals formed by the irradiation of vitrified polymers[88]. This allows us to carry out separately irradiation and subsequent graft polymerisation on the surface of the irradiated polymer placed in a medium containing the monomer.

By applying radiation-grafting methods to a polyethylene–vinylcarbazole surface, materials are obtained which surpass the individual polymers in several properties; such copolymers have a higher softening point and a greater electrical resistivity than either unexposed or irradiated polyethylene, together with a greater impact strength than polyvinylcarbazole. When films of polytetrafluoroethylene (Teflon) are irradiated in the presence of styrene, a graft copolymer is formed on the polymer surface. A graft of 1–10% of styrene increases the adhesion of Teflon to polymers and to aluminium.

Interesting results are achieved in the radiation grafting of polyacrylonitrile to films of vulcanised polydimethylsiloxane[87]. Such a graft copolymer exhibits, together with the heat resistance characteristic of polysiloxanes, considerably less swelling in petrol, aromatic hydrocarbons, and other organic solvents.

Graft polymerisation at film surfaces can yield strong cation- and anion-exchange membranes of high exchange capacity. Cation-exchange membranes are prepared by sulphonating films of polyethylene containing a graft copolymer of polyethylene and styrene on the surface.

For anion-exchange membranes, polyvinylpyridine is grafted on the surface of a polyethylene film, with subsequent conversion of the pyridine groups in the side branches into quaternary ammonium bases.

A sulphonated film containing 20% of polystyrene grafted to polyethylene has a wet strength of 80.5 $kg\,cm^{-2}$. The strength of the industrial membrane Amberplex S-1 is 17.5 $kg\,cm^{-2}$. It may be assumed that the polyethylene restricts the swelling of sulphonated graft-copolymer membranes, and to a considerable extent determines the strength of such films[87]. A still greater increase in strength and stability towards aqueous solutions of electrolytes may be achieved by the graft copolymerisation of polyethylene films with divinylbenzene and its mixtures with styrene.

The widespread use of graft copolymerisation by ionising radiation is impeded by (1) difficulties associated with ensuring safety and controlling the process when working with γ-rays, and (2) lack of methods for eliminating side reactions, which result in degradation or cross-linking of the polymer macromolecules during grafting.

Recently, therefore, attention has been turned to the possibility of effecting graft polymerisation by means of ultra-violet radiation (λ = 254–280 mμ). When films of polyethylene containing benzophenone are irradiated in acrylonitrile medium, surface grafting occurs, producing an increase in hydrophilic character, a diminution in swelling in hydrocarbons, and a change in the adsorption of dyes by the polymeric film[90,91].

Grafting by means of ultra-violet radiation enables degradation of the polymer and formation of homopolymer to be avoided; together with its safety, this is the great advantage of the method.

3. Graft Copolymerisation of Polymers Containing Active Centres in the Macromolecules

In addition to the above methods based on chain transfer, processes of graft copolymerisation based on the introduction into the macromolecules of groups which readily form active centres of polymerisation are acquiring practical importance. Such groups are usually introduced by auto-oxidation[92], ozonolysis[93,94], direct chemical synthesis (e.g. by the reaction of polyacryloyl chlorides with alkyl hydroperoxides)[92,95], irradiation with X-rays or γ-rays in air, and electrolysis of polyacrylic acid or carboxyl-containing elastomers[96-97]. Among these a very promising method is based on separate ozonisation, with subsequent graft copolymerisation of a monomer and the ozonised polymer. Mild ozonisation enables grafts to be made on polymeric films and fibres[98]. The principle of the method consists in treating the film (polyethylene, polystyrene, etc.) at room temperature with ozonised oxygen and subsequently keeping the material in a solution or an emulsion of the monomer at an elevated temperature in an inert gas. Graft polymerisation occurs on the surface of the film, as a result of which its weight increases by 2–20%.

By grafting acrylonitrile on crystalline polyethylene, obtained by the Ziegler method, it is possible to reduce markedly its permeability to gases and to increase its stability to light. A graft of 15% of acrylic acid on polyethylene fibres and films yields materials which are stronger and more hydrophilic in character, and capable of being dyed with basic dyes.

