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# Progress in the synthesis of grafted materials using radiation graft polymerisation

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ABSTRACT. The current state of research into graft polymerisation processes that are initiated by ionising radiation is examined. Particular attention is given to new radiation grafting methods, such as low-temperature graft post-polymerisation, grafting with plasma chemical initiation, grafting in the presence of complexing agents, and grafting of metal-containing monomers. The mechanism of the radiation graft polymerisation process is also discussed.

The bibliography includes 188 references.

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## I. Introduction

Graft polymerisation is currently one of the most promising methods for obtaining modified polymer materials which combine different, and often contrasting, properties. There is an extensive literature, including a number of monographs and reviews,[1–24] which is devoted to different aspects of graft polymerisation — the procedural method, a study of its basic principles, its kinetics and mechanism, the structure and physicochemical properties of graft polymer materials, and problems in carrying out the processes on a pilot and industrial scale.

Amongst the many methods for obtaining graft copolymers, radiation graft polymerisation plays an important role. The radiation method for initiation of grafting is the most versatile method, and it can be used to carry out the process in virtually any system of matrix–grafted monomer. The radiochemical initiation of graft polymerisation has a number of advantages over a material method.[25]

Radiation graft polymerisation has up to the present time evolved as an independent branch of science with its own methodology and wide range of problems that can be resolved by it relating to the overall task of obtaining materials with a given set of production and operating properties. Considerable progress has been made in the practical realisation of processes based on radiation graft polymerisation. Thus, radiation finishing of textile materials is widely used.[15,16,21,22] Radiation grafting is used to obtain biocompatible polymer materials for medical application and materials for the immobilisation of biologically active compounds and samples,[26–44] adhesive polymers,[45–54] ion-exchange materials,[55–63] and supported catalysts and other materials.[24]

In the present review the most recent advances in the development of methods for obtaining radiation grafted polymer materials and a study of the mechanism of radiation graft polymerisation are examined.

## II. Direct grafting

The main methods of radiation graft polymerisation had already been developed by the start of the 1960s and are covered in sufficient detail in review articles.[1–4,6,8,10–12,14–17,19,21,22,24] There are four main methods of radiation grafting: 1) the direct method, i.e., direct irradiation of the system: polymer being modified–monomer being grafted; 2) post-