97. A. I. Lainer, "Proizvodstvo Glinozema" (The Production of Alumina), Metallurgizdat, Moscow, 1961.
98. T. Parker, "Proceedings of the Third International Congress on the Chemistry of Cement" (Translated into Russian), Gosstroiizdat, 1958, p. 307.
99. A. E. Fersman, "Geokhimiya" (Geochemistry), Vol. IV, Goskhimizdat, 1939.
100. G. Erwin and E. Osborn, "Experimental Studies in the Field of Petrography and Ore-Formation" (Translated into Russian), Inostr. Lit., 1954.
101. I. S. Lileev, "Khimiya i Tekhnologiya Okisi Alyuminiya" (The Chemistry and Technology of Aluminium Oxide), Part 1, Leningrad.Tekhnol. Inst. im. Lensoveta, Leningrad, 1940.
102. K. M. Fedot'ev and S. S. Batsanov, Zap. Vses. Miner. Obshch., 86, No. 4 (1957).
103. L. Pauling, "The Nature of the Chemical Bond" (Translated into Russian), Goskhimizdat, 1947.
104. S. I. Kuznetsov, "Proizvodstvo Glinozema" (The Production of Alumina), Metallurgizdat, Sverdlovsk, 1956.
105. A. M. Samarin and L. A. Shvartsman, Zhur. Fiz. Khim., 20, 189 (1946).
106. P. Pfeiffer, Ber., 40, 4036 (1908).
107. A. Werner, "Neuere Aussthauungen in anorganischen Chemie" (Translated into Russian), ONTI, 1936.
108. V. A. Pazukhin, "Metallurgiya Tsvetnykh Metallov, Sbornik Trudov Moskovskogo Instituta Met. i Zolota im. M. K. Kalinina i VNITO Metallurgov" (The Metallurgy of Non-Ferrous Metals, Collected Papers of the Kalinin Moscow Institute for Metals and Gold and the All-Union Scientific, Engineering, and Technical Society for Metallurgists), Metallurgizdat, 1952, p. 159.
109. V. I. Vernadskii, "Ocherki Geokhimii" (Essays on Geochemistry), Gosizdat, Moscow–Leningrad, 1927.
110. S. A. Mironov, O. M. Astreeva, and L. A. Marinina, Tsement, No. 2, 9 (1957).
111. D. Roy and R. Roy, "Abstracts of Reports to the 4th International Conference on the Chemistry of Cements, Washington, 1960" (Translated into Russian).
112. P. Niggli, "Stereochemistry" (Translated into Russian), Inostr. Lit., Moscow, 1949.
113. N. V. Belov, "Mineralogicheskii Sbornik L'vovskogo Geologicheskogo Obshchestva" (Mineralogical Symposium of the Lvov Geological Society), Lvov, 1962, No. 16, p. 14.
114. V. A. Tikhonov and Z. G. Klimenko, "Issledovaniya Vyazhushchikh Veshchestv i Izdeliya na ikh Osnove" (Studies of Cements and Articles Made from Them), Nos. 2 and 3, Lvov, 1962, p. 10.
115. Z. G. Klimenko and V. A. Tikhonov, "1-ya Nauchnaya Konferentsiya po Khimii i Khimicheskoi Tekhnologii" (First Scientific Conference on Chemistry and Chemical Technology), Izd. L'vov. Univ., Lvov, 1963, p. 41.
116. P. P. Budnikov, "Gips" (Gypsum), Izd. Akad. Nauk SSSR, Leningrad, 1933.
117. A. A. Grinberg, "Vvedenie v Khimiyu Kompleksnykh Soedinenii" (Introduction to the Chemistry of Complex Compounds), Goskhimizdat, 1945; *ibid.*, 1951 Edn.
118. Yu. S. Cherkinskii, "Neorganicheskie Polimernye Stroitel'nye Materialy. Otchet VNIINSM, 1963, Reg. No. 42 050, Goskomiteta po Delam Izobretenii i Otkrytii pri SM SSSR." (Inorganic Polymeric Building Materials. Report of the All-Union Research Institute for New Constructional Materials, 1963, Reg. No. 42 050, USSR Council of Ministers' State Committee for Inventions and Discoveries).

All-Union Research Institute
for New Constructional
Materials

U. D. C. 547.458.81

GRAFT COPOLYMERS OF CELLULOSE AND ITS DERIVATIVES

R. M. Livshits and Z. A. Rogovin

CONTENTS

I. Introduction 459
II. Synthesis of graft copolymers by polycondensation 460
III. Synthesis of graft copolymers by the interaction of two polymers 460
IV. Synthesis of graft copolymers by the polymerisation of rings 461
V. Synthesis of graft copolymers by ionic polymerisation 461
VI. Synthesis of graft copolymers by radical polymerisation 461
1. Synthesis of graft copolymers by chain transfer 461
2. Synthesis of graft copolymers by the copolymerisation of unsaturated esters of cellulose with vinyl monomers 462
3. Mechanicochemical method of synthesising block and graft copolymers 463
4. Synthesis of graft copolymers under the influence of radiation 463
5. Synthesis of graft copolymers by the preliminary introduction of groups which break down to form macroradicals 465
6. Synthesis of graft copolymers on redox systems in which the polymer acts as reducing agent 466

I. INTRODUCTION

The controlled modification of the properties of cellulose and its derivatives by the synthesis of graft copolymers based on them undoubtedly provides one of the most promising and effective methods for improving the quality and extending the range of application of cellulosic materials.

Several cellulosic materials possessing valuable new properties have already been obtained by the synthesis of graft copolymers. For example, cellulosic materials which are completely resistant to the action of microorganisms can be prepared by grafting on various carbon-chain polymers, and improved stability to light and heat is achieved by the synthesis of graft copolymers with polyacrylonitrile. Non-flammable cellulosic materials can be obtained by the grafting on of polymers containing phosphorus or chlorine; the grafting of water-repellent carbon-chain or silicon-containing polymers confers water-repellent properties and improved resistance to acids. The synthesis of graft copolymers of cellulose with a definite class of synthetic polymers makes it possible to

have cellulosic materials possessing specific new properties, in particular ion-exchange and bactericidal properties. The possibility of a controlled variation in the properties of cellulosic materials by the synthesis of graft copolymers is responsible for the interest taken by research workers in this method of modifying the properties of cellulose and its derivatives [1-16].

It is possible to envisage two main ways in which graft copolymers of cellulose and its esters can be synthesised — (1) by the synthesis of graft copolymers which are then processed into materials (fibres, films, etc.), and (2) by direct grafting to ready-made articles.

Each of these methods has its advantages and disadvantages. The advantages of the first method are — (*a*) the production in most cases of materials (fibres, films) having improved physical and mechanical properties, since in this case not only the macromolecules of the original cellulose derivative but also graft chains of synthetic polymers are involved in forming the supermolecular structures, and (*b*) the possibility of using a mixture of the graft copolymer and the homopolymer joined to it. A serious defect of the method is the impossibility of using it to obtain fibres and films of graft copolymers of cellulose, since such products are not usually soluble and do not show viscous flow.

The second method is considerably more promising and versatile. If certain requirements, indicated below, are satisfied, this method may find wide practical application in the immediate future. A method of synthesising graft copolymers which is acceptable in practice for the modification of ready-made goods must evidently satisfy the following requirements: (1) graft copolymerisation should occur without formation of the homopolymer; in isolated cases the homopolymer may be formed directly on the cellulosic material (not in the reaction medium), and then the homopolymer should not be removable when the goods are in service; (2) the synthesis of graft copolymers must be achieved without the use of organic solvents; and (3) the grafting process should not be accompanied by appreciable degradation of cellulose or its derivatives. It is also desirable that the method should permit ready control of the length and number of the graft chains, so that the properties of the graft copolymers can be varied without changing their composition.

In principle the synthesis of graft copolymers, like that of polymers in general, can be effected by the known reactions of polycondensation, polymerisation of rings, and chain polymerisation. A specific method for the synthesis of graft copolymers is the possibility of their production by the interaction of two polymers.

Below are considered the principal methods which have been proposed for the synthesis of graft copolymers of cellulose. These methods can be employed also to obtain graft copolymers based on other macromolecular compounds. The present review is confined to results obtained in the synthesis of graft copolymers of cellulose and its derivatives.

II. SYNTHESIS OF GRAFT COPOLYMERS BY POLYCONDENSATION

Rogovin and his coworkers have synthesised graft copolymers of cellulose and its esters with polyamides by polycondensation of the monomer as a result of interaction with the functional group of the cellulose derivatives.

Polycondensation of methyl 7-aminoheptanoate, in the presence of methyl ethers of carboxy-containing polysaccharides (carboxymethylcellulose, dicarboxycellulose, alginic acid) or their amides with methyl 7-aminoheptanoate, yields graft copolymers of the cellulose derivatives with polyamides, together with a large quantity of the homopolyamide [17,18]. The reaction takes place according to the scheme

$$\text{poly-saccharide}\text{—COOCH}_3 + n\text{H}_2\text{N(CH}_2)_6\text{COOCH}_3 \xrightarrow[\text{Ar}]{100-110^\circ} \text{polysaccharide—CONH(CH}_2)_6\text{COOCH}_3 \rightarrow$$
$$\rightarrow \text{polysaccharide—CO[NH(CH}_2)_6\text{CO]}_x\text{OCH}_3 + \text{H[NH(CH}_2)_6\text{CO]}_y\text{OCH}_3 + (n-2)\,\text{CH}_3\text{OH} \quad (1)$$
(where $x+y=n$).

Graft copolymers of cellulose and polyamides have been synthesised [18] by treating cellulose with the hydrochloride of 7-aminoheptanoyl chloride in an organic base

$$\text{Cell—OH} + n\text{ClOC(CH}_2)_6\text{NH}_2\cdot\text{HCl} \rightarrow$$
$$\rightarrow \text{Cell—OCO(CH}_2)_6\text{NH[CO(CH}_2)_6\text{NH]}_x\text{H} + \text{H[NH(CH}_2)_6\text{CO]}_y\text{OH} + n\text{HCl} \quad (2)$$
(where $x+y=n$).