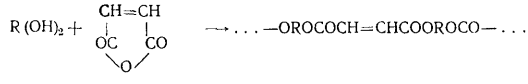
By using the ozonisation method, it has recently been possible to graft vinyl monomers on a polyamide[99] and to obtain graft copolymers of starch and polystyrene. Such

copolymers are prepared by ozonising an aqueous suspension of starch and subsequently polymerising styrene on the ozonised starch in an atmosphere of nitrogen at 70°–100°.[100] Depending on the relative proportions of starch and styrene and the duration of ozonisation, products were obtained with different physical and mechanical properties. These copolymers were shown to be excellent stabilisers for emulsions of water and styrene.

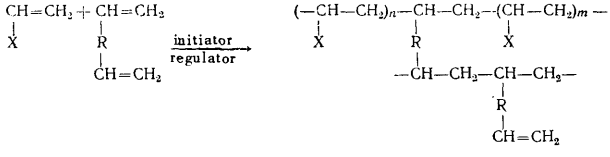
Ozonisation is also a very promising method for modifying the properties of many other natural polymers. Thus the ozonisation of cellulose (cotton fibre, viscose cord) enables an acrylonitrile graft to be made by treating the fibre or cord with a solution of the monomer in a high vacuum (10^{-6} mm Hg) on a boiling water bath[101].

4. Graft Copolymerisation of Unsaturated Polymers. Three-Dimensional Copolymers

Polymers containing double bonds in the main chain are prepared by polycondensation of α,β-unsaturated dibasic acids or their anhydrides (maleic, aconitic, itaconic, etc.) with glycols[102,103]:



Polymers containing double bonds in the side chains were first synthesised in the USSR (1946–1947)[104]. The method consists in principle in copolymerising unsaturated bi- and quadri-functional monomers under conditions which hamper the formation of three-dimensional structures. To avoid the formation of a network polymer, the process is carried out in a non-solvent medium (water, methanol, etc.) in the presence of an initiator and a regulator for the polymerisation process (an amine, a thiol, or a phenol)[104]. Allyl esters of dibasic acids can be used as the quadrifunctional monomers. This reaction can be represented as



The yield of soluble unsaturated copolymer is 75–85%. The content of double bonds is ~20–25% of the theoretical, which indicates that the copolymer macromolecules have a branched structure.

Compounds of high molecular weight containing reactive double bonds can be prepared also by esterifying hydroxyl-containing polymers with unsaturated acids or by etherifying them with unsaturated alcohols. Thus the reaction of cellulose or the so-called "secondary" cellulose acetate with methacrylic anhydride yields methacrylic or acetomethacrylic esters containing 0.1–1.0 methacryloyl group per glucose unit[105].

The initiated polymerisation of bi- or quadri-functional monomers in the presence of polymers containing double bonds generally yields insoluble three-dimensional graft copolymers. Such products are therefore most conveniently made not in advance but during the manufacture of various articles. Thus mixtures of poly(ethylene glycol maleates) with styrene and an initiator are employed as binders in the production of reinforced plastics, protective coatings, and insulating compounds[102]. Compositions based on polyacrylates or branched copolymers of acrylic esters and biscarboxyallyl ethers of ethylene glycols with polyester-acrylates or dimethacrylic esters of di- and poly-hydric alcohols have found practical application as adhesives and special pastes which harden at room or elevated temperatures (60°–80°). Such adhesives form strong joints between metals, and between metals and various non-metallic materials[76,106].

The three-dimensional graft copolymerisation of acetomethacrylic and nitromethacrylic esters of cellulose with acrylic and methacrylic esters is of considerable interest for the preparation of new types of plastics and protective coatings.

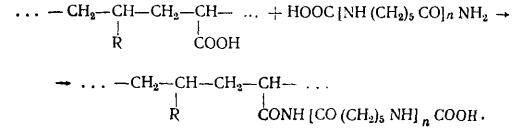
The surface methacrylation of cellulose fibres with subsequent surface grafting of acrylonitrile enables cotton cloth to be given improved crease-resistance and increased wet strength[107].

The development of the principle of three-dimensional graft copolymerisation, first worked out in the USSR in 1946, to remake polymer-monomer bonds in finished articles will in the future undoubtedly lead to new and more systematic methods for making casting resins, binders, protective coatings, gas-filled plastics, and other polymeric materials[104].

