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Institute of Organic Chemistry,
Academy of Sciences of the
Armenian SSR

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THE SYNTHESIS OF MACROMOLECULAR COMPOUNDS BY RADIATION POLYMERISATION

V. S. Ivanov

CONTENTS

Introduction 43
1. Radiation polymerisation of alkenes 44
2. Alkadienes 45
3. Halogeno-derivatives of alkenes and alkadienes 46
4. Unsaturated carboxylic acids and their derivatives 47
5. Vinyl esters and ethers 48
6. Vinyl derivatives of carbocyclic compounds 48
7. Vinyl derivatives of heterocyclic compounds 49
8. Allyl monomers 49
9. Alkyne monomers 49
10. Carbonyl compounds 50
11. Nitriles of saturated carboxylic acids 50
12. Isocyanates 50
13. Cyclic monomers 51
14. Organoelemental monomers 52
15. Inorganic monomers 53

INTRODUCTION

At the present time, polymerisation is initiated chiefly by chemical methods in which the monomers or their solutions are treated with initiators for polymerisation taking place by a radical mechanism, or catalysts for ionic polymerisation. The use of thermal and photochemical method of initiation is limited — for the first because of the unfavourable conditions for the development of chains at elevated temperatures and the secondary processes which take place, and for the second because of the low efficiency and the complexity of the technological layout, associated chiefly with the influence of the optical properties of the medium on the course of photochemical reactions.

Recently, the attention of many research workers has been drawn to a new method of polymerisation — radiation polymerisation — in which the chain process is initiated by the action of ionising radiation. The first observations of the formation of polymeric (resinous) substances under the influence of the radiation from radium and radon were made at a very early date, but the development of radiation polymerisation as an independent branch of the chemistry of macromolecular compounds is a recent phenomenon. It appears that in a few years this new method will be recognised as an effective industrial method for the synthesis of certain polymeric products.

Problems of radiation polymerisation have been examined in a number of general papers and reviews[1-17], which give data characterising chiefly the fundamental features of the method, in particular the mechanism of radiation-chemical initiation, the influence of various factors (including such specific factors as the dose and dose rate) on the reaction rate, sensitisation in multicomponent systems, polymerisation in inclusion compounds, etc. Special reviews devoted to radiation polymerisation in the solid phase[18-23] and a review of the patent literature[24] have been published. No systematic review of data on the use of radiation-chemical initiation for the polymerisation of various monomers according to classes has

been published, however. The aim of the present work is to fill this gap.

Radiation polymerisation has a number of advantages over other methods for the preparation of polymers.

1. It makes it possible to obtain polymeric products based on monomers whose polymerisation under ordinary conditions either does not take place at all or can be achieved only with considerable difficulty. Such monomers include, in particular, certain fluorine-containing monomers which give valuable heat-resistant and chemically stable polymers of practical importance[14], monomers with a symmetrically-substituted double bond[25-27], and allyl monomers[28].

2. Radiation polymerisation is the simplest and most effective method for polymerising monomers in the solid phase[14], and also in channel[29] and layer[30] inclusion compounds.

3. The radiation method makes it possible to obtain highly pure polymers containing no residual initiators, catalysts, or other auxiliary polymerisation agents, whereas this is unavoidable in polymerisation by the usual methods[2]. These impurities are often responsible for a significant deterioration in the operational properties of the polymers; this is of particular importance for polymers used in radio-electronics and medicine, where these impurities have a harmful influence[31].

4. With radiation initiation, polymerisation can be carried out at reduced temperatures, at which the conditions of chain growth are favourable for the formation of macromolecules with only minimal degrees of branching; this leads to an improvement in the properties of the polymeric materials[2].

5. Radiation polymerisation takes place more smoothly than ordinary polymerisation and enables the reaction rate to be regulated[2]. In "material" initiation the rate decreases as the initiator (or catalyst) is used up, and with an exothermic process increase in temperature leads to an increased rate of dissociation of the initiator, resulting in a change in the rate of the process[9]. With radiation initiation, however, analogous increase in temperature has almost no influence on the concentration of radicals or ions initiating the polymerisation, since this concentration is determined chiefly by the intensity of the irradiation (dose rate). By varying the latter, it is possible to polymerise monomers with appreciable quantities of inhibiting additives, whose action is suppressed[2].

6. The radiation method sometimes makes it possible to produce polymer manufactured parts "in situ" in construction where access is difficult ("imprinting" linings, one-piece parts, etc.)[31].

7. Radiation polymerisation in certain instances makes it possible to obtain finished textile fibres in a single operation by irradiating the crystalline monomer[32].

The use of radiation-chemical initiation naturally involves a number of difficulties, of which the following may be noted: special requirements have to be satisfied in the design of the apparatus, associated with the use of penetrating radiation (safety precautions), and also with the need, in most instances, to create in the reaction zone a field with uniform radiation density; the possibility of secondary processes and side-reactions: cross-linking or degradation of the resulting polymers and radiolysis of the monomers.

These difficulties are not insuperable, however. It appears to be possible to find solutions to the engineering and technological problems and to choose reaction conditions which will satisfy the requirements made of the apparatus and will make it possible to carry out the process with maximal rate of polymerisation and relatively low yields of side products. Sometimes it is possible in principle to make the process continuous, with removal of the resulting polymer from the irradiation zone. In individual instances it is possible to make use of the cross-linking of the resulting polymer and to combine the preparation of the polymer and its vulcanisation in a single process. It should also be noted that the radiolysis products contaminating the finished polymer do not lead to a deterioration in its electrophysical properties, although they may sometimes have a plasticising action.

We shall examine the results of published work on the use of ionising radiation for the synthesis of polymeric products from monomers of different type. The problems of radiation copolymerisation, including graft copolymerisation and telomerisation, are not examined here, since they are of independent interest. The monomers are grouped according to the usual classification of organic compounds with allowance for the nature of the structural elements by which polymerisation is brought about.

1. RADIATION POLYMERISATION OF ALKENES

Ethylene, depending on the polymerisation conditions, forms products with different molecular weights, from liquid oils and waxy substances to hard plastics with a fairly high degree of crystallinity[1]. Macromolecular products are obtained only under pressure (~ 300–400 atm), but this pressure is much lower than the pressures used in the production of ordinary "high pressure" polyethylene (1500–3000 atm at 150–250°). The properties (density, degree of crystallinity, degree of branching) of "radiation" polyethylene are similar to those of polyethylene obtained at low pressures. It has excellent dielectric properties including, in particular, low dielectric loss at high frequencies[1]. To give ordinary "low pressure" polyethylene these properties, special purification of the polymer from traces of catalysts is necessary. The cost of low-pressure polyethylene purified in this way is 1.5–2 times greater than the cost of radiation polyethylene. The radiation process is free from the danger of explosion, is readily controlled, and takes place at low temperatures[33] with values of G up to 1 130 000 (at 200° and 850 atm)[34]. Economic calculations show that when fuel elements are used, the radiation method for preparing polyethylene can compete with ordinary methods[35]. The requirements to be satisfied by the chief technological characteristics of apparatus for the radiation polymerisation of ethylene on the industrial scale have been formulated[36]. The polymerisation of ethylene under the influence of γ-radiation is carried out from the gaseous phase[37-41] and in liquid medium[24,42]. Study of the heterogeneous polymerisation of ethylene[43,44] under a pressure of 300–400 atm at temperatures below the melting point of polyethylene (25°) showed that the process takes place in the kinetic range[45]. The radiation polymerisation of ethylene in solutions has been studied[41,46], but here products with molecular weight not exceeding 40 000 are formed. In aqueous solutions in

the presence of Ag salts the radiation yield G reaches 60 000 molecules per 100 eV.[47] Irradiation of ethylene in the solid state (-196°) in a Van de Graaf electrostatic generator (3 MeV) gives a negligibly low yield of polymer (G = 2.5). The results of experiments on the irradiation of a mixture of ethylene and deuteroethylene lead to theories of an ion-molecular mechanism[48].