When sodium cellulose xanthate is employed as starting material, the process can be carried out at the interface [18].

The complicated preparation of the initial cellulosic derivatives, the necessity of employing organic solvents, and the formation of a considerable quantity of homopolymer together with the graft copolymer at the present time prevent the practical application of these methods of synthesising graft copolymers.

III. SYNTHESIS OF GRAFT COPOLYMERS BY THE INTERACTION OF TWO POLYMERS

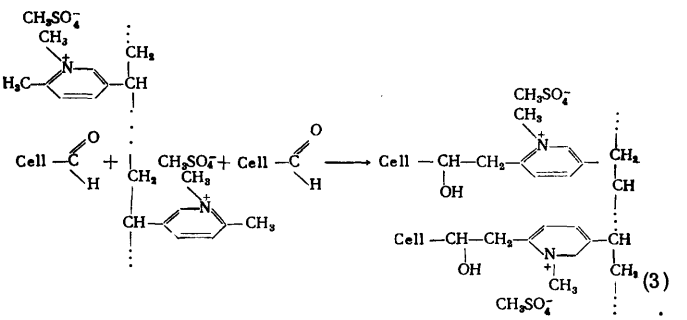
The chief advantage of this method is the possibility of synthesising graft copolymers having main and graft chains of specified length. The method is used to obtain graft copolymers based on synthetic polymers, but finds limited application for the modification of cellulosic derivatives.

Graft copolymers having a main chain of cellulose and protein side-chains have been obtained by condensation. These products are of great interest for polymer chemistry. In order to synthesise cellulose–protein graft copolymers, cellulose azide is condensed with proteins containing free amino-groups:

$$\text{Cell—CON}_3 + \text{H}_2\text{N—Prot} \rightarrow \text{Cell—CONH—Prot.}$$

Graft copolymers differing in composition can be obtained according to the concentrations of the two components in the reaction mixture. If the concentration of protein is considerably increased, insoluble products are formed [19].

Copolymers of three-dimensional structure have been synthesised by the interaction of cellulose acetate toluene-*p*-sulphonate and dialdehydocellulose with poly-2-methyl-5-vinylpyridine or a quaternary salt thereof [20]. When dialdehydocellulose is used, the reaction proceeds according to the scheme



(3)

Reaction between cellulose acetate toluene-*p*-sulphonate and poly-2-methyl-5-vinylpyridine is brought about by a method similar to that used to synthesise graft copolymers of poly(vinyl chloride) and methylvinylpyridine rubber[21]. Practical application of this method for the modification of cellulose is made difficult by the complexity of the synthesis of the initial cellulose derivatives and the insolubility of the final product.

IV. SYNTHESIS OF GRAFT COPOLYMERS BY THE POLYMERISATION OF RINGS

When strained rings (ethylene oxide, ethyleneimine, β-propiolactone) are polymerised in the presence of alkali-cellulose, homopolymerisation and formation of cellulose ethers are probably accompanied by the formation of graft copolymers[22-25]:

$$\text{Cell}-\text{OH}+n\text{CH}_2-\text{CH}_2 \begin{cases} \rightarrow \text{Cell}-\text{O}(\text{CH}_2\text{CH}_2\text{O})_x\text{H} \\ \rightarrow \text{Cell}-\text{OCH}_2\text{CH}_2\text{OH} \end{cases} \quad (4)$$

Formation of a graft copolymer by the interaction of aziridine (ethyleneimine) and alkali-cellulose has been demonstrated experimentally by isolating the grafted polyethyleneimine by hydrolysis of the cellulose followed by esterification of the glucopyranose end-group with benzoyl chloride[26]. The degree of polymerisation of the isolated polymer did not exceed 6.

It is of interest to undertake similar investigations on the products formed by cellulose with oxiran (ethylene oxide). The simplicity of their preparation and their several valuable properties (in particular solubility in water) of such products have provided reasons for their practical utilisation[27].

Graft copolymers of cellulose and polyethyleneimine are also of definite practical interest for obtaining cellulosic materials possessing specific properties (bactericidal power, non-flammability, etc.).[26,28-30] A final conclusion concerning the advisability of the practical application of products formed by the interaction of cellulose with ethyleneimine may be reached after determining the relative quantities of monomer which have reacted with the cellulose and have been used up in homopolymerisation.

American research workers, having studied the conditions for the synthesis of derivatives of cellulose and poly-β-propiolactone, and also the properties of these products, concluded that their practical application would serve no useful purpose[31-34].

The principal defect in the above methods for synthesising graft copolymers is the considerable loss of monomer by homopolymerisation.

Rogovin and Wu Jung-jui proposed a method for obtaining graft copolymers of carboxymethylcellulose and polycaprolactam which excludes formation of the homopolyamide[35]. Synthesis of the graft copolymer is effected by polymerising caprolactam in the presence of chloroformylmethylcellulose and sodium caprolactam. In the first stage of the reaction an imide of caprolactam and carboxymethylcellulose is formed, with polymerisation of the caprolactam, in the presence of which graft copolymers are formed:

$$\text{Cell}-\text{OCH}_2\text{COCl} \xrightarrow{\text{NaN}(\text{CH}_2)_5\text{CO}} \text{Cell}-\text{OCH}_2\text{CON}(\text{CH}_2)_5\text{CO} \xrightarrow[70-80^\circ,\ \text{Ar}]{n\text{HN}(\text{CH}_2)_5\text{CO}} \xrightarrow[70-80^\circ,\ \text{Ar}]{n\text{HN}(\text{CH}_2)_5\text{CO}} \text{Cell}-\text{OCH}_2\text{CO}[\text{HN}(\text{CH}_2)_5\text{CO}]_{n-1}\text{N}(\text{CH}_2)_5\text{CO}. \quad (5)$$

The employment of chloroformylmethylcellulose and sodium caprolactam for the synthesis of graft copolymers by this method precludes its practical application, although the synthesis of graft copolymers of cellulose and polyamides is of considerable interest.

V. SYNTHESIS OF GRAFT COPOLYMERS BY IONIC POLYMERISATION

Only one attempt has been reported[36] to use ionic polymerisation to modify cellulose with carbon-chain polymers. The cellulosic material is wetted out at low temperatures in a solution of boron trifluoride in an organic solvent (boron trifluoride forms a complex with cellulose), and then the material is placed in the monomer. However, the paper gives no evidence to indicate the formation of a graft copolymer.

Ionic polymerisation can probably be used to obtain graft copolymers of cellulose by a scheme suggested for the synthesis of block copolymers of poly(ethylene oxide)[37] (with hydroxyethylcellulose as starting material). The complexity of the process for obtaining the starting materials and the necessity of carrying out the reaction in an organic solvent or in the 100% monomer make the method unpromising for practical application.

VI. SYNTHESIS OF GRAFT COPOLYMERS BY RADICAL POLYMERISATION

The modification of cellulosic materials by the synthesis of graft copolymers by radical polymerisation has been investigated most. The following methods may be used — (1) chain transfer, (2) copolymerisation of unsaturated esters of cellulose with vinyl monomers, (3) a mechanico-chemical method, (4) exposure to high-energy and low-energy particles, (5) preliminary introduction of groups which break down to form macroradicals, and (6) by redox systems in which the polymer acts as reductant.

1. Synthesis of Graft Copolymers by Chain Transfer

The synthesis of graft copolymers by chain transfer presupposes that, as a result of detachment of a labile atom by interaction with a radical, the polymer molecule is converted into a macroradical capable of initiating the graft copolymerisation of a vinyl monomer in contact with it.

In principle chain transfer to a polymer can be effected by the interaction of (*a*) a growing macroradical or (*b*) an initiator radical with the polymer macromolecule. The composition of the product of graft copolymerisation will depend on which of these two mechanisms of chain transfer is operating. It is therefore useful to examine the two possibilities separately, but it must be borne in mind that such separation is arbitrary, and cases may occur in which chain transfer is accomplished by both mechanisms.

(*a*) Synthesis of graft copolymers by chain transfer from a growing macroradical. We include here those methods of graft copolymerisation in which an initiator is added to a solution of the monomer containing the polymer. Under these conditions interaction of the initiator radicals is thermodynamically more favourable with the monomer than with the polymer.

Graft copolymers have been synthesised by the initiated polymerisation of acrylonitrile in the presence of starch[38], methylcellulose, gelatin, cellulose acetates[39], and hydroxyethylcellulose[40].

A systematic investigation of the effect of process conditions on the quantity of homopolymer formed during the graft copolymerisation of 2-methyl-5-vinylpyridine and cellulose has been made by Kryazhev and Rogovin[41]. The efficiency of chain transfer to the polymer is increased if the reaction is carried out with the cellulose in a considerably swollen state. Even in this case, however, the quantity of monomer involved in graft copolymerisation does not exceed 25% of that which has reacted.

To improve the efficiency of chain transfer, groups containing labile atoms are introduced into the cellulose macromolecule, which markedly increases the possibility of this process. Mixed esters of cellulose with acetic and 11-bromoundecanoic acids[1] or cellulose preparations containing thiol groups[42,43] are used for this purpose.

The preliminary introduction of thiol groups for the synthesis of graft copolymers was first suggested by Gluckman[44,45]. J. J. Hermans and his coworkers obtained products containing thiol groups by treating modified cellulose and secondary cellulose acetate with ethylene sulphide. Graft copolymers can be obtained by the polymerisation of vinyl monomers in the presence of such esters[42,43]. The efficiency of chain transfer with preparations containing thiol groups is five times that with materials which have not been treated with ethylene sulphide.