5. Synthesis of Graft Copolymers by Polycondensation and Stepwise Polymerisation

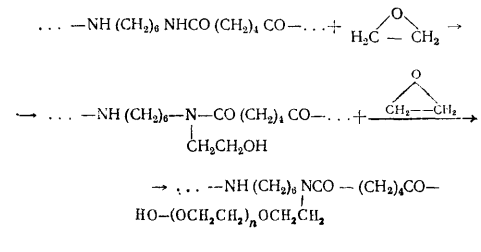
To obtain graft copolymers by polycondensation or stepwise polymerisation, polymers containing NH_2, COOH, OH, $CONH_2$, SH, and CHO groups are used[1,43]. As regards stepwise polymerisation, great interest attaches to polymers containing isocyano groups or epoxide or cyclooxabutane rings in the side chains[1,108].

When polyacrylic acid or copolymers containing carboxyl groups are condensed with polycaprolactam, copolymers of the following type are formed[109]:



Such copolymers possess an extremely wide range of properties, including moisture absorption, ability to take dyes, and increased resistance to light. Development of this process may yield extremely interesting graft copolymers of polyacrylonitrile and polycaprolactam.

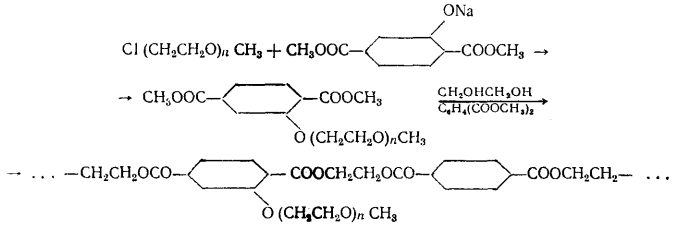
Stepwise graft copolymerisation is beginning to acquire practical significance for modifying the properties of nylon. Thus grafting polyethylene oxide side chains on polycaprolactam, 6,6-nylon, and other types of polyamides has enabled their moisture absorption and ability to take dyes to be improved without lowering the softening point or reducing the strength[110,111]. The nature of this reaction is evident from the scheme



The change in the hydrophilic character of nylon with its content of ethylene oxide units can be seen from the following data[110].

C_2H_4O content in nylon, %.	Moisture permeability, $g\,m^{-2}\,h^{-1}$.
10.6	3.13
32.0	31.0
42.2	32.3
49.5	52.8

A more hydrophilic Terylene has been synthesised by reaction of the methyl ether of polyethylene chlorohydrin with the sodium derivative of dimethyl hydroxyterephthalate and subsequent reaction of the resulting product with ethylene glycol and dimethyl terephthalate:



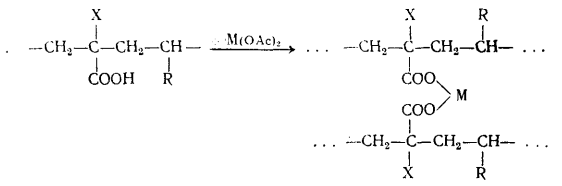
Three-dimensional graft copolymers can also be obtained by polycondensation and stepwise polymerisation methods. Such copolymers have been prepared[112] by the reaction of polymers containing a carboxyl or an amide group with caprolactam, and of polyamides with Resol resins, epoxypolyethers, and polyurethanes.

6. Cross-Linking Reactions

The presence in macromolecules of carboxyl, aldehyde, hydroxyl, sulphoxyl, isocyanato, amide, epoxy, and several other functional groups leads to various types of three-dimensional polymers, with increased heat resistance, strength, a permanent colour, selective ionic adsorption, ionic conduction, etc.

For example, as early as 1947 a process was suggested for converting carboxyl-containing polymers, obtained by copolymerisation of unsaturated acids with various monomers (methacrylates, acrylates, acrylonitrile, etc.), into an infusible and insoluble condition by reaction with bi- and multi-valent metal ions and with diamines[1,113].