The molecular weight of radiation polyethylene may reach 800 000[41] and even 1.5 million.[33] The polymer has a higher density (0.945–0.975 g cm^{-3}) and crystallinity than high-pressure polyethylene but its tensile strength is about the same. The macromolecular chain of radiation polyethylene has a low degree of branching[49].

Of particular interest is the polymerisation of ethylene on Ziegler catalysts — halides of Ti, V, Cr, Co, Fe, Zr, etc. — in which the part of cocatalyst is played by the ionising radiation. A solution of the metal halide (for example, a solution of $TiCl_4$ in heptane) is irradiated at low temperature, after which gaseous ethylene is passed through the irradiated solution; under these conditions the ethylene polymerises. Studies of this type are directed towards an investigation of the role of the components and the mechanism of action of the Ziegler–Natta catalysts[50–53]. The action of γ-radiation on a mixture of ethylene and carbon dioxide at temperatures from -78° to +204° gives liquid and paste-like polymers of carboxylic acids with a linear carbochain structure and molecular weight up to 660 ($G_{-C_2H_4} \simeq 310$ molecules per 100 eV).[53] The radiation-catalytic method has been used to prepare higher carboxylic acids with m.p. 121–123° and M = 3000.[54]

The polymerisation of propene at pressures up to 160 atm, temperatures from -75° to +200° and a dose rate of 400 r s^{-1} gives oily products with low molecular weights in the range 112–200 (G varies in the range 800–4400 molecules per 100 eV).[55] Work has also been carried out on the radiation polymerisation of propene at high pressures of 5000–17 000 atm and 21–83°.[56,57] The maximal degree of polymerisation reached 75 and the values of G reached 108 000. The results obtained indicate that this process takes place by a radical mechanism[56]. Radiation polypropene is soluble in benzene at room temperature.

2-Methylpropene is a convenient material for studying the cationic mechanism of radiation polymerisation[58–69]. 2-Methylpropene does not polymerise at 0° and higher temperatures. Polymerisation from the gaseous phase gives only low-molecular-weight products[70]. At low temperatures (-78°) in the presence of electron-accepting solid additives or solvents, 2-methylpropene gives a polymer with high molecular weight and the same properties as that obtained by ordinary polymerisation. The influence of the purity of the monomer on the yield and molecular weight of radiation polyisobutene [poly-(2-methylpropene) (Ed. of Translation)] has been established[55]. Oxygen and more particularly water have an inhibiting influence. G may be increased to 2 million by polymerisation under sterile conditions in the presence of specially treated zinc oxide[12]. A polymer with M = 3.759 million was obtained at -110° and a dose of 24 Mrad.[67]

The radiation polymerisation of higher alkenes — pentenes[71], hex-1-ene[72], n-heptene (in the presence of $TiCl_4$)[73], oct-1-ene[72–74], oct-2-ene, 2,2,4-trimethylpent-2-ene[74], 2,4,4-trimethylpent-1-ene[75,76], and hexadec-1-ene[77] — leads to the formation, for the most part, of liquid and viscous polymers of low molecular weight.

2. ALKADIENES

Diene hydrocarbons are polymerised with low radiation-chemical yields. The radiation polymerisation of butadiene "in bulk"[78–80] at temperatures from 0° to -196° gives a polymer containing the same relative quantities of *cis*-1,4-, *trans*-1,4-, and 1,2-linkages as the product obtained by the cationic mechanism. This indicated that at low temperatures the radiation polymerisation of butadiene also takes place by a cationic mechanism[79]. In all instances, including those where halogen-containing solvents were used[81] (apart from one[78], where the degree of conversion was very small), low-molecular-weight viscous polymers are formed. Channel polymerisation in urea complexes leads to the 1,4-*trans*-structure with m.p. 135°.[82]

A method has been described in a patent[83] for preparing macromolecular polybutadiene ($[\eta]$ = 1.8) at +40° and a dose of 0.5 Mr in an emulsion; the product has the microstructure: 1,4-*trans* 57%, 1,4-*cis* 20%, and 1,2 23%. A polymer with M = 100 000 was obtained by irradiation in nitromethane at -100°.[84]

The radiation polymerisation of isoprene "in bulk" gives viscous polymers[85–88]. As for butadiene, the possibility of polymerisation at low temperatures by an ionic mechanism has been demonstrated[85,87]. The microstructure (at 20°) includes up to 8% 1,2- and 3,4-linkages and up to 84% 1,4-linkages, including 15% 1,4-*cis*-linkages. The concentration of 1,4-*cis*-linkages increases to 36.4% with increase in temperature to 40°. Irradiation in the presence of $TiCl_4$ increases the rate of the process, which takes place by a cationic mechanism[89]. The sensitisation of the polymerisation of isoprene by carbon tetrachloride has been studied[86,90]. The radiation polymerisation of isoprene in clathrate complexes with 4,4′-dihydroxytriphenylmethane gives a polymer with a ratio of *cis*-1,4- to *trans*-1,4-linkages equal to 1 : 9, with almost complete absence of the 1,2- and 3,4-structures[91]. A polymer with M = 200 000 was obtained by irradiating isoprene in a Van de Graaf generator at -100°.[84]

Piperylene "in bulk" under the influence of radiation also forms a viscous polymer with $G \simeq 20$–30 molecules per 100 eV. The sensitisation of its radiation polymerisation by noble gases (argon and krypton) and also by carbon tetrachloride has been noted. The decreased concentration of double bonds in the polymer is due to possible cyclisation[92].

The microstructure of the polymer, studied by infrared spectroscopy[92,93] and ozonisation[93], consists chiefly of the 1,4- and 1,2-*trans*-linkages (64–67%). The concentration of 1,2-linkages is 17.4% and that of 3,4-linkages (vinyl group) is 3–6.5%. "Channel" polypiperylene, prepared in the complex with urea[94], is more regular and contains no 3,4- or *cis*-linkages.

2,3-Dimethylbuta-1,3-diene and cyclohexa-1,3-diene give high-melting crystalline polymers with the *trans*-structure when their complexes with thiourea are irradiated[29,95,96]. Ammonia has a marked inhibiting action on the polymerisation of cyclopenta-1,3-diene at -78°;[97,98] this may be due to the transfer of a proton from the hydrocarbon ion to NH_3 and also to aminolysis of carbonium ions[99]; methylene dichloride has a marked sensitising influence on the polymerisation[100].

In the irradiation of dienes, polymerisation is accompanied to some extent by radiolysis[101]. It has been suggested that

the radiolysis products may inhibit the polymerisation.