In all cases of the synthesis of graft copolymers by chain transfer from a growing macroradical a considerable quantity of homopolymer is formed, which, together with the need to introduce groups to ensure a high efficiency of chain transfer, prevents the practical application of these methods.

(*b*) Synthesis of graft copolymers by chain transfer from initiator radicals. Chain transfer from initiator radicals is considerably more useful than the above. It probably occurs in the polymerisation of vinyl monomers in the presence of cellulose on the Fe^{2+}–H_2O_2 redox system[46–53]. In this case formation of a cellulose macroradical probably occurs by the following mechanism

$$Fe^{2+}+H_2O_2 \rightarrow Fe^{3+}+OH^-+\dot{O}H,$$

$$\text{Cell}-OH+\dot{O}H \rightarrow \text{Cell}-O^{\bullet}+H_2O. \qquad (6)$$

Graft copolymerisation takes place when a cellulosic material is wetted out in a solution containing Fe^{2+} ions and then immersed in a solution of a monomer containing 0.03% of hydrogen peroxide. Under the conditions chosen, however, the quantity of monomer involved in graft copolymerisation does not exceed 12.5% of the amount which has reacted[47]. The formation of considerable quantities of homopolymer is probably due to diffusion of Fe^{2+} ions into the aqueous solution, where homopolymerisation of the monomer is initiated. The efficiency of chain transfer is considerably increased if the initiator or a component of the redox system is bound to the cellulosic material by a salt link, and its diffusion into the monomer solution is impeded. In this case initiator radicals are formed directly on the cellulosic material, and the probability of their interacting with the cellulose macromolecules is increased. This principle forms the basis of the method for synthesising graft copolymers proposed by Bridgeford, in which a cellulose preparation containing a small quantity of carboxy-groups is wetted with a solution of an iron(II) salt (when Fe^{2+} is sorbed by the carboxy-groups of the cellulose) and, after excess Fe^{2+} cations have been eluted, is immersed in an aqueous solution or an emulsion of the monomer containing hydrogen peroxide insufficient to initiate polymerisation in the absence of Fe^{2+} ions. In this case formation of homopolymer in the reaction medium is not observed[53]. The efficiency of graft copolymerisation is determined by the nature of the cellulosic material. The amount of homopolymer formed within the cellulosic material is considerably lower with hydrocellulose fibres than with cotton fibres, constituting only 4–5% of the monomer which has reacted.

Chain transfer from initiator radicals also occurs when potassium peroxodisulphate is employed as initiator under conditions which make diffusion of the initiator into the monomer solution difficult[6,54,55]. The possibility of formation of a cellulose macroradical by interaction of the cellulose with radicals produced by decomposition of the persulphate is confirmed by investigations with alcohols of low molecular weight. When aqueous solutions containing peroxodisulphate ions are heated, these ions break down according to the equation[56]

$$S_2O_8^{2-} \rightarrow 2SO_4^{-}. \qquad (7)$$

When $K_2S_2O_8$ decomposes in the presence of an alcohol, $SO_4^{-}\cdot$ ion-radicals react with the alcohol molecule according to the equation[56–58]

$$CH_3OH+SO_4^{-}\cdot \rightarrow \dot{C}H_2OH+HSO_4^{-}. \qquad (8)$$

The probability of reaction (8) diminishes in the presence of a free-radical acceptor (monomer). Thus the synthesis of graft copolymers of cellulose is possible on reaction under conditions which impede interaction of $SO_4^{-}\cdot$ with the monomer. In fact, if a cellulosic material is wetted with a solution of potassium peroxodisulphate and then brought into contact with a monomer (by being kept in the monomer vapour or immersed in the pure monomer) under conditions which make diffusion of $S_2O_8^{2-}$ or $SO_4^{-}\cdot$ into the monomer phase difficult, graft copolymers of various compositions can be synthesised[54,55].

When graft copolymers are synthesised by chain transfer from initiator radicals, homopolymer is formed only directly on the cellulosic material. Therefore such methods can be expected to be applied in practice for the modification of ready-made goods in cases in which the presence of homopolymer on the cellulosic material does not impair the properties of the resulting materials in service. Among the defects of these methods must be reckoned the difficulty of controlling the degree of polymerisation and the number of graft chains.

2. Synthesis of Graft Copolymers by the Copolymerisation of Unsaturated Esters of Cellulose with Vinyl Monomers

The synthesis of graft copolymers by this method is based on the fact that, in the presence of initiators of radical polymerisation, the double bond of the polymer is opened to form a macroradical, which initiates polymerisation of the monomer or combines with the growing macroradical of the monomer. Both processes result in the formation of a graft copolymer. The presence of an initiator in the system makes simultaneous homopolymerisation of the monomer possible. Thus a considerable quantity of homopolymer is formed in all cases of graft copolymerisation by this method.

The possibility of synthesising graft copolymers by the copolymerisation of unsaturated esters of cellulose with various vinyl monomers was first pointed out by Ushakov[59]. Berlin and Makarova developed a method for preparing cellulose acetate methacrylates by the acetylation of cellulose monomethacrylate with acetic anhydride or by the esterification of secondary cellulose acetate with methacrylic anhydride. The resulting mixed esters of cellulose are copolymerised in the presence of benzoyl peroxide with methyl methacrylate and ethylene dimethacrylate to form graft copolymers of three-dimensional structure[60]. Graft copolymers containing 6–8% of polystyrene have been synthesised[61] by the copolymerisation with styrene of mixed esters of cellulose containing unsaturated bonds. Grafting is accompanied by the formation of a large quantity of homopolymer. Unsaturated groups are readily introduced into the macromolecule of cellulose nitrates by treating their solutions with

$$\left[\begin{array}{l}-ONO_2\\-ONO_2\\-OH\end{array}\right. + OCNRNHCOOCH{=}CH_2 \rightarrow \left[\begin{array}{l}-ONO_2\\-ONO_2\\-OCONHRNHCOOCH{=}CH_2\end{array}\right. \quad (9)$$

Graft copolymers are formed by the polymerisation of acrylonitrile in solutions of modified cellulose nitrates[62].

The formation of a considerable quantity of homopolymer, the low yields of graft copolymer, and the need for preliminary treatment of the cellulose to introduce unsaturated groups evidently make the synthesis of graft copolymers by this method unpromising.

3. Mechanicochemical Method of Synthesising Block and Graft Copolymers

The degradation of cellulose and its derivatives by mechanical energy is accompanied by the formation, at the ends of the newly produced chains, of free macroradicals[63] capable of initiating the block copolymerisation of monomers in contact with them. Formation of a macroradical by rupture of a bond with a substituent results in the formation of graft copolymers. The mechanicochemical method is the only method for the synthesis of block copolymers of polysaccharides which has yet been put into practice under laboratory conditions.

Ceresa obtained methylcellulose–polyacrylonitrile, ethylcellulose–poly(methyl methacrylate), benzylcellulose–polystyrene, and cellulose acetate–poly(vinyl acetate) block copolymers by vigorous grinding of the polymers, plasticised with the monomer, in the absence of atmospheric oxygen[64]. He prepared block copolymers also by swelling cellulose acetates in acrylonitrile[64]. Block copolymers of water-soluble polysaccharides are obtained by repeatedly freezing and thawing out aqueous emulsions of the polymer and monomer[64-66]. Block copolymers can probably be obtained also by the intense mechanical working of thermoplastic cellulose ethers with other thermoplastic polymers (as a result of the combination of macroradicals of the different polymers). In the synthesis of block copolymers by this method, a complicated mixture of products is obtained, containing both homopolymers and block and graft copolymers.

This last fact, the difficulties associated with controlling the composition and size of the blocks, and the impossibility of employing this procedure for modifying ready-made goods have so far prevented the practical realisation of these methods for modifying cellulose and its derivatives.

4. Synthesis of Graft Copolymers under the Influence of Radiation

(*a*) Synthesis of graft copolymers by exposure to high-energy particles. When cellulose[67,68], its ethers and esters[69], and other polysaccharides[70] are irradiated with high-energy particles, the main process is degradation. Completely water-soluble products are formed by the exposure of cellulose[68] to a dosage of only ~ 100 Mr. Degradation under the influence of radiation takes place by a free-radical mechanism. The formation of macroradicals of cellulose and its derivatives by the action of high-energy particles can be used to initiate graft copolymerisation. Depending on the conditions, there are four ways in which graft copolymers can be synthesised by this method — (i) simultaneous irradiation of polymer and monomer in the absence of air, (ii) simultaneous irradiation of polymer and monomer in air, (iii) irradiation of the polymer in an inert gas atmosphere with subsequent interaction with the monomer, and (iv) irradiation of the monomer in the presence of air with subsequent interaction with the monomer.

(i) When polymer and monomer are exposed together in the absence of air, graft copolymerisation is initiated by macroradicals of the polymer formed under the influence of the high-energy particles. In the synthesis of graft copolymers of cellulose, macroradicals can be formed either at the end of a chain (by cleavage of the bond between monomeric units in the cellulose macromolecule) or in the middle of a chain[67-69,71].

Rupture of the bond between monomeric units should result in the formation of considerable quantities of block copolymers together with the graft copolymers.

(ii) When polymer and monomer are irradiated together in air, graft copolymerisation is initiated both by macroradicals formed by the direct action of radiation and by macroradicals resulting from the breakdown of peroxy- or hydroperoxy-groups formed by the addition of oxygen to macroradicals obtained in the first stage of irradiation.

When graft copolymers are synthesised by simultaneous irradiation of polymer and monomer, considerable quantities of the homopolymer are formed, since production of polymer macroradicals is accompanied by that of radicals of low molecular weight as a result of exposure of the monomer, and these initiate homopolymerisation[72-84]. One procedure for the simultaneous exposure of polymer and monomer is to irradiate the polymer swollen in the monomer. In this case the homopolymer is formed only on the treated polymer, not in the reaction medium, as is observed when the polymer is irradiated in the monomer solution[85]. One of the most acceptable ways of synthesising graft copolymers by the simultaneous irradiation of polymer and monomer is probably to expose the polymer in the presence of the monomer vapour (vapour-phase copolymerisation)[86,87].