Carboxyl-containing polymers, when mixed with oxides of bi- or multi-valent metals or their salts (stearates, oleates), react when pressed at elevated temperatures (120°–140°) to form three-dimensional structures:



The resulting material is infusible, withstands heating to 250°–300°, and is stable to the action of solvents. The physicochemical and mechanical properties of such polymers can be changed within wide limits by varying the chemical nature of the copolymer or the cross-linking metal oxides or salts. The inorganic oxides used to convert carboxyl-containing polymers into three-dimensional products can be replaced by glycols, polyhydric alcohols, diamines, or compounds of high molecular weight containing OH or NH_2 groups (partly hydrolysed polyvinyl acetate, polyvinyl acetal, polyamides[113]. This method has recently attracted the attention of investigators and technologists. For example, copolymers of butadiene and methacrylic acid are finding increasing practical application for the preparation of raw rubbers convertible into high-strength rubber by reaction of the COOH groups with metal oxides[114].

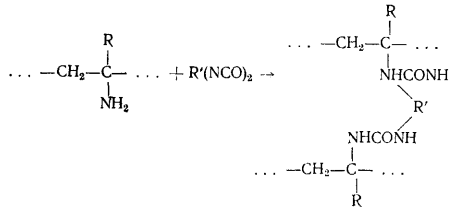
Copolymers of methyl methacrylate with methacrylic acid mixed with partly hydrolysed polyvinyl acetate are recommended as thermosetting coatings and binders which adhere well to metals, wood, and plastics. Compositions consisting of carboxyl-containing copolymers[115] (e.g. copolymers of butyl methacrylate with 5–10% of methacrylic acid) and hydroxymethyl derivatives of urea or melamine[116] are important in varnish technology.

Coatings based on such compositions, when heated at 80°–120°, acquire great hardness, elasticity, and adhesion to metals, glass, wood, etc. During the baking process the COOH groups of the copolymer react with the CH_2OH groups of the melamine or urea derivatives to form an infusible and insoluble polymer, which apparently has a three-dimensional structure.

Work on the preparation and application of carboxyl-containing polymers has led to the production of cation-exchange resins which can adsorb ions of the alkaline-earth metals; insoluble copolymers of polyacrylohydroxamic acid are employed as cation-exchange resins for the selective adsorption of ions of the heavy metals (e.g. Fe^{2+}).[26,117] The reactions of polymers containing chelating groups[26] can be successfully used to convert the soluble and fusible polymers into insoluble, infusible, heat-resistant products.

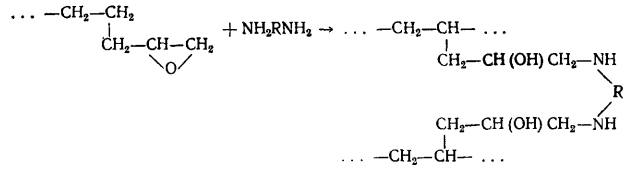
Cross-linking reactions of macromolecules due to polycondensation or migration polymerisation can be effected also with hydroxyl-containing polymers by their reaction with multivalent-metal oxides, dibasic acids, diisocyanates, and di- or poly-epoxy compounds. Such processes are widely used in the technology of protective coatings, adhesives, and plastics.

Instead of the hydroxyl-containing products of the partial hydrolysis of polyvinyl acetate or acetals, copolymers of various monomers (acrylates, methacrylates, vinyl acetate, etc.) with glycol monoesters of acrylic or methacrylic acid have been suggested[118] for the preparation of protective coatings which can be hardened by heat or chemical treatment. Equally great possibilities arise with polymers containing amino groups and in particular with polyvinylamines[119]. An example of three-dimensional copolymerisation of polyamines of high molecular weight is the reaction with alkyl or aryl diisocyanates, which usually occurs at moderate temperatures (20°–80°):

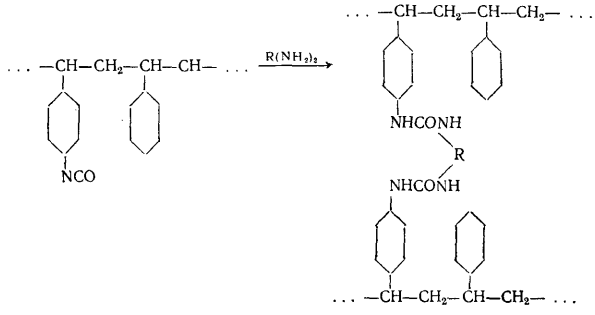


A polymer having oxygen-containing three-membered heterocycles in its side chains forms infusible and insoluble products, with high adhesion to metals and glass, by reaction with organic diamines, dibasic acids, glycols, and poly-

condensates containing amino groups (urea- and melamine--formaldehyde resins[108]):