3. HALOGENO-DERIVATIVES OF ALKENES AND ALKADIENES

Of the halogeno-derivatives of the alkenes, the fluoroalkenes have been most extensively studied. Tetrafluoroethylene is one of the monomers most readily polymerised under the influence of radiation. The radiation polymerisation yield is exceptionally high and reaches 800 000 molecules per 100 eV; the organisation of an industrial process for the radiation polymerisation of Fluoroplast can thus be regarded as one of the first tasks in radiation technology. The radiation polymerisation of tetrafluoroethylene takes place from the gaseous phase [102,103], "in bulk", in chloroform [102,104], in aqueous medium [104], at low temperature in the liquid phase [105], and in the solid phase [106-108]. A post-effect is observed [102,104]. The radiation polymerisation of trifluorochloroethylene "in bulk" has been studied over a wide range of dose rate and temperature [104,109,110]. The polymerisation was first studied by Lazar [111]. The polymer forms a solid phase insoluble in the monomer. G reaches values of 10 000 molecules per 100 eV. In halogen-containing solvents ($CHCl_3$, CCl_4, $CFCl_2-CF_2Cl$), polymers with melting point of the crystalline phase in the range 80–200°, have been obtained [112] depending on the dose rate. The polymerisation takes place by a radical mechanism and gives a product of the Fluoroplast-3 type. A post-effect is observed. Vinylidene difluoride also polymerises under the influence of γ-radiation [113-115]. The rate of polymerisation decreases in the order: tetrafluoroethylene–vinylidene difluoride–trifluorochloroethylene [114]: the corresponding values of G (molecules of monomer per 100 eV) are 10^6, 10^5, and 10^4. The marked induction effect is due to contaminants, particularly oxygen [114]. The activation energy (6–8 kcal mole^{-1}) and dose rate exponent (0.6) indicate a radical mechanism. Complete conversion of the monomer requires a dose of 24 Mr. Radiation polymerisation of vinyl fluoride at a dose rate of 34 r s^{-1} leads to the formation of waxy products. A radical mechanism is indicated [116]. $G \simeq 10^3$ molecules per 100 eV. [115] C_3-Fluoroalkenes with different degrees of fluorination and the monomer $CH_2=C<^{CF_3}_{CF_3}$, under the influence of radiation, form polymers with M = 510–800 in the form of viscous liquids and wax-like products with G = 9–350 molecules per 100 eV. [117] Perfluoropropene, [118,119] perfluoro-2-methylpropene, [119] and perfluoropentylpropene [119] form oligomers at extremely high doses (~200–600 Mr). These liquid "radiation" fluoropolymers can be used as heat-resistant lubricants. Irradiation of n-perfluorohept-1-ene under a pressure of 10 000–15 000 atm gives a solid polymer with M = 5000. [120] The highest degree of polymerisation, equal to 76 ± 8, was observed at a pressure of 17 000 atm, 189°, and dose rate 0.0027 Mrad h^{-1}. [56] It should be emphasised that for most of the fluorinated monomers examined, radiation polymerisation provides the only possible method of conversion into polymers.

Vinyl chloride in the gaseous phase has been polymerised by α-particle bombardment [121,122] with the formation of liquid and solid polymers and radiolysis products — hydrogen and methane. The polymer formed under the influence of γ-radiation consists of a white powder which swells readily in the reaction medium, and on further irradiation forms a red solid monolithic material. Oxygen inhibits the polymerisation [123,124] but mercury at 10–95° sensitises it [123]. At a pressure of 1.5 atm and room temperature, $G \simeq 900$ molecules per 100 eV. In the liquid phase ("in bulk") at room temperature a polymer analogous to that obtained by ordinary polymerisation is formed [78,125-128]. The kinetics of polymerisation are typical of those for a hetero-phase process [127,129]. A post-effect is observed. "In bulk" at -20° with a dose of 0.2–0.5 Mrad, a product with glass point 100° is formed (with "material" initiation, the glass point of the polymer is 75–80°) [127]. Radiation poly(vinyl chloride) has not only an increased heat resistance, but also a high purity, which distinguishes it from the polymers obtained by the usual methods [125,130]. It may find application in fields where prolonged stability to high temperatures is required [1]. There are patents on the continuous production of poly(vinyl chloride) with initiation by γ-radiation [125,131]. Vinyl chloride polymerises in the vitreous state in a solid dispersion (mineral oil, etc.) [132]. Polymerisation of the monomer itself in the solid phase is not observed, however [133,134].

Channel polymerisation of vinylidene dichloride (complex with thiourea) [95] gives a brown polymer identical with that obtained in the usual way. No polymerisation of vinylidene dichloride is observed in the solid phase at -196° under the influence of γ-radiation [18]. The formation of polymeric products by the γ-irradiation of *cis*- and *trans*-1,2-dichloroethylenes has been studied [26,135]. Only the *trans*-isomer forms solid polymers. The total radiation yield for *trans*-1,2-dichloroethylene amounts to 204–239 molecules per 100 eV; the concentration of solid polymer in the polymeric products reaches 24.8%. For *cis*-1,2-dichloroethylene, G = 134–138. Trichloroethylene and tetrachloroethylene have values of G (molecules per 100 eV) equal to 31–34 and 9 respectively [26]. Liquid and waxy oligomers are formed from trichloroethylene. Thus increase in the number of chlorine atoms in the ethylene molecule leads to an increase in the stability of the monomer towards radiation.

Vinyl iodide in the pure state or in concentrated solutions does not polymerise under the influence of X-rays. In solutions in CCl_4 (concentration less than 80%), $CHCl_3$ (concentration less than 60%), and CH_2Cl_2 (concentration less than 45%), however, it forms solid white polymers which are stable in air in diffused light for a period of two months; the temperature of decomposition in a vacuum is 97°. [136]

Perfluorobutadiene at a dose of 225.6 Mr forms an oligomer in 55% yield [40,119] and 4-chlorodecafluorohepta-1,6-diene forms a polymer with 100% conversion at 150°, a pressure of 1 atm, and a dose rate of 0.2 Mrad h^{-1} with irradiation for 71 h. The low characteristic viscosity of the polymer (0.09) can be increased to 0.60 by carrying out the polymerisation at a dose rate of 0.003 Mrad h^{-1} for 113 h at 147° and a pressure of 13 600 atm; [56] here a solid product is formed.

When irradiated "in bulk", Chloroprene [2-chlorobuta-1,3-diene (Ed. of Translation)] forms a cross-linked product (μ-polymer). Formation of soluble α-poly(chloroprene) is achieved by the addition of stabilisers which regulate the molecular weight and the process of structure formation [137,138]. The properties of the radiation elastomer are similar to those of GN Neoprene [137]. 2,3-Dichlorobuta-1,3-diene in its complex with urea and thiourea is polymerised completely in an electron

beam (800 keV, dose rate 2.3×10^5 r s^{-1}) in several seconds with the formation of a highly crystalline *trans*--1,4-polymer with regular structure [82,95].

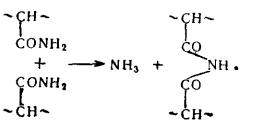
4. UNSATURATED CARBOXYLIC ACIDS AND THEIR DERIVATIVES

Acrylic, methacrylic, and butadiene-1--carboxylic acids polymerise under the influence of γ-radiation in the solid phase [133,134,139]. In the case of acrylic and methacrylic acids at -18° the polymerisation is very rapid (rate of conversion 400% h^{-1}) [133]. Butadiene-1--carboxylic acid polymerises spontaneously and forms a cross-linked product [139]. Its closest homologue — sorbic acid — undergoes 1,4-polymerisation in the solid phase and in solvents by a radical mechanism yielding amorphous soluble polymers with $[\eta]$ up to 1.0. [140] Potassium, sodium, and lithium acrylates and methacrylates, rubidium and calcium acrylates, and barium methacrylate also polymerise in the solid phase [18,141,142]. The difference in the crystalline structure of the monomers determines their relative rates of polymerisation. Marked differences are observed between the ease of polymerisation of the hydrated salts and the anhydrous forms. For example, at a dose of 0.8 Mrad under identical conditions, the conversion of barium methacrylate dihydrate amounts to 55%, while that of the anhydrous monomer is 1%. [142] The sodium, potassium, and barium butadiene-1-carboxylates are fairly stable to γ-radiation [139].