The synthesis of graft copolymers by the irradiation of polymer and monomer together probably involves the formation of strongly branched polymers, since the possibility remains that a macroradical capable of initiating polymerisation will be formed on the grafted chain[88]. Swelling of the cellulosic material is of great importance for the reaction to be efficient, since it increases the rate of diffusion of the monomer. Usmanov and his coworkers investigated the graft copolymerisation of cellulose with acrylonitrile. The reaction was carried out by irradiating

cellulose suspended in a solution of acrylonitrile in water, methanol, or benzene or in pure acrylonitrile. A graft copolymer was obtained only when the cellulose was swollen (no grafting occurred when cellulose was exposed in benzene solution)[72]. Other workers have noted the effect of degree of swelling on rate of graft copolymerisation[71,74,75]. Shapiro and Stannett found that the rate of the graft copolymerisation of cellulose with vinyl monomers is increased by increasing the water content of the reaction medium[74]. Leavitt suggested that the effect of water is not limited to increasing the degree of swelling of the cellulosic material, but involves the generation of OH radicals on irradiation, which split off a hydrogen atom from the cellulose macromolecule to form a cellulose macroradical, as is presumably confirmed by the possibility of the "cross-linking" of water-soluble ethers of cellulose and gelatin in the presence of water. No cross-linking effect is observed when the dried polymers are irradiated[89].

(iii) When cellulose is irradiated in an atmosphere of an inert gas, "long-lived" macroradicals are formed (cellulose which has been exposed in the absence of atmospheric oxygen gives paramagnetic resonance signals for several days after irradiation)[88], which initiate graft copolymerisation on subsequent interaction with a monomer[71,76,90-92]. However, degradation of the cellulose is more intense in this case than on exposure in the presence of a monomer which is an acceptor for free radicals[71].

(iv) When a polymer is irradiated in air, peroxy- or hydroperoxy-groups are formed, which on subsequent heating in the presence of a monomer break down and initiate graft copolymerisation[77,90,91]. Thus exposure of the polymer in the presence of air can be regarded as one way of introducing hydroperoxy-groups; the synthesis of graft copolymers by means of these groups is discussed below. Irradiation of the polymer with subsequent interaction with the monomer has certain technical advantages compared with the above procedure, since it permits the processes of irradiation and of subsequent grafting to be separated.

Wide practical application of methods for synthesising graft copolymers based on the use of ionising irradiation with particles of high energy is made difficult by the absence of methods for eliminating secondary processes resulting in the formation of homopolymer, degradation of the initial polymer, and the production of strongly branched graft copolymers, as well as by the difficulties involved in ensuring the safety of the process.

This last obstacle largely disappears when graft copolymerisation is induced by ultraviolet radiation or by radiation of longer wavelength in the presence of sensitisers. Carrying out grafting by this method enables considerable degradation of the polymer to be eliminated, which, together with its safety, constitutes the advantage of this method of synthesising graft copolymers.

(*b*) Synthesis of graft copolymers by means of low-energy particles. A systematic investigation of graft copolymerisation induced by visible light in the presence of anthraquinonoid dyes as sensitisers have been undertaken by Geacintov[93,94].

The mechanism of graft copolymerisation in the presence of sensitisers is that radiation of a wavelength absorbed by the sensitiser excites its molecule to a state in which it reacts with the polymer, converting the latter into a macroradical which initiates graft copolymerisation. Interaction between the excited sensitiser molecule and the monomer results in the formation of a radical of low molecular weight, which initiates homopolymerisation.

When an anthraquinonoid dye is employed as sensitiser, the mechanism of the process can be represented as follows:

$$AQ^a + h\nu \longrightarrow AQ^{*b}, \quad (10)$$

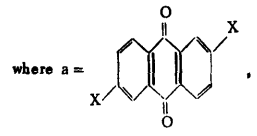
$$AQ^{*b} + \text{Cell}\!>\!\underset{\displaystyle H}{\overset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}} \longrightarrow AQH^c\cdot + \text{Cell}\!>\!\overset{\displaystyle OH}{\overset{|}{C}}\cdot, \quad (11)$$

$$\text{Cell}\!>\!\overset{\displaystyle OH}{\overset{|}{C}}\cdot + n CH_2{=}CHR \longrightarrow \text{Cell}\!>\!\overset{\displaystyle OH}{\overset{|}{C}}\!-\!(CH_2\!-\!CHR)_n, \quad (12)$$

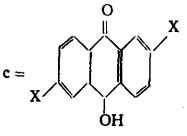
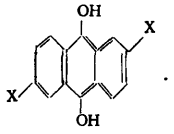
$$AQ^{*b} + CH_2{=}CHR \rightarrow AQH^c\cdot + CH_2{=}\dot{C}R, \quad (13)$$

$$CH_2{=}\dot{C}R + (n-1)\,CH_2{=}CHR \rightarrow (CH_2\!-\!CHR)_n, \quad (14)$$

$$2\,AQH^c\cdot \rightarrow AQH_2^d + AQ^a, \quad (15)$$

where a = ,

the X being groups which confer on the sensitiser solubility in water (SO_3Na) or organic solvents, b is an excited sensitiser molecule,

c = , d = .

Such a mechanism is supported by work on related systems using alcohols of low molecular weight[6].

The rate of graft copolymerisation by this method is greater in the presence of air than in an inert gas, since in the presence of oxygen the above reactions are accompanied by the formation of peroxides, hydroperoxides, or both, which break down to form a cellulose macroradical[93].

Graft copolymerisation by this method is carried out under conditions of considerable swelling of the cellulose (in a solution of the monomer in a mixture of dimethylformamide and water or in an aqueous solution of the monomer) with minimum concentrations of the sensitiser (up to 0.01 M). The quantity of monomer grafted on is proportional to the time of exposure and the concentration of the dye.

Geacintov employed the above method to synthesise graft copolymers of cellulose with polyacrylonitrile, poly(vinyl acetate), polystyrene, and poly(methyl methacrylate), employing as starting material regenerated cellulose film, paper, etc.

A considerable amount of homopolymer — cf. reactions (13) and (14) — is formed in all cases of the synthesis of graft copolymers by this method. A further defect of the method is the difficulty of controlling the length and number of graft chains.

5. Synthesis of Graft Copolymers by the Preliminary Introduction of Groups which Break Down to Form Macroradicals

Under certain conditions hydroperoxy(or peroxy)-, diazo-, azonitrile, and diazoamino-groups break down to form radicals capable of initiating the polymerisation of vinyl monomers in contact with them [95-100]. If these groups are chemically combined with a polymer molecule, their decomposition produces macroradicals which initiate graft copolymerisation.

The synthesis of graft copolymers of cellulose and its derivatives is effected only by first introducing hydroperoxy- and diazo-groups into the cellulose macromolecule.

(*a*) Synthesis of graft copolymers of cellulose and its derivatives by the preliminary introduction of hydroperoxy-groups. Hydroperoxy- or peroxy-groups can be introduced into the macromolecule of cellulose and its ethers by treating the polymer with ammonium peroxodisulphate [101], irradiating it with high- and low-energy particles in the presence of air [77,99,102], and also by passing a stream of air through a solution of the cellulose ether containing azoisobutyronitrile [103] or a stream of oxygen or oxygen enriched with ozone [99,100,104,105]. The oxidation of cellulose and its derivatives for the purpose of introducing peroxy- or hydroperoxy-groups is almost always accompanied by considerable degradation of the polymer [102,103,105].

Ozonisation is a method frequently employed in laboratory investigations for introducing hydroperoxy-groups. The rate of accumulation of peroxy- and/or hydroperoxy--groups during ozonisation is increased by the presence of water, although hydrogen peroxide is not formed under the experimental conditions [106].

When a stream of oxygen containing 6% of ozone is passed through a cellulosic material, it is possible after 6 h to introduce 1 peroxy-group per 20 monomeric units. Peroxy-groups introduced into cellulose do not break down at 20° even on storage of the oxidised cellulose for 3 months. Appreciable diminution in the content of available oxygen is observed only at 75–80°; at 100° complete breakdown of peroxy-groups occurs after 2 h. [99]

A systematic investigation of ozonisation and of the properties of oxidised cellulose acetates has been made by Radchenko and his coworkers [105].

When cellulose preparations containing hydroperoxy--groups are heated in the presence of a monomer at 80–100°, the groups break down to form a macroradical, which initiates graft copolymerisation, and a hydroxy--radical, which causes homopolymerisation of the monomer:

$$\text{Cell}-\text{OOH} \rightarrow \text{Cell}-\text{O}^{\cdot} + {}^{\cdot}\text{OH}. \qquad (16)$$

In the presence of metals of variable valency the hydroxy--radical is reduced to a hydroxide ion:

$$\text{Cell}-\text{OOH} + \text{Fe}^{2+} \rightarrow \text{Cell}-\text{O}^{\cdot} + \text{OH}^{-} + \text{Fe}^{3+}. \qquad (17)$$

When, however, the process takes place in a heterogeneous system (as is almost always the case in the synthesis of graft copolymers of cellulose and its ethers), some of the hydroperoxy-groups break down by reaction (16) even in the presence of such metals. This results in the formation of considerable amounts of homopolymer.

The preliminary introduction of hydroperoxy-groups and/or peroxy-groups into the polymer has been used to synthesise graft copolymers of cellulose with polyacrylonitrile, polystyrene [99], poly(methyl methacrylate), poly(vinyl acetate), and polyvinylpyridine, of cellulose nitrates with poly(butyl methacrylate) [102], of benzyl- and ethyl--cellulose with polystyrene, and of carboxymethylcellulose with polyacrylonitrile [92].