Interesting cross-linked and branched polymers can be prepared from products of the polymerisation of *m*- and *p*-formyl, amino-,[121] and hydroxy-styrene[122,123], as well as of *m*- and *p*-styrene isocyanates[124]. These monomers, in the presence of peroxide initiators in an inert atmosphere at 110°–120°, are able to form copolymers with styrene and acrylates. The side chains of such copolymers contain some hydroxyphenyl, formylphenyl, or phenyl isocyanate groups which can undergo various reactions leading to the formation of network polymers. Thus copolymers containing 10–15 parts by weight of *p*-formylstyrene or styrene isocyanate and 85–90 of styrene can be instantaneously hardened by the addition of very small amounts of diamines:



Analogous copolymers of *m*- or *p*-hydroxystyrene at elevated temperatures react vigorously with hydroxymethyl derivatives of phenol and urea to form strong, heat-resistant plastics with good electrical insulating properties.

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CATALYTIC SYNTHESIS OF ALKYLPHENOLS

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INTRODUCTION

The chemistry of phenols has developed rapidly during the last two decades. One of the lines of work in this field has been the synthesis of alkyl derivatives, the investigation of their properties, and the search for methods of effective application of the alkylphenols in industry.

Among the most important uses of alkylphenols, their application, due to their easy oxidisability, as antioxidants for aviation fuels[1-5], lubricants[6-9], various fats[10-13], natural rubber, synthetic rubber[13-17], and other organic compounds[18-23], is of interest. Alkylphenols are also used as depressors for lubricants[24-27], as starting materials for the preparation of herbicides and fungicides[28], bactericides[29], insecticides[30] and as disinfectants[31]. This list of examples of the practical application of the alkylphenols shows the wide prospects for their utilisation in the national economy.

In the present article an attempt is made to give a survey of the numerous investigations on the catalytic synthesis of alkylphenols, which possesses a number of advantages over other methods by virtue of the simplicity of the starting materials, the accessibility of catalysts, and the high yields of alkylated products.

Since the most frequently used starting materials are unsaturated hydrocarbons, alcohols and alkyl halides, it is useful to systematise the literature according to the nature of the phenolic substances being alkylated. In the individual sections, the subject is considered in relation to the catalysts, the nature of which to a considerable extent determines the structures and relationships of the alkylated products.

The catalysts are usually various acid agents: sulphuric, phosphoric, boric, hydrohalogenic, and perchloric acids, boron fluoride and its molecular compounds, zinc and aluminium chlorides, natural clays and industrial aluminium silicates, ion-exchange resins, aluminium phenoxide, etc.

I. ALKYLATION OF PHENOLS BY UNSATURATED HYDROCARBONS

1. The Use of Acids as Alkylation Catalysts

One of the first catalysts to find application in the alkylation of phenols by alkenes was sulphuric acid[32-34], which has been used in this reaction not only as such, but also in mixtures with other substances — acetic[32-37] and boric[38] acids, and also with salts, for example ammonium sulphate[39].

The quantity of sulphuric acid used has varied a lot. Thus, Koenings[32-34] used for the alkylation of phenols by isopentene and styrene ten volumes of a solution of 1 part of concentrated sulphuric acid in 9 parts of glacial acetic acid. However, in subsequent work, the quantity of sulphuric acid was considerably diminished, and at the present time it amounts to 3–10% of the weight of phenol[40-44].

Mamedaliev[42] investigated the influence of the quantity of sulphuric acid on the yield in the alkylation of *o*-cresol by alkenes. It was shown that the use of above 5% of the acid led to a reduction of the yield, particularly that of monoalkylated products.

In the literature there is no mention of the preparation of ethylphenols by the alkylation of phenol by ethylene in