The polymerisation of methyl acrylate "in bulk", initiated by γ-radiation, is very rapid at room temperature and is accompanied by a marked gel-effect [78,143]. Polymerisation in an atmosphere of air (dose 40 Mr) gives a colourless transparent elastomer. Its density is 25% greater than that of the ordinary polymer. The increase in weight of a specimen immersed in water for 24 h is 0.4%. [40] Very slight sensitisation is observed in CCl_4 solution [144]. Polymerisation takes place by a radical mechanism at -78° in polar solvents [145]. Almost no polymerisation takes place in the solid phase (at -78° and -196°) [18]. Ethyl acrylate polymerises readily at low temperatures [12] and in an emulsion at 25°. [146] Methyl methacrylate (MMA) has been studied fairly systematically. For polymerisation "in bulk" the degree of conversion and molecular weight of the polymer are increased at higher temperatures. The gel-effect is very marked and is appreciable even at a degree of conversion equal to 2%. [78] The polymerisation of MMA has been studied in the presence of solid additives [147-149] and in various solvents: methyl acetate [150-152], ethyl acetate [150], carbon tetrachloride [150-153], benzene [78,150-152], its mixture with acetone [154], methanol [78], isopropylamine [155], and dimethylformamide [156]. The rate is decreased in benzene, whereas sensitisation is observed in CCl_4, $CHCl_3$, and dioxan [157]. Special technological apparatus has been developed and tested under different conditions [158], indicating an attempt to introduce a radiation method for the polymerisation of MMA. The monomer itself does not polymerise in the solid phase [18,156] but polymerisation can be achieved by adding alkanes [132,156]. A kinetic study has been made of the radiation polymerisation of cetyl methacrylate in the liquid and solid phases [159-161]. The rate of polymerisation of the crystalline monomer is fairly high initially and decreases with increase in the degree of conversion, indicating degeneration of the autocatalytic nature of the polymerisation in the solid phase [162]. The degree of polymerisation at 60° reaches about 30 000.

Diacrylates and dimethacrylates (octamethylene diacrylate, ethylene dimethacryalte, and octamethylene dimethacrylate) are polymerised under the influence of fast electrons (800 keV) [163]. The polymerisation of octamethylene dimethacrylate has been studied in more detail than that of the others. Its rate at room temperature is 45 times that of the polymerisation of MMA. A crosss-linked polymer in the form of a gel is produced in several seconds. Since the diffusion of the growing chains in such a short time interval is almost negligible, the shape of the resulting polymer reproduces exactly the geometry of the electron beam falling on the monomer [1]. 2,2,3,3,4,4,4-Heptafluorobutyl acrylate at a dose of 220 Mfer is converted completely into a cross-linked rubber-like polymer which softens and undergoes degradation at 150°. [119] Here the polymerisation takes place at both the C=C and the C=O bonds.

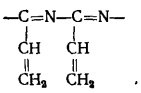
The radiation polymerisation of acrylamide in aqueous solutions has been studied [164,165]. Irradiation of solutions with a monomer concentration greater than 10% gives cross-linked products with liberation of ammonia, apparently as a result of reaction between the chains with the formation of an imide bridge



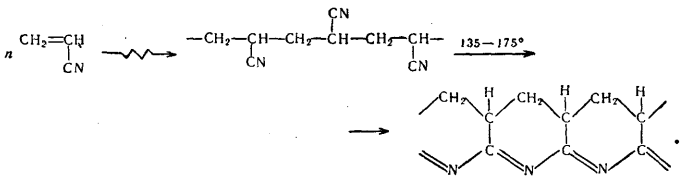
Acrylamide polymerises readily in the solid phase [133,134,166-175]; under pressure the rate increases close to the melting point of the monomer [176,177]. It is suggested that the solid-phase polymerisation takes place by a radical mechanism [178,179]. Methacrylamide also polymerises in the solid phase [168,175,180]. The yield of polymer is much greater for irradiation in air at 32° than for irradiation in nitrogen [181]. Post-polymerisation is observed [180]. *N*-Arylmethacrylamides (the *o*-chloro-, *o*-butyl-, and *o*-ethoxy-derivatives) also polymerise in the solid phase at 20° ± 3°. [180] The solid-phase polymerisation of the *N*-phenyl- and *p*-biphenylylene-derivatives was observed directly in an electron microscope under the initiating influence of the electron beam [182].

Detailed studies have been made of the radiation polymerisation of acrylonitrile "in bulk" [183-186] and in various solvents: dimethylformamide [156,187-191], triethylamine [187,192], isopropylamine, acetone, toluene [87], ethyl chloride, acetonitrile [58,192], butyronitrile [192], methanol [1], and water [193-195]. In polymerisation "in bulk" the polymer separates in the form of aggregates of particles [78]. A clearly defined post-effect is observed. In polymerisation in aqueous solutions under the influence of γ-radiation, a number of sulphates exhibit an inhibiting influence [195]. The addition of substances with electron-acceptor character (ethyl chloride, ethyl acetate, acetonitrile, and butyronitrile) to a solution of acrylonitrile in triethylamine at -78° inhibits polymerisation but the addition of substances with electron-donor character (pyridine) [192] or the addition of semiconducting oxides of the *p*-type [147,148], accelerate the polymerisation. It has been shown that the radiation polymerisation of acrylonitrile may take place both by a radical mechanism and by an ionic mechanism; these mechanisms predominate in the ranges of elevated and reduced temperatures respectively [196]. A patent [197] has proposed that the efficiency of radiation polymerisation be

increased by using a platinum electrode in contact with the polymerisation system to remove the electrons which accumulate during irradiation. In this way the yield of polyacrylonitrile is increased from 6.5% to 19.6% for a dose of 7.3 Mr and a dose rate of 0.09 Mr h^{-1}. In the opinion of Japanese authors[196], the polymerisation of acrylonitrile in liquid ethylene gives a product which contains, in addition to polyacrylonitrile with ordinary structure, chains with the following structure:



A post-effect is observed in the solid-phase polymerisation of acrylonitrile[156,175,196,199-207]. The molecular weight of the polymer reaches 200 000 or more. Polyacrylonitrile obtained at temperatures from -94° to -196° is a syndiotactic polymer; on thermal treatment the $-C\equiv N$ group is readily converted into the $-C=N-$ group[208]:



At a dose of ~200 Mr perfluoroacrylonitrile forms a polymer with low molecular weight in 20% yield[119]. The behaviour of methacrylonitrile is analogous to that of acrylonitrile[209]. In the solid phase at low temperature, the polymer is formed, in the opinion of the authors, by opening of the double carbon–carbon and triple carbon–nitrogen bonds[210]. It is suggested that the product is a syndiotactic polymer whose $-C\equiv N$ groups, unlike the analogous groups of the acrylonitrile polymer, are converted into $-C=N-$ groups without the use of elevated temperatures, apparently due to the influence of the methyl group[208].

5. VINYL ESTERS AND ETHERS

The radiation polymerisation of vinyl acetate is extremely sensitive to traces of contaminants. The polymerisation "in bulk" has been studied under conditions of initiation by γ-radiation[78,150] and in a reactor with filtered-neutron irradiation[211]. Studies have been made of the influence of 70 different additives, of which the most effective were found to be acids and their anhydrides[212]. It was established that the molecular weight of the polymer decreases with increase in temperature[213]. A patent[214] has proposed a method for carrying out the polymerisation in different solvents using various radiation sources with subsequent hydrolysis of the polymer to poly(vinyl alcohol). Study of the polymerisation in the solid phase with irradiation by 1.6 MeV electrons showed that the reaction rate is much less than that in the liquid phase; the rate of polymerisation of the solid monomer in the vitreous state is greater by one order of magnitude than that in the crystalline state[203,204]. It has been shown that the polymerisation takes place only in the beam; there is no post-effect. Vinyl stearate[133] and octadecyl vinyl ether[215] are polymerised under the influence of ^{60}Co γ-radiation above and below the melting point.

The polymerisation of pentafluorophenyl trifluorovinyl ether and phenyl trifluorovinyl ether was achieved only by using radiation initiation (γ-radiation) under a pressure of 12 000–14 000 atm at 100–103°.[56] The radiation polymerisation yield for a dose rate of 0.003 Mrad h^{-1} is 283 molecules per 100 eV for the first and 1190 molecules per 100 eV for the second.