This method has the advantages that it makes possible the synthesis of graft copolymers based on almost any derivative of cellulose, the number of grafted chains can be readily varied (by varying the content of available oxygen in the polymer), and the process is comparatively simple to carry out. Among its disadvantages are the formation of a certain amount of homopolymer together with the graft copolymer, and the degradation of the original polymer on oxidation. These defects can be eliminated by using preparations of cellulose containing a small quantity of diazo--groups.

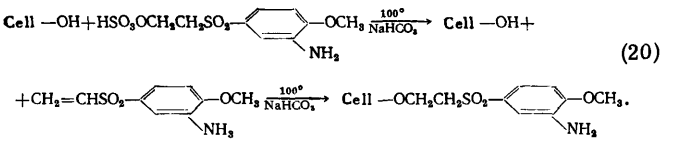
(*b*) Synthesis of graft copolymers by the preliminary introduction of diazo-groups. This method was suggested almost simultaneously and independently by Richards [107] and by Rogovin [108]. According to Richards, aromatic amino-groups can be introduced by treating alkali-cellulose with *p*-amino-ω-chloroacetophenone

$$\text{Cell}-\text{ONa} + \text{ClCH}_2\text{COC}_6\text{H}_4\text{NH}_2 \rightarrow \text{Cell}-\text{OCH}_2\text{COC}_6\text{H}_4\text{NH}_2, \qquad (18)$$

or by heating an aqueous solution of the sodium salt of carboxymethylcellulose with a solution of *p*-aminochloroacetophenone in dimethylformamide:

$$\text{Cell}-\text{OCH}_2\text{COONa} + \text{ClCH}_2\text{COC}_6\text{H}_4\text{NH}_2 \rightarrow \text{Cell}-\text{OCH}_2\text{COOCH}_2\text{COC}_6\text{H}_4\text{NH}_2. \qquad (19)$$

Rogovin et al. proposed a simpler single-stage method for introducing aromatic amino-groups into the cellulose macromolecule. When cellulose is treated in weakly alkaline medium at 100° with a 2-sulphonylethyl sulphate, the sulphate group is split off, and a vinylsulphonyl group is formed which, in the nascent state, adds on to the hydroxy--groups of the cellulose molecule to form a cellulose ether (Michael reaction). To introduce aromatic amino-groups into the cellulose macromolecule, use was made of the water-soluble sulphuric esters of 2-(3-amino-4-methoxyphenylsulphonyl)ethanol and 2-*p*-aminophenylsulphonylethanol. The alkylation of cellulose proceeds according to the scheme



(20)

Diazotisation of the cellulose macromolecule effects the introduction of diazo-groups, which break down on subsequent heating to form a macroradical, which initiates graft copolymerisation, and a radical of low molecular weight, which diffuses into the monomer solution and initiates homopolymerisation [107]:

$$\text{Cell}-\text{OAr}-\text{NH}_2 \xrightarrow[\text{HCl}]{\text{NaNO}_2} \text{Cell}-\text{OArN}_2\text{Cl} \xrightarrow{t} \text{Cell}-\text{OAr}^{\cdot} + \text{N}_2 + \text{Cl}^{\cdot}. \qquad (21)$$

Formation of homopolymer can be avoided by decomposing the diazo-group in the presence of a metal of variable valency. The role of the metal cations is to convert

the Cl· radical into a Cl^- ion, and they are probably involved in chain termination by interaction of the growing macroradical with the oxidised form of the metal cation:

$$Cell\text{–}OArN_2Cl + Fe^{3+} \rightarrow Cell\text{–}OAr^{\cdot} + N_2 + Cl^- + Fe^{3+}, \quad (22)$$

$$\text{–}CH_2\text{–}\dot{C}HR + Fe^{3+} \rightarrow \text{–}CH{=}CHR + Fe^{3+} + H^+. \quad (23)$$

In order to synthesise graft copolymers by this method it is sufficient to obtain a cellulose ether having $\gamma = 3$–10. The quantity of polymer grafted depends on the activity of the radical formed, the degree of alkylation, and the nature of the initial monomer [108]. This method has been used to synthesise graft copolymers of cellulose with polyacrylonitrile, poly(vinylidene chloride), poly(methyl methacrylate), and polyacrylic and polyvinylphosphinic acids. In no case is the homopolymer formed [107–114].

It must be noted that the synthesis of graft copolymers by this method always yields coloured products [108]. The probable explanation is that the main reaction of diazotisation of the amino-groups with subsequent formation of a macroradical is accompanied by azo-coupling, in which some of the unchanged amino-groups take part.

In spite of the considerable advantages of this method (the possibility of synthesising graft copolymers from aqueous solutions or aqueous emulsions of the polymer without homopolymer formation, and the ease of regulating the number of graft chains), the necessity of first introducing aromatic amino-groups, with the associated considerable consumption of a relatively expensive compound and the production of coloured materials, prevents the widespread practical application of this method.

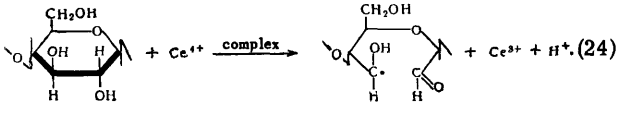
The synthesis of graft copolymers of cellulose and its derivatives on redox systems in which the cellulose or its derivative acts as reducing agent is a considerably more promising method.

6. Synthesis of Graft Copolymers on Redox Systems in which the Polymer Acts as Reducing Agent

The principle underlying the synthesis is that the oxidation with some oxidising agents of polymers containing reducing groups involves a stage in which macroradicals are formed; these are capable of initiating the graft copolymerisation of vinyl monomers in contact with them.

This principle was first exploited for the synthesis of graft copolymers by Mino, who proposed a quadrivalent cerium salt as oxidant [115]. This method has been investigated systematically by Japanese workers [116–127] and in our laboratory [128–136]. Work has also been done on the oxidation of compounds of low molecular weight [137–141], as well as of poly(vinyl alcohol) [142] and cellulose [120], with Ce^{4+} ions, and on the polymerisation of vinyl monomers on redox systems formed by an alcohol of low molecular weight with Ce^{4+}. [140,143,144]

The initiation of the graft copolymerisation of cellulose by this method takes place according to the scheme



This mechanism of initiation is supported by the following experimental results:

(i) In all cases of the oxidation of alcohols of low and high molecular weight, and of polymerisation by means of alcohol–Ce^{4+} redox systems, a complex of reductant and oxidant is formed, the rate of oxidation being determined by the rate of disproportionation of this complex [140].

(ii) The oxidation of compounds containing a glycol grouping by cerium(IV) salts involves the intermediate formation of free radicals, with cleavage of the bond between the carbon atoms having attached hydroxy-groups [138,140,142].

(iii) Polymers synthesised on the redox system formed by an alcohol of low molecular weight with Ce^{4+} contain a terminal hydroxy-group [145].

(iv) When highly substituted methyl ethers of cellulose containing no free glycol groups are employed as initial polymer, graft copolymers cannot be synthesised, whereas with methylcelluloses of low degree of substitution graft copolymerisation is rapid [131].

Termination of the material chain is achieved in this method mainly by interaction of the growing macroradical with an oxidant cation. This hypothesis is supported by the lack of dependence of reaction velocity on initiator concentration and the almost complete absence of homopolymer formation [115,128,146]. By this method it is possible to vary the number and degree of polymerisation of the graft chains without changing the total quantity of graft component [133].

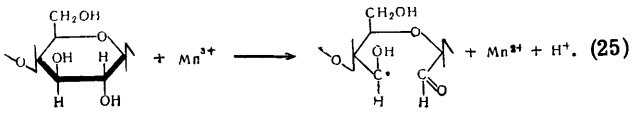
It must be noted that the use of cerium(IV) salts for the synthesis of graft copolymers may cause polymerisation of the monomer even in the absence of a reducing agent. However, polymerisation of the monomer begins after a definite induction period, whereas oxidation of the polymer, and hence initiation of graft copolymerisation, take place without an induction period. Thus by keeping the duration of the synthesis shorter then the induction period it is possible to obtain graft copolymers practically without formation of homopolymer. The synthesis of graft copolymers using cerium(IV) salts is carried out in aqueous solutions or aqueous emulsions of the monomer with minimum amounts of oxidant [128,129]. This method has already been employed to synthesise copolymers of cellulose with polyacrylonitrile [120,121,128,132,147,148], poly(methyl methacrylate) [117,119,133], poly(vinyl acetate) [118], poly(butyl acrylate) [136], polystyrene [122], polyacrylamide [116,148], poly-(2,3-epoxypropyl methacrylate) [123,145], and poly(methyl acrylate) [121,148], and of cellulose nitrates and acetates with poly(methyl acrylate) [130,134].

The appearance of Mino and Kaizerman's paper stimulated attempts to find other redox systems, not involving the use of the scarce and expensive cerium salts.

Japanese workers have proposed the use of potassium permanganate and cobalt(III) salts [127] for the synthesis of graft copolymers of polyvinyl alcohol, starch, and block copolymers containing the terminal hydroxy-groups of a polyethylene glycol, and sodium periodate [149] or cobalt(III) salts [127] for the synthesis of graft copolymers of cellulose. Graft copolymerisation by means of these oxidants is accompanied by the formation of considerable quantities of homopolymer, resulting from oxidation of the monomers with formation of radicals of low molecular weight.

Rogovin and Livshits suggested the use of manganese(III) pyrophosphate [150] for the synthesis of graft copolymers of cellulose, and vanadium(V) compounds [151–154] for modified cellulosic preparations containing small quantities of aromatic amino-groups or aldehyde groups.

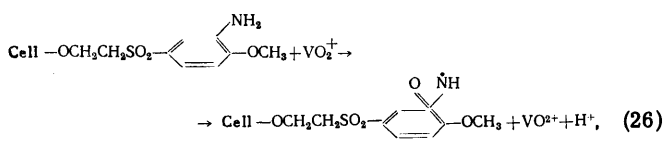
When manganese(III) pyrophosphate is used, initiation of graft copolymerisation is effected, as with cerium(IV) salts, by free-radical oxidation of a glycol group in the cellulose macromolecule [154], and chain termination occurs by interaction between the growing macroradical and an oxidant cation.



(25)

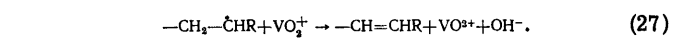
With manganese(III) pyrophosphate as oxidising agent, as with cerium(IV) salts, graft copolymers can be synthesised without homopolymer formation, and also without the use of organic solvents, while the number and length of the graft chains can be readily varied by changing the oxidant concentration. A further advantage of using the pyrophosphate is its ready availability.

In the synthesis of a graft copolymer based on modified cellulose preparations containing aromatic amino-groups — the ether of cellulose and 2-(3-amino-4-methoxyphenylsulphonyl)ethanol — with vanadium(V) compounds as oxidants, initiation of graft copolymerisation is accomplished according to the scheme



(26)

and chain termination is probably represented by the equation



(27)

In the synthesis of graft copolymers of modified cellulose preparations containing aromatic amino-groups or aldehyde groups, with a vanadium(V) compound as oxidant, formation of homopolymer does not occur, however long the contact between oxidising agent and monomer, if the conditions have been chosen correctly, in contrast to what occurs in methods involving the use of Ce^{4+} or Mn^{3+}. This together with the ready availability of the oxidising agent constitutes an important advantage of this method, since it enables the process to be carried out continuously using aqueous solutions or emulsions of the monomer. One defect of the method is the necessity of first introducing a small quantity of amino-groups or aldehyde groups into the cellulosic materials. The method is applicable not only to cellulose but also to all other polymers containing these groups.

From this survey of the various methods for synthesising graft copolymers of cellulose and its derivatives we can conclude that the most promising methods are — (1) syntheses of graft copolymers on redox systems in which the polymer acts as reductant, and (2) in several cases chain transfer from initiator radicals.

In spite of the considerable amount of research on the synthesis of graft copolymers of cellulose and its derivatives, several fundamental questions relating to the characterisation and properties of graft copolymers have not yet been settled. Systematic investigations have still not been made to elucidate the effect of the conditions of graft copolymerisation on the length and number of graft chains, and especially on the quantity of cellulose entering into the graft copolymer. The quantity of homopolymer formed from the synthetic compound of high molecular weight has been determined in most published work, but the fact that not all the cellulose macromolecules become incorporated in the graft copolymer has been ignored. The quantity of cellulose homopolymer undoubtedly has an important influence on the properties of the products resulting from grafting. Nor has the effect of the degree of polymerisation and the number of graft chains on the properties of graft copolymers of cellulose and its derivatives been investigated, except in one paper [133]. Carrying out the reaction in a heterogeneous medium, as is almost always the case in grafting to cellulose and its derivatives, results in the production of graft copolymers containing a small number of graft chains of high molecular weight (with degrees of polymerisation up to 30 000), and sometimes, therefore, graft copolymers do not differ in their fundamental properties from mechanical mixtures of the homopolymers. The development of methods yielding graft copolymers having a small number of relatively short graft chains is an urgent task. An investigation of these questions has recently been undertaken in our laboratory.

---o0o---

Since this paper was submitted to the Editors, several publications have appeared on the synthesis of graft copolymers of cellulose by the radiation method [155-164], by the use of cerium salts [165-171], by chain transfer from initiator radicals [172-174], and by ionic polymerisation [175,176]. Several papers have been published on the properties of graft copolymers of cellulose and its derivatives [168,173,174,176-179].

1. E. H. Imergut and H. Mark, Makromol. Chem. 18–19, 322 (1956).
2. W. I. Burlant and A. S. Hoffman, "Block and Graft Copolymers", Reinhold, New York, 1960.
3. S. H. Pinner and W. Wycherly, Plastics (London), 22, 456 (1957).
4. Z. A. Rogovin, J. Polymer Sci., 48, 443 (1960).
5. E. Schwab, V. Stannett, and J. J. Hermans, Tappi, 44, 251 (1961).
6. J. J. Hermans, Pure Appl. Chem., 5, 147 (1962).
7. Ya. L. Raskin and R. M. Livshits, Lakokrasochnye Materialy i Ikh Primenenie, No. 5, 33 (1960).
8. K. Schurz, Papier, 16, 525 (1962).
9. Kh. U. Usmanov, Khim. Nauka i Prom., 6, 706 (1959).
10. Z. A. Rogovin, Khim. Nauka i Prom., 6, 690 (1959).
11. Z. A. Rogovin, Uspekhi Khim., 28, 853 (1959).
12. A. N. Pravednikov and Yu. S. Lipatov, "Metody Sinteza i Svoistva Blok- i Privitykh Sopolimerov" (Methods of Synthesising and Properties of Block and Graft Copolymers), Izd. Akad. Nauk SSSR, Moscow, 1958.
13. Z. A. Rogovin, Zhur. Vses. Khim. Obshch. Mendeleeva, No. 2, 154 (1962).
14. A. A. Berlin, Uspekhi Khim., 29, 1189 (1960) [Russ. Chem. Rev., 541 (1960)].
15. S. H. Pinner, Brit. Plastics, 35, 518 (1962).
16. G. Odiane and W. H. Chandler, Adv. Nucl. Sci. Technol., 1, 85 (1962).
17. Sun T'un, V. A. Derevitskaya, and Z. A. Rogovin, Vysokomol. Soed., 1, 1625 (1959).
18. Sun T'un, Candidate's Thesis, Moscow Textile Institute, Moscow, 1961.

19. F. Michel and J. Evers, Makromol. Chem., 3, 200 (1949).
20. Yu. G. Kryazhev, A. I. Polyakov, and Z. A. Rogovin, Collected Papers, "Tsellyuloza i Ee Proizvodnye" (Cellulose and Its Derivatives), Izd. Akad. Nauk SSSR, Moscow, 1963, p. 48.
21. A. A. Berlin, A. G. Kronman, D. M. Yanovskii, and V. A. Kargin, Vysokomol. Soed., 2, 1188 (1960).
22. S. N. Ushakova, Zhur. Prikl. Khim., 27, 71 (1954).
23. Z. A. Rogovin and N. N. Shorygina, "Khimiya Tsellyulozy i Eë Sputnikov" (The Chemistry of Cellulose and Its Associated Materials), Goskhimtekhizdat, Moscow, 1953.
24. S. Schroeder and F. Condo, Textile Res. J., 27, 135 (1957).
25. P. P. Shorygin and Yu. A. Rymashevskaya, Iskusstv. Volokno, No. 4, 62 (1932).
26. G. L. Drake, W. A. Reeves, and J. D. Guthrie, Textile Res. J., 23, 639 (1953).
27. Chem. Eng. News, 39, 39 (17th April 1961).
28. L. Soffer and E. Carpenter, Textile Res. J., 24, 847 (1954).
29. H. Fink and K. Stahn, French P. 793 179 (1936).
30. T. S. Gardner, J. Polymer Sci., 1, 289 (1946).
31. R. Reinhardt, J. Reed, and G. Daul, Textile Res. J., 26, 1 (1956).
32. G. Daul, R. Reinhardt, and J. Reed, Textile Res. J., 25, 330 (1955).
33. N. Gocal and J. K. Skelly, J. Soc. Dyers and Colourists, 75, 486 (1959).
34. E. Natt and J. Grant, Textile Res. J., 27, 673 (1957).
35. Z. A. Rogovin and Wu Jung-jui, Vysokomol. Soed., 11, 1630 (1959).
36. G. Rausing and S. Sinner, Tappi, 45, 203A (1962).
37. J. Furukawa and J. Salgusa, Makromol. Chem., 38, 244 (1960).
38. B. P. 715 194 (1954) (see Ref. 6).
39. USSR P. 135 641.
40. E. A. Kuril'chikov, M. P. Pen'kova, and A. V. Vidisheva, Khim. Volokna, No. 4, 15 (1960).
41. Yu. G. Kryazhev and Z. A. Rogovin, Vysokomol. Soed., 3, 1847 (1961).
42. D. K. R. Chaudhuri and J. J. Hermans, J. Polymer Sci., 48, 159 (1960).
43. D. K. R. Chaudhuri and J. J. Hermans, J. Polymer Sci., 51, 373 (1961).
44. M. S. Gluckman, M. J. Kampf, J. L. O'Brien, T. G. Fox, and R. K. Graham, J. Polymer Sci., 37, 411 (1959).
45. T. G. Fox, M. S. Gluckman, F. Gornick, R. K. Graham, and S. Gratch, J. Polymer Sci., 37, 397 (1959).
46. K. P. Shen and F. R. Eirich, J. Polymer Sci., 51, 81 (1961).
47. G. N. Richards, J. Appl. Polymer Sci., 5, 539 (1961).
48. S. Hirosi, Ts. Kadzuhiko, and I. Akira, Ann. Report Eng. Res. Inst. Fac. Eng. Univ. Tokyo, 20, No. 2, 31 (1962).
49. G. Landells and C. S. Whewell, J. Soc. Dyers and Colourists, 67, 338 (1951).
50. G. Landells and C. S. Whewell, J. Soc. Dyers and Colourists, 71, 171 (1955).
51. B. K. Lohani, L. Valentine, and C. S. Whewell, J. Textile Inst., 49, T265 (1958).
52. N. K. Boardman and M. Lipson, J. Soc. Dyers and Colourists, 69, 335 (1953).
53. D. J. Bridgeford, Khim. Tekhnol. Polimerov, No. 9, 61 (1962) [Translated into Russian].
54. C. H. Haydell, J. J. Lanssen, L. F. Seal, H. L. Vix, and E. A. Gastrox, Textile Res. J., 27, 975 (1957).
55. S. M. Sankalia, D. K. R. Chaudhuri, and J. J. Hermans, Canad. J. Chem., 40, 2249 (1962).
56. I. M. Kolthoff and I. K. Miller, J. Amer. Chem. Soc., 74, 4419 (1952).
57. C. Marie and L. J. Bunel, Bull. Soc. chim. France, [3], 29, 930 (1930).
58. I. M. Kolthoff, E. F. Mechan, and E. M. Carr, J. Amer. Chem. Soc., 75, 1439 (1953).
59. S. N. Ushakov, "Trudy I i II Konferentsii po Vysokomolekulyarnykh Soedineniyakh" (Proceedings of the First and Second Conferences on Macromolecular Compounds), Izd. Akad. Nauk SSSR, 1945, p. 35.
60. A. A. Berlin and T. A. Makarova, Zhur. Obshch. Khim., 21, 1267 (1951).
61. G. Faraoni, G. Parsacco, and C. Gogrossi, J. Appl. Polymer Sci., 5, 16 (1961).
62. A. A. Blagonravova, I. A. Pronina, and I. I. Bondarevskaya, Lakokrasochnye Materialy i Ikh Primenenie, No. 2, 4 (1962).
63. H. Staudinger, Ber., 63, 926 (1930).
64. R. J. Ceresa, Polymer, 2, 217 (1961).
65. A. A. Berlin and E. A. Penskaya, Dokl. Akad. Nauk SSSR, 110, 585 (1956).
66. A. A. Berlin and E. A. Penskaya, "Tezisy Dokladov na IX Vsesoyuznoi Konferentsii po Vysokomolekulyarnykh Soedineniyakh" (Abstracts of Papers at the Ninth All-Union Conference on Macromolecular Compounds), 1956.
67. L. F. Saeman, M. A. Millett, and E. J. Lawton, Ind. Eng. Chem., 44, 2848 (1952).
68. A. Shapiro, Khim. Tekhnol. Polimerov, No. 2, 3 (1958) [Translated into Russian].
69. A. Shapiro, J. Chim. phys., 53, 295 (1956).
70. F. P. Price, W. D. Bellamy, and E. J. Lawton, J. Phys. Chem., 58, 821 (1954).
71. V. Kabayashi, J. Polymer Sci., 51, 359 (1961).
72. Kh. U. Usmanov, B. I. Aikhodzhaev, and U. O. Azizov, Vysokomol. Soed., 1, 1570 (1959).
73. Kh. U. Usmanov, B. I. Aikhodzhaev, and U. O. Azizov, J. Polymer Sci., 53, 87 (1961).
74. A. Shapiro and V. Stannett, Internat. J. Appl. Radiation Isotopes, 8, 164 (1960).
75. J. C. Arthur and R. J. Demint, Textile Res. J., 30, 505 (1960).
76. R. A. Mock and V. N. Vauderkooi, J. Polymer Sci., 56, 69 (1962).
77. M. Tatsuo, H. Kiyoshi, and K. Kaoru, Fourth Japan Conference on Radioisotopes (I.R.I.A.), 1961.
78. A. J. Restaino, "Effect of Radiation on Materials", Reinhold, New York, 1958, p. 287.
79. I. A. Arifov, G. A. Klein, A. N. Filippov, Yu. Yu. Amirova, G. A. Aikhodzhaeva, G. S. Okun', and L. Kh. Osipova, Izv. Akad. Nauk Uzbek SSR, Ser. Fiz.-Mat. Nauk, No. 4, 56 (1960).
80. W. H. Rapson, R. Huang, and E. H Imergut, Angew. Chem., 73, 123 (1961).
81. J. Sakurada, T. Okada, S. Hatakeyama, and F. Kimura, Khim. Tekhnol. Polimerov, No. 12, 67 (1963) [Translated into Russian].
82. O. Seidzo and K. Yosio, Japanese P. 13 947.
83. V. Stannett, J. D. Wellons, and H. Yasuda, Khim. Tekhnol. Polimerov, No. 12, 58 (1963) [Translated into Russian].
84. E. S. Putnam, J. Polymer Sci., 55, 377 (1963).
85. J. C. Arthur and R. J. Demint, Textile Res. J., 30, 505 (1960) [this is identical with Ref. 75].
86. A. A. Armstrong and H. A. Rutherford, Textile Res. J., 33, 264 (1963).
87. H. A. Rutherford, A. A. Armstrong, L. H. Kiser, and R. D. Kirby, Textile Res. J., 30, 546 (1960).
88. A. Shapiro, Khim. Tekhnol. Polimerov, No. 3, 3 (1958) [Translated into Russian].
89. F. C. Leavitt, J. Polymer Sci., 51, 349 (1961).
90. R. J. Abraham and D. H. Whiffen, Trans. Faraday Soc., 54, 1291 (1958).
91. K. P. Shen and E. R. Eirich, J. Polymer Sci., 53, 81 (1961).
92. C. Simionescu, D. Feldman, and C. Vasiliu, Simposium Chimia ai Tehnologia Cellulosei, Iassi, 1961.
93. N. Geacintov, V. Stannett, E. W. Abrahamson, and J. J. Hermans, J. Appl. Polymer Sci., 3, 54 (1960).

94. N. Geacintov, V. Stannett, and E. W. Abrahamson, Makromol. Chem., 36, 52 (1959).
95. L. Valentine and B. Chapman, Ricerca sci., Suppl., Simposio intern. Chim. macromol., 25, 276 (1955).
96. W. Hahn and A. Fisher, Makromol. Chem., 21, 77 (1956).
97. T. Otsu, J. Polymer Sci., 26, 236 (1957).
98. B. Vollmert and H. Bolte, Makromol. Chem., 36, 17 (1959).
99. V. A. Kargin, Kh. U. Usmanov, and B. I. Aikhodzhaev, Vysokomol. Soed., 1, 149 (1959).
100. Ya. L. Raskin, R. M. Livshits, and A. A. Berlin, Lakokrasochnye Materialy i Ikh Primenenie, No. 4, 8 (1960).
101. O. Ditz, Chem.-Ztg., 31, 833 (1907).
102. O. P. Koz'mina, V. I. Kurlyankina, E. N. Matveeva, and M. K. Aleksandrovich, Zhur. Obshch. Khim., 28, 3202 (1958).
103. E. Gleason and V. Stannett, J. Polymer Sci., 44, 183 (1960).
104. C. Dorée, J. Chem. Soc., 1347 (1913).
105. G. O. Radchenko, L. S. Sletkina, and G. I. Larina, Collected Papers, "Tsellyuloza i Ee Proizvodnye" (Cellulose and Its Derivatives), Izd. Akad. Nauk SSSR, Moscow, 1963, p. 25.
106. V. A. Kargin, P. V. Kozlov, A. A. Plate, and I. I. Konoreva, Vysokomol. Soed., 1, 114 (1959).
107. G. N. Richards, J. Appl. Polymer Sci., 5, 533 (1961).
108. Z. A. Rogovin, Sun T'un, A. D. Virnik, and N. M. Khvostenko, Vysokomol. Soed., 4, 571 (1962).
109. A. G. Ispravnikova, L. S. Sletkina, and Z. A. Rogovin, Vysokomol. Soed., 4, 12, 1790 (1962).
110. Sun T'un, Li Jui, and Z. A. Rogovin, Vysokomol. Soed., 5, 18 (1963).
111. Wu Mei Yen and Z. A. Rogovin, Vysokomol. Soed., 5, 706 (1963).
112. Yu. S. Kozlova, A. A. Pogadaeva, and Z. A. Rogovin, Collected Papers, "Tsellyuloza i Ee Proizvodnye" (Cellulose and Its Derivatives), Izd. Akad. Nauk SSSR, Moscow, 1963, p. 3.
113. Yu. G. Kryazhev, Z. A. Rogovin, and V. V. Chernaya, *ibid.*, p. 94.
114. A. A. Gulina, R. Marunov, R. G. Zhbankov, Yu. G. Kryazhev, and Z. A. Rogovin, Vysokomol. Soed., 6, 1997 (1964).
115. G. Mino and S. Kaizerman, J. Polymer Sci., 31, 242 (1958).
116. H. Kamogawa and V. Sekiya, Textile Res. J., 31, 585 (1961).
117. L. Fumio and U. Takayama, J. Chem. Soc. Japan, Ind. Chem. Sect., 64, 213 (1961).
118. I. Fumio, J. Chem. Soc. Japan, Ind. Chem. Sect., 64, 925 (1961).
119. I. Fumio, J. Chem. Soc. Japan, Ind. Chem. Sect., 64, 1489 (1961).
120. T. Iwao and M. Matsuo, J. Soc. Textile Cellulose Ind. Japan, 18, 147 (1962).
121. I. Fumio, J. Chem. Soc. Japan, Ind. Chem. Sect., 65, 82 (1962).
122. I. Fumio, J. Chem. Soc. Japan, Ind. Chem. Sect., 65, 88 (1962).
123. K. Hisaiti and I. Esio, Khim. Tekhnol. Polimerov, No. 1, 65 (1963) [Translated into Russian].
124. S. Kimura and M. Imoto, Makromol. Chem., 42, 140 (1960).
125. I. Fumio, J. Chem. Soc. Japan, Ind. Chem. Sect., 64, 1676 (1962).
126. M. Negishi, V. Nakamura, and R. Kitamura, J. Appl. Polymer Sci., 5, 563 (1961).
127. M. Hideiti and U. Sigesi, Khim. Tekhnol. Polimerov, No. 1, 113 (1963) [Translated into Russian].
128. R. M. Livshits and Z. A. Rogovin, Collected Papers, "Tsellyuloza i Ee Proizvodnye" (Cellulose and Its Derivatives), Izd. Akad. Nauk SSSR, Moscow, 1963, p. 12.
129. A. A. Movsum-zade, R. M. Livshits, Z. A. Rogovin, and A. A. Konkin, *ibid.*, p. 186.
130. R. M. Asimova, V. N. Egorova, P. V. Kozlov, R. M. Livshits, and Z. A. Rogovin, *ibid.*, p. 100.
131. R. M. Livshits, V. P. Alachev, M. V. Prokof'eva, and Z. A. Rogovin, Vysokomol. Soed., 6, 655 (1964).
132. R. M. Livshits, E. G. Tokar', I. A. Domiteeva, and Z. A. Rogovin, Izv. Vys. Ucheb. Zaved., Ser. Tekhnol. Tekstil. Prom., No. 4, 95 (1963).
133. A. A. Movsum-zade, R. M. Livshits, E. N. Goryainova, Z. A. Rogovin, and A. A. Konkin, Vysokomol. Soed., 6, 1340 (1964).
134. P. V. Kozlov, N. A. Ivenkova, A. T. Frolova, R. M. Livshits, A. A. Movsum-zade, and A. A. Konkin, Vysokomol. Soed., 6, 1965 (1964).
135. L. S. Gol'braikh, Yu. G. Kryazhev, and R. M. Livshits, "Khimiya i Tekhnologiya Proizvodnykh Tsellyulozy" (Chemistry and Technology of Cellulose Derivatives), Verkhne-Volzhskoe Izd., 1964, p. 241.
136. R. M. Livshits, V. V. Chernaya, and Z. A. Rogovin, Izv. Vys. Ucheb. Zaved., Ser. Tekhnol. Tekstil. Prom., No. 2, 96 (1964).
137. F. R. Duke and R. F. Bremer, J. Amer. Chem. Soc., 73, 5179 (1951).
138. F. R. Duke and A. A. Forist, J. Amer. Chem. Soc., 71, 2790 (1949).
139. G. Hargreaves and L. H. Sutcliffe, Trans. Faraday Soc., 51, 105 (1955).
140. G. Mino, S. Kaizerman, and F. Rasmussen, J. Amer. Chem. Soc., 81, 1494 (1959).
141. M. Ardon, J. Chem. Soc., 1811 (1957).
142. G. Mino, S. Kaizerman, and F. Rasmussen, J. Polymer Sci., 39, 523 (1959).
143. J. Lalitha and M. Santappa, Res. J. Hindi Sci. Acad., 4, 139 (1961).
144. G. M. Gusman, Anales real Soc. españ. Fís. Quím., A 57, 189 (1962).
145. U. Iwakura, T. Kurosaki, and Nakabayashi, Khim. Tekhnol. Polimerov, No. 1, 123 (1964) [Translated into Russian].
146. G. Mino, S. Kaizerman, and F. Rasmussen, J. Polymer Sci., 38, 393 (1959).
147. J. H. Daniel, S. T. Moore, and N. R. Sergo, Tappi, 45, 53 (1962).
148. S. Kaizerman, G. Mino, and L. F. Meinhold, Textile Res. J. 32, 136 (1962).
149. T. Toda, J. Polymer Sci., 58, 414 (1962).
150. R. M. Livshits and Z. A. Rogovin, Khim. Volokna, No. 12, 45 (1963).
151. R. M. Livshits and Z. A. Rogovin, Vysokomol. Soed., 4, 854 (1962).
152. R. M. Livshits, D. A. Predvoditelev, and Z. A. Rogovin, Collected Papers, "Tsellyuloza i Ee Proizvodnye" (Cellulose and Its Derivatives), Izd. Akad. Nauk SSSR, Moscow, 1963, p. 60.
153. R. M. Livshits, R. Marunov, R. G. Zhbankov, and Z. A. Rogovin, *ibid.*, p. 65.
154. R. M. Livshits, M. Levites, and Z. A. Rogovin, Vysokomol. Soed., 6, 1624 (1964).
155. S. Hiroshi, T. Sacko, and H. Iosicadzu, J. Chem. Soc. Japan, Ind. Chem. Sect., 269 (1963).
156. V. Stannett, J. D. Wellons, and H. Uasuda, J. Polymer Sci., Part C, 551 (1964).
157. H. Voshikazu and S. Hiroshi, Technol. Reports Osaka Univ., 12, 451 (1962).
158. K. H. Usmanov and U. Azizov, J. Polymer Sci., Part C, 579 (1964).
159. K. E. Kesting and V. Stannett, Makromol. Chem., 65, 248 (1963).
160. J. Sakurada, T. Okada, and S. Hatakeyama, J. Polymer Sci., Part C, 1233 (1964).
161. I. Suzuki and S. Ogawa, J. Appl. Polymer Sci., 7, 2067 (1963).

162. J. Arthur and D. J. Daigle, Textile Res. J., 34, 653 (1964).
163. H. A. Krässig, Tappi, 46, 654 (1963).
164. W. H. Rapson and E. Kvasnicka, Tappi, 46, 662 (1963).
165. I. Sakyia, K. Tosio, and N. Tacuia, J. Soc. Textile Cellulose Ind. Japan, 19, 547 (1963).
166. N. Bergem, Ø. Ellefsen, K. Kringstad, and P. Kroken, Norsk Skogind., 17, 347 (1963).
167. N. Hirosi, U. Norito, and M. Saisi, J. Soc. Textile Cellulose Ind. Japan, 19, 225 (1963).
168. U. Iwakura, T. Kurosaki, K. Uno, and U. Imai, J. Polymer Sci., Part C, 673 (1964).
169. F. K. Guthrie, Tappi, 46, 656 (1963).
170. S. Kai, I. Kindzo, and M. Kaidzo, J. Soc. Textile Cellulose Ind. Japan, 19, 177 (1963).
171. G. N. Richards and F. F. White, J. Polymer Sci., Part C, 1251 (1964).
172. D. J. Bridgeford, Tappi, 46, 673 (1963).
173. A. V. Kulkarni, A. G. Chitale, B. K. Vaidia, and P. C. Mehta, J. Appl. Polymer Sci., 7, 1891 (1963).
174. G. N. Richards and F. F. White, Textile Res. J., 34, 810 (1964).
175. S. A. Sunner, Swiss P. 180 155.
176. R. F. Schwenker and E. Pacsu, Tappi, 46, 665 (1963).
177. F. L. Saunders and R. S. Sovish, J. Appl. Polymer Sci., 7, 357 (1963).
178. A. J. Kulkarni and P. C. Mehta, J. Polymer Sci., Part A, 509 (1963).
179. K. Kh. Razikov, Kh. U. Usmanov, and U. O. Azizov, Vysokomol. Soed., 6, 1959 (1964).

Moscow Textile Institute

U. D. C. 543.544

REACTION GAS CHROMATOGRAPHY IN ANALYSIS

V. G. Berezkin and O. L. Gorshunov

CONTENTS

1. Introduction 470
2. Pyrolysis 471
3. Cracking 473
4. Hydrogenation and dehydrogenation 473
5. Dehydration and decarboxylation 474
6. Esterification 474
7. Saponification 475
8. Formation of non-volatile compounds 475
9. Oxidation of organic compounds 477
10. Determination of water 478
11. Qualitative chemical reactions 478

1. INTRODUCTION

Gas chromatography is now an effective method for the analysis of organic and inorganic compounds. Fairly frequently, however, particularly in the analysis of complex organic mixtures, the oridinary methods of gas chromatography are unsatisfactory.

The efficiency of gas chromatography as an analytical method can be increased considerably by the simultaneous use of chromatographic separation and chemical reactions. Chemical reactions in gas chromatography can be carried out for different purposes, in particular: (1) the analysis of substances for which direct use of the methods of gas chromatography is impossible (e.g. the analysis of polymers, non-volatile compounds, etc.); (2) the reduction of a difficult analytical problem to a simpler problem which has previously been resolved (e.g. the conversion of alcohols into alkenes or alkanes or esters of nitrous acid, followed by chromatographic analysis of the reaction products); (3) the identification of peaks due to unknown components by the use of group (individual) selective absorbers (e.g. sulphuric acid for the absorption of alkenes from hydrocarbons) or group qualitative reactions; and (4) the simplification of quantitative calculations and increase in the sensitivity and accuracy of analysis by the conversion of all the organic compounds being analysed into one or two simple compounds at the outlet from the separating column (e.g. conversion to carbon dioxide and water or hydrogen with the use of a thermal-conductivity detector).

Thus the use of chemical reactions in gas chromatography is extending appreciably the range of the ordinary chromatographic separation and exhibits a number of specific features. It is therefore appropriate to deal with the use of chemical reactions in gas chromatography as a separate field — reaction gas chromatography. This term was first used by Drawert[1,2], who at first, however, gave a too narrow definition of reaction gas chromatography, restricting himself to the case where the substance being analysed undergoes changes in a reaction vessel placed before the separating column (in order to convert the compounds being analysed into definite compounds whose chromatographic analysis presents no difficulties).

In a later paper, Drawert[3] correctly pointed out that in a wider sense the term "reaction gas chromatography" can be taken to mean the use of chemical reactions together with chromatographic separation. It is necessary only to emphasise that the chemical changes should take place in a single chromatographic scheme. The present review considers only the analytical applications of the combined use of chemical reactions and chromatographic separation. Another important independent field of reaction gas chromatography involves the study of the kinetics and mechanism of chemical reactions under chromatographic conditions. Work on these lines, which is now being successfully developed, was begun by Roginskii and coworkers[4,5].

A promising development is the use of the mathematical methods of the theory of reactions under chromatographic conditions to determine the initial concentration of a substance in a specimen, some components of which undergo chemical changes as a result of chemical reactions in the chromatographic column.

Thus analytical reaction gas chromatography is a form of gas chromatography in which chemical reactions in a single gas-phase chromatographic process are used for analytical purposes. The chemical reactions may take