6. VINYL DERIVATIVES OF CARBOCYCLIC COMPOUNDS

The radiation polymerisation of styrene "in bulk" has been studied under conditions of initiation by γ-radiation[216,217]. The polymer formed by complete conversion has a higher heat resistance than the ordinary polymer[2]. Polymerisation "in bulk" by radiation from an atomic reactor (neutron irradiation filtered with cadmium foil) shows a low degree of conversion (0.79% after 60 min)[211]. Macromolecular radiation polystyrene with an average molecular weight of 70 000 was obtained by Abkin and coworkers by the polymerisation of styrene in ethyl chloride solution at -78°.[61,218] The efficiency of the ionic polymerisation of styrene is increased in solvents with high dielectric constant (methylene dichloride)[219,220], in the presence of SiO_2 and other mineral additives at -78°.[221-223] Bromoform is an extremely effective sensitiser[224]; white phosphorus accelerates the polymerisation slightly[225]. The radiation polymerisation of styrene in the presence of the initiator benzoyl peroxide has also been studied[226]; the rate of polymerisation is ten times the value calculated assuming additivity, indicating effective transfer of excitation energy from the styrene to the benzoyl peroxide. Data have been obtained indicating an ionic mechanism for the polymerisation of styrene under ordinary conditions[227] and a radical mechanism in the solid phase (vitreous state in mineral oil)[132]. It has been shown that the polymerisation of styrene and 2,4-dimethylstyrene takes place simultaneously by ionic and radical mechanisms[228,229].

α-Methylstyrene at room temperature forms low-molecular-weight polymers with an exceptionally low rate of polymerisation[230]; the author considers that the polymerisation takes place by a radical mechanism. At -78° the reaction takes place by an ionic mechanism[59]. The anhydrous monomer gives a polymer with degree of polymerisation 15–45 and G = 8000 molecules per 100 eV.[231] Macromolecular poly-(α-methylstyrene) (average molecular weight 50 000) is formed by the action of γ-radiation at 25° and a pressure of 10 000 atm (G = 18 molecules per 100 eV)[129]. In solution, m- and p-methylstyrenes polymerise by a radical mechanism at 25° and by a cationic mechanism at -65°.[232]

p-Acetamidostyrene polymerises instantly under the influence of γ-radiation in the solid phase; this may be of practical importance for the production of textile fibres in a single operation by irradiation of the crystalline monomer[32].

β-Pinene also polymerises under the influence of radiation[231,233,234]. Traces of water decrease the rate of the process considerably. When the β-pinene is dried the values of G increase to 370–1055 molecules per 100 eV.[231] Attention has been drawn to the need to purify the monomer not only from traces of moisture but also from oxygen. Irradiation of the liquid monomer with a dose of ~4 Mrad gives a solid polymer in 45% yield; this is precipitated during the polymerisation and is stable at 230° in a vacuum. The polymerisation apparently involves opening of the double bond and it is suggested that elements of a camphene structure may be formed by rearrangement. Data

obtained by infrared spectroscopy and NMR also indicate the presence of unsaturated groups in the microstructure[233].

7. VINYL DERIVATIVES OF HETEROCYCLIC COMPOUNDS

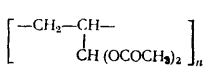
The radiation polymerisation of vinylpyrrolidone has been carried out in aqueous, alcoholic, and chloroform solutions[1]. Poly(vinylpyrrolidone) is important in medicine (blood plasma substitute). It can also be used in the dyestuffs industry, for cosmetics, and for other purposes. Advantages of its production by radiation polymerisation include the slightly narrower molecular-weight distribution and the possibility of organising a continuous process[1,9]. Vinylpyrrolidone also polymerises in the solid phase[18,235]. The radiation polymerisation of *N*-vinylcarbazole[133,154,236,237], *N*-vinylcaprolactam[159,238], *N*-vinylsuccinimide[159,238-241], and *N*-vinylphthalimide[18] has been carried out in the liquid and solid phases. According to data obtained by thermal analysis, the last two monomers in the solid phase polymerise autocatalytically and explosively. For the solid-phase polymerisation and post-polymerisation of *N*-vinylsuccinimide, two alternatives have been observed, differing in their dependence on the temperature, dose rate, and dimensions of the specimen: that involving a uniform thermal polymerisation stage and that involving thermal explosion[160]. The rate of polymerisation of *N*-vinylcarbazole changes little on going from the solid phase to the liquid phase[237]. The polymerisation of *N*-vinylcaprolactam in the solid phase is very slow, whereas the process is rapid in the supercooled state[160]. *N*-Vinylpyridinium salts also polymerise under the influence of ^{60}Co γ-radiation in solution (water of dimethylformamide) and in the solid phase[242,243]. The polymers are amorphous and in aqueous solution have the properties of a polymeric electrolyte. It is suggested that the reaction in the liquid and solid phases takes place by a radical mechanism.

It should be emphasised that the polymerisation of this group of monomers involves the double bond of the vinyl group, the heterocycle being preserved.

8. ALLYL MONOMERS

Allyl derivatives, with the exception of allylsilanes and allyl hydrocarbons do not polymerise under ordinary conditions. Only a few form oligomers. In this case radiation initiation is the only means of obtaining polymers. The action of γ-radiation has made it possible to obtain macromolecular products from allyl alcohol, allyl chloride and bromide, allyl acetate, allyl ethyl ether, allylamine, allyl nitrile, and other monomers[28,244-246]. The polymerisation takes place by opening of the double carbon–carbon bond, but with allyl nitrile, the nitrile functional group also takes part. The radiation-chemical yield is low (up to 50 molecules per 100 eV). Despite the large doses used (up to 10^9 r g^{-1}), almost, no radiolysis of the monomers or cross-linking of the polymeric products takes place, however[28].

Allylidene diacetate polymerises when irradiated "in bulk".[247] The polymer

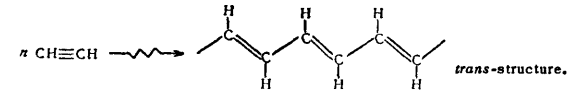


consists of a white powder with molecular weight up to 2750 and m.p. 130–140°; it is soluble in the monomer, acetone, benzene, and dioxan. It can be hydrolysed.

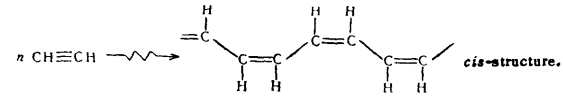
9. ALKYNE MONOMERS

The polymerisation of acetylene and its homologues gives polyvinylenes — structures with a conjugated system of double bonds. These substances have a high heat resistance and electrical conductivity.

The influence of α-radiation on gaseous acetylene was one of the first examples of radiation polymerisation to be observed. The resulting insoluble yellow powder is similar to cuprene, but subsequent electron-microscope study showed that it differs from cuprene and the name "alprene" was proposed for the product[248,249]. Benzene is formed in addition to the solid polymer ($G_{polymer}$ = 60 molecules per 100 eV and $G_{benzene}$ = 5.1 molecules per 100 eV). The polymerisation of acetylene also takes place under the influence of β-radiation from tritium[250]. Sensitisation of the polymerisation in gaseous medium by noble gases has been observed when α-radiation from radon[251,252] and X-rays[253,254] were used. The radiation polymerisation of acetylene in the liquid and solid phases has also been studied[208,210,255,256]. The possibility of formation of a polymer with regular structure has been noted (*trans*--configuration for irradiation of acetylene in the solid state):



trans-Polyacetylene is insoluble and is dark red. To explain the solid-phase polymerisation, the authors suggest an "electronic polymerisation" mechanism[257] (see Section 12 below). In the liquid phase, in the authors' opinion, the polymerisation takes place by a cationic mechanism with the formation of a *cis*-structure[256]:

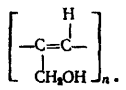


cis-Polyacetylene is soluble and brown.

Phenylacetylene polymerises under the influence of electrons (1.5 MeV) in an atmosphere of air and in a vacuum[258-262]. The value of G is low: 9 molecules per 100 eV. The number-average molecular weight of the polymer is 1100. Atmospheric oxygen accelerates the polymerisation and the yield increases by a factor of 1.5–2. Radiation poly(phenylacetylene)[260] is yellow--orange and soluble in acetone, benzene, esters, and carbon tetrachloride. It is insoluble in petroleum ether and alcohol. The purified product melts at 170–190°. Atmospheric oxygen does not influence the polymerisation of hex-1-yne and cyclohexylacetylene[259], unlike phenylacetylene.

The polymerisation of perfluorobut-2-yne (^{60}Co γ-radiation, dose rate 0.36 Mr h^{-1}, duration of irradiation 67 h) leads to the quantitative formation of a heat-resistant solid white polymer which is not attacked or even wetted by boiling concentrated sulphuric acid, concentrated nitric acid, or 50% sodium hydroxide solution. The polymer is

insoluble in ether, CCl_4, methanol, benzene, and other common solvents[263]. Thermographic analysis shows that its decomposition in nitrogen begins at 425° and that the point of 50% degradation is 75 deg higher than for poly(tetrafluoroethylene). The rate of polymerisation of prop-2-ynyl bromide and prop-2-ynyl alcohol is unaffected by the presence of air[261]. The prop-2-ynyl alcohol polymer is a dark red product with structural unit[208,210]:



Macromolecular products are obtained by the radiation polymerisation of 2,2-dimethyltrimethylene dipropiolate and acetylenedicarboxylic acid[264].

10. CARBONYL COMPOUNDS

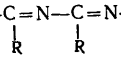
Characteristic features of the radiation polymerisation of aldehydes involving opening of the C=O bonds are the very high rates and the consequent use of extremely small doses. According to a patent taken out by a Japanese firm, anhydrous formaldehyde, emulsified at -16° in n-hexane solution, polymerises under the influence of ^{60}Co γ-radiation at a dose rate of 900 r h^{-1}.[265] According to another patent[266], absolutely anhydrous liquid formaldehyde (m.p. -118°) at -30° and -100° and high dose rates of 10^2–10^8 r h^{-1} forms a polymer which is more stable than that obtained by ordinary polymerisation. Under the influence of γ-rays and X-rays, the polymerisation in the solid phase[267–269] develops satisfactorily at temperatures from -75° to -196° at very small doses (less than 2000 r); this requires extremely low-power sources. Explosive polymerisation was observed at lower temperatures. The values of G are exceptionally high and amount to 5.4×10^6 molecules per 10 eV; $[\eta]$ for the polymer is 3.5–4.0.[269] Comparison of the polymerisation of acetaldehyde in the liquid[270,271] and solid[270,272,273] phases showed that, as for formaldehyde, the process takes place readily in the solid phase and the product is a rubber-like polymer with high molecular weight (up to 1.5 million). In the liquid phase a polymer with M = 140 000–500 000 is formed. No post-effect is observed. In the solid phase the radiation polymerisation takes place by a mechanism involving propagation through the crystal lattice[272]. Radiation polyacetaldehyde is apparently as unstable as the polymer obtained by ordinary polymerisation. Propionaldehyde at -196°, at a dose of 0.57 Mr and a dose rate of 4750 r × × min^{-1} (X-rays) gives an elastomer (degree of conversion 3%) extremely similar to radiation polyacetaldehyde[267,270,271]. The polymerisation of acrolein[274–276] "in bulk" gives an extensively cross-linked (by polymerisation at the C=C and C=O bonds) vitreous polymer insoluble in aqueous sulphuric acid solution. The rate of polymerisation is increased in solutions, particularly aqueous solutions. The product is a polymer which is soluble in sulphuric acid and contains reactive aldehyde groups[274]. The same effect is achieved by polymerisation "in bulk" at -78°.[276] Radiation polymerisation in aqueous medium leads to the formation of a water-insoluble polymer[277]. The γ-irradiation of chloral at a dose rate of 0.068 r h^{-1} at low temperatures gives a colourless solid polymer[278].

The γ-irradiation of dimethylformamide with ^{60}Co at low temperatures gives a polymer in the form of a reddish orange oil, immiscible with water[279]. The polymerisation apparently involves opening of the C=O bonds.

Acetone has been polymerised in the solid phase at -136° and -196° under the influence of γ-radiation[280]. The yield of polymer is 0.1–1% and G amounts to 30–500 molecules per 100 eV. The polymer is a yellow unstable elastomer. Data obtained by infrared spectroscopy indicate the presence of polyether units (–O–C–O–). Chloroacetone and bromoacetone have also been polymerised in the solid phase[280]. For chloroacetone at -78°, G = 8.4 molecules per 100 eV. For bromoacetone under the same conditions, G = 470 molecules per 100 eV. The polymerisation of methyl vinyl ketone "in bulk" at temperatures from 22° to -78° takes place by a radical mechanism with monomolecular termination[281].

11. NITRILES OF SATURATED CARBOXYLIC ACIDS

Polymerisation of nitriles at the triple bond should give hetero-chain polymers with a conjugated system of bonds



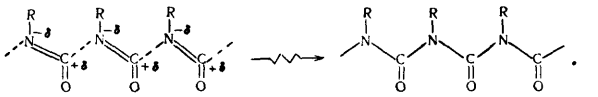
These polymers have a high heat-resistance and semiconductor properties[282]. The radiation polymerisation of acetonitrile[208,261,283] takes place by an anionic mechanism, as established by comparison of radiation polyacetonitrile with polymers obtained using cationic and anionic catalysts and by radical polymerisation. The polymers (dark brown adhesive or elastic products) are formed with low values of G (10–50 molecules per 100 eV). The degree of polymerisation is also low (~10–50). The acetonitrile polymer is soluble in the monomer and in dimethylformamide. The infrared spectrum of radiation polyacetonitrile indicates the presence of C=N–C=N and N=C=N bonds. According to data given in a patent[284], G for the polymerisation of acetonitrile at a dose of ~4.35 Mr and a dose rate of 0.0195 Mr h^{-1} has the values (molecules per 100 eV) 8.4 and 12.6 at 20° and -78° respectively. The radiation polymerisation of propionitrile, isobutyronitrile[208,283], and n-butyronitrile[208] in the solid phase has been observed. Experiments with the addition of ethylene showed that it acts as a sensitiser[208]. The results of the radiation polymerisation of propionitrile, butyronitrile, and benzonitrile in the liquid and solid phases[284] are analogous to the results obtained in the polymerisation of acetonitrile.

12. ISOCYANATES

It is suggested that in the radiation polymerisation of isocyanates[285,286], as in the case of "material" initiation, the polymers are formed by opening of the N=C bonds with units:

Methyl and phenyl isocyanates in the liquid and solid phases give amorphous polymers[286]. Polymethyl isocyanate is a white solid, melting with decomposition at 210°.[285] Butyl isocyanate forms an amorphous polymer in the liquid phase and a crystalline stereoregular polymer at low temperature in the solid phase[286]. The rate of polymerisation is much higher in the solid phase

than in the liquid phase. It is assumed that at low temperature with radiation initiation, stereospecific polymerisation takes place, as happens under analogous conditions for acrylonitrile, methacrylonitrile [208], and acetylene [208,255]. The process takes place by an anionic mechanism in the liquid phase. To explain the process taking place in the solid phase, the authors introduce the so-called "electronic" mechanism of polymerisation, with the assumption that here the process is neither ionic nor radical [286]. These ideas are essentially based on the concept previously put forward in principle by Semenov [287]. The Japanese authors emphasise the importance of the electronic state of the crystal as a whole at low temperature, pointing out the strong electronic interaction between the molecules of the monomer in the crystalline state:



From this examination of the electronic state, in the authors' opinion, it follows that the monomer in the crystal at low temperature is present in an excited state produced by the strong collective interaction. Under the influence of ionising radiation the ordered molecules give corresponding macromolecular compounds.

13. CYCLIC MONOMERS

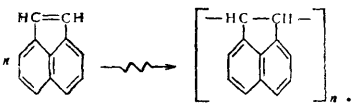
The polymerisation of this group of monomers is brought about either by opening of the ring or at an unsaturated bond in the ring.

Among the carbocyclic compounds, the aromatic hydrocarbons and acenaphthylene are noteworthy. The formation of polymers by the irradiation of benzene has been noted [288-291]. The value of G for the polymerisation is negligibly small (0.76 [288] or 0.91 [290]). The polymeric products are unsaturated yellow oils with M = 250–530. It has been suggested that the polymers are formed by opening of the benzene ring when benzene is irradiated in the liquid and solid phases [210,280]:

$$-CH=CH-CH=CH-CH=CH- \quad [210, 280]$$

As for benzene, irradiation of toluene produces a polymer with low radiation yield (0.92 molecules per 100 eV) [288]. The formation of a p-xylene polymer on irradiation in a reactor (yield 8%) has been noted [291]. Polynuclear aromatic hydrocarbons (biphenyl, terphenyl, etc.) are extremely stable to radiation and on prolonged irradiation form only traces of polymers [292]. Their stability to radiation increases and their tendency to polymerise decreases with increase in the number of aromatic rings in the molecule.

The polymerisation of acenaphthylene takes place under the influence of X-rays in the solid phase in an atmosphere of air or nitrogen and in a vacuum [293]:

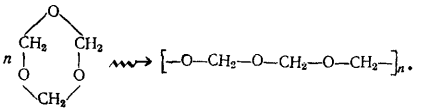


For irradiation in the liquid phase at 125° with a dose of 1.6 Mr the yield is 51.7%. The polymer is a white or yellow solid amorphous product with molecular weight 606 000. Thermal analysis shows no change in the polymer on heating in an atmosphere of air or nitrogen to 350°.

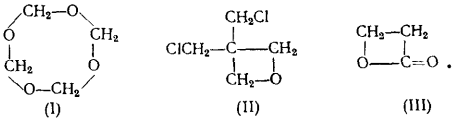
Study of the radiation polymerisation of heterocyclic compounds, particularly in the solid phase, has led to important results.

Sylvan (2-methylfuran) is relatively stable to radiation because of its conjugated system of double bonds: the pure monomer is not polymerised even at doses of 25 Mr. [294] The addition of 30–40 rel.% CCl_4 or $CHCl_3$ at doses above 5 Mr leads to the formation of resinous products (yield 70–80 wt.%) which are soluble in acetone and give lacquer coatings [294]. The formation of a polymer from furfuryl alcohol under the influence of ^{60}Co γ-rays has been reported [295].

Trioxan (m.p. 62°) polymerises readily in the solid state under the influence of γ-radiation or electrons with the formation of poly(oxymethylene) [296-302]:



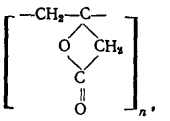
At a dose of 0.44 Mr for polymerisation in the liquid phase at 80° the yield of polymer is ~ 1%, whereas in the solid phase it increases to 16% at 50° and to 22% at 55°. [19] The degree of conversion of the monomer increases when it is subjected to high pressure before irradiation [302]. The polymerisation takes place more readily in large single crystals than in fine crystals [296] and the polymers have a higher melting point (198° and 186° respectively) [303]. The post-polymerisation has been noted and studied [302,304-306]. Radiation poly(oxymethylene) prepared from trioxan has a higher melting point and better heat resistance than the polymer from formaldehyde [297]. Microscope studies show that this product, like the radiation polymers from 3,3-bischloromethyloxacyclobutane, β-propiolactone, and diketen described below, can be obtained in the form of fibres. The sulphur-containing analogue of trioxan — trithian — forms polythioformaldehyde under the influence of γ-radiation at room temperature at doses up to 10 Mrad with subsequent heating at 180° (35 deg below the melting point of trithian) [307-309]. Tetraoxan (tetraoxymethylene) (I) (m.p. 120°) in the form of single crystals was exposed to ^{60}Co γ-radiation at a dose of 0.45 Mr at 80° and gave poly(oxymethylene) in 94% yield [310,311].



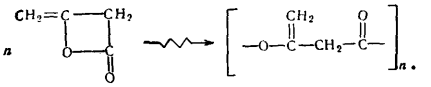
(I) (II) (III)

3,3-Bischloromethyloxacyclobutane (3,3-bischloromethyloxetan) (II) — the monomer of "Penton" — forms a polymer with linear structure [296,297,312]. The yield is greater from a large single crystal than from fine crystals [296,297]. Post-polymerisation has been noted [304,312]. The monomer polymerises only in the solid state (from 16° to -78°). The melting point of the polymer is 171–176°, that is 8–10 deg higher than for polymerisation with BF_3. [313] The solid-phase polymerisation of 3,3-bisbromomethyloxacyclobutane and 3,3-bisiodomethyloxacyclobutane has also been studied. The chlorine-containing monomer is the most reactive and the reactivity of the iodine derivative is very low (Cl > Br ≫ I). [314]

Of the lactones, β-propiolactone (III) polymerises in the solid phase with opening of the ring under the influence of γ-rays and electrons. The yield at -78°, a dose of 143 000 r, and a dose rate of 9000 r h^{-1} is 13.2% from a large single crystal and 10.9% from fine crystals[296,297]. Data characterising the kinetics of polymerisation indicate an ionic mechanism[315]. The polymer obtained from single crystals shows a high orientation of the crystalline regions[303,310]; its crystallinity and melting point are higher than those of the polymer obtained by ordinary polymerisation with ionic catalysts. With chemical initiation, diketen is capable of polymerising either at the $CH_2=C<$ bond in the case of radical initiation with the formation of a polymer of the vinyl type



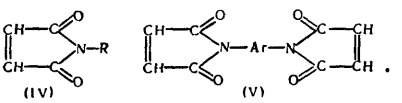
or with opening of the ring under the influence of ionic catalysts with the formation of polymeric products of the ester type. In radiation polymerisation in the solid state, a polymer of the polyester type is formed[296,297]:



The radiation polymer has a higher melting point and better crystallinity than the polymers obtained using ionic catalysts[297].

Maleic anhydride polymerises under the influence of ^{60}Co γ-radiation "in bulk" and in solution in benzene and acetic anhydride. In the latter at a dose of 40 Mr and a dose rate of 0.195 Mr h^{-1} the degree of conversion reaches 90%.[27] The polymerisation apparently involves opening of the double carbon–carbon bond in the ring.

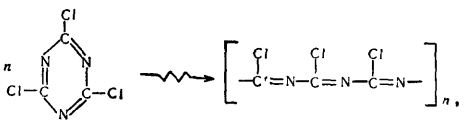
The imides of maleic acid (maleimides) polymerise readily in the solid phase. Studies have been made of the polymerisation, under the influence of ^{60}Co γ-radiation, of various *N*-substituted monomaleimides (IV) and dimaleimides (V):



(IV) (V)

N-phenylmaleimide[316–320], *N*-*p*-tolylmaleimide, *N*-2,4-dimethylphenylmaleimide, *N*-benzylmaleimide[320], *N*-carbamylmaleimide[320,321], *NN'*-*p*-phenylenedimaleimide, and *NN'*-4,4'-biphenylylenedimaleimide[322,323]. The degree of conversion is high close to the melting point of the monomers, for example up to 95% at a dose of up to 3 Mrad for *N*-*p*-tolylmaleimide[320]. The solid-phase polymerisation at 20° is sensitised by solid trichloroacetic acid[318–320] and liquid trifluoroacetic acid[320]. The monomaleimides form soluble polymers[316–321] with softening temperatures from 168° for *N*-benzylmaleimide to 330° for *N*-2,4-dimethylphenylmaleimide[320]. Polymerisation takes place at the C=C bonds with preservation of the imide rings in the chain[318–320]. The dimaleimides form heat-resistant insoluble polymers[322,323].

The triazine derivative cyanuric chloride (the chloride of cyanuric acid), a crystalline substance with m.p. 154°,



is polymerised in the solid phase under the influence of γ-radiation[324]. The yield of polymer is 70% at 16°, a dose rate of 0.03 Mr h^{-1}, and a dose of 14 Mr. Opening of the triazine ring was confirmed by infrared spectroscopy. The polymer is soluble in dimethylformamide and does not melt below 260°.

Of the heterocyclic spiro-compounds, dioxaspiro-[3,3]heptane has been studied. It polymerises in the solid phase with the formation of an amorphous, insoluble, and infusible polymer, but the rate of polymerisation is lower than in the case of trioxan and 3,3-bischloromethyloxetane. Air sensitises the polymerisation under the beam and the post-effect[325].

14. ORGANOELEMENTAL MONOMERS

These monomers can in turn be divided into cyclic, vinyl, and allyl monomers. The formation of the macromolecular chains is here analogous to that for the corresponding groups of monomers previously examined.

Hexamethylcyclotrisiloxane polymerises in the solid phase under the influence of fast electrons (800 keV)[326] or ^{60}Co γ-radiation[327] by different mechanisms corresponding to its two crystalline modifications[328]. The polymerisation product at doses below 0.5 Mr, a dose rate of 0.05–0.25 Mr h^{-1}, and a temperature of 40° is a soluble polymer, whose infrared spectrum is analogous to that of linear polysiloxane[327]. It is suggested that the polymerisation takes place with opening of the ring according to an ionic mechanism, since this monomer is not polymerised with radical initiators[327]. The post-polymerisation has been studied[306]. Octamethylcyclotetrasiloxane polymerises in a very narrow temperature range in the solid phase close to the melting point of the monomer[329,330]. Heptamethylvinylcyclotetrasiloxane is polymerised in the liquid and solid phases. The polymerisation in the latter takes place at the vinyl groups to give fibrous polymers soluble in benzene[331]. The radiation polymerisation of allyldiethylsilane, allylethylphenylsilane, allyldiphenylsilane, diallylethylsilane, and triallylsilane has been studied[332,333]. The ease of polymerisation increases in the order given, due to the increase in the number of allyl groups and in the monoallylsilanes the activity of the monomers increases with the introduction of phenyl groups into the molecules. The polymerisation takes place at the double bond of the allyl group by a radical mechanism. Di- and tri-allylsilanes form cross-linked products by polymerisation "in bulk"; polymerisation of diallylsilanes in 20% benzene solution gives soluble polymers[334]. The latter are also obtained from the divinyl-derivatives[335,336] and trivinyl-derivatives[336,337].

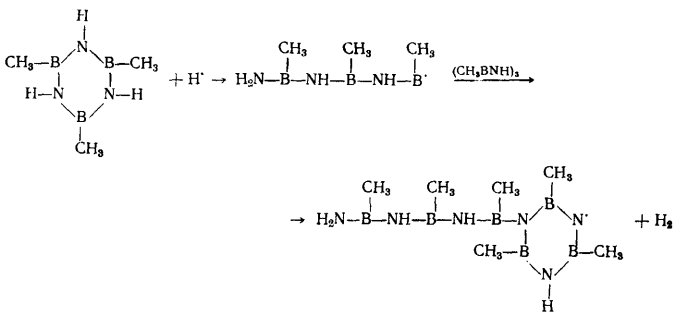
The radiation polymerisation of diethylvinylphosphine oxide and diphenylvinylphosphine oxide gives polymers with molecular weight 30 000–60 000 in

80–90% yield[338–340]. The molecular weight of the polymers obtained from these monomers by usual polymerisation methods does not exceed 3000–4000.

The study of the solid-phase polymerisation of the two polymorphic modifications of tributylvinylphosphonium bromide is of interest[341]. Under the influence of X-rays at temperatures from 30° to -80° and a dose rate of 0.28 Mrad h^{-1}, the radiation yield for 50% conversion varied in the range (molecules of monomer per 100 eV) 1147–9872, depending on temperature. An unusual effect was shown by atmospheric oxygen, which inhibits the polymerisation at 30° and -80° but sensitises the polymerisation at 0°. The polymer is amorphous, soluble in water, and hygroscopic. Its weight-average molecular weight is 50 000–96 000, glass point 5–16°, and heat resistance 340–396° (in air) or 396–411° (in nitrogen). Tributylvinylphosphonium iodide also polymerises in the solid phase under the influence of X-rays[342].

The radiation polymerisation of vinylsulphonamide has been studied in the liquid and solid phases[343,344]. The process is extremely rapid: at a dose rate of 0.25 Mr h^{-1} and 22° the rate of conversion of the monomer amounts to 75% h^{-1}, whereas for other monomers the rate is 1–17% h^{-1}.

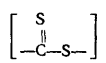
Among the organoboron monomers, the polymerisation of the borazoles has been studied. *BB'B''*-Trimethylborazole was irradiated in an electron accelerator (800 keV) and in an X-ray apparatus (800 kV, 200 mA)[345]. The polymer is a transparent resin with a low degree of polymerisation, readily soluble in benzene. A scheme of polymer formation by a radical mechanism has been proposed. The authors assume the formation of linear macromolecules from borazole rings and in some instances opening of the rings to form linear units, which may alternate with the rings in the chain:



BB'B''-Triphenylborazole and *BB'B''*-triphenyl-*NN'N''*-trimethylborazole (the latter on irradiation in the solid phase) form polymers which are insoluble in benzene but soluble in cresol. The polymers are brown powders which do not melt up to 300°.[345] Analogous polymerisation is undergone by the phosphorus-containing analogue of borazole — the cyclic dimethylphosphineborine trimer. The molecular weight of the polymer is 5200.[346]

15. INORGANIC MONOMERS

The polymer of dichlorophosphazene or so-called "inorganic rubber" has high heat resistance. With irradiation by electrons (4 MeV) the cyclic oligomers of dichlorophosphazene are more stable; the oligomers with an open chain polymerise more readily[347]. The polymerisation of the trimer has been described; in an electron accelerator (1–1.2 MeV) in an atmosphere of air at 130° the trimer can be completely polymerised to a sticky rubber-like mass containing a trace of the tetramer[348]. In the polymerisation of dichlorophosphazene in the solid phase at 100° under the influence of X-rays (dose rate 1.2 Mr h^{-1}) a degree of conversion of 10% is reached in 40 h.[349] The tetramer does not polymerise under the influence of γ-radiation either in the solid or in the liquid phase[350]. On irradiation of the trimer in the solid phase the rate of polymerisation increases with increase in temperature to the melting point but above this temperature it decreases to almost zero[350]. In the polymerisation of dicyan (cyanogen) $(CN)_2$ from the gaseous phase, it was found that argon, krypton[253], and xenon[253,351] have a sensitising influence. Analogous studies were carried out with hydrogen cyanide[253]. A carbon disulphide polymer was previously obtained by thermal polymerisation at 185° and a pressure of about 55 000 atm[352]. Infrared spectroscopy indicated that the solid black polymer had the microstructure



The action of ^{60}Co γ-radiation gives a brown product at a pressure of 1 atm and a black product at high pressures (up to 15 000 atm). The polymer is insoluble in the monomer but swells in it. The yields of polymer are very low. The maximum yield of 4.1% (G = 1.5) was obtained at a dose of 400 Mr, a dose rate of 3.2 Mr h^{-1}, a temperature of 98° and a pressure of 10 000 atm.[120,352] It is reported that carbon monoxide forms a polymer under the influence of ionising radiation[34].

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Leningrad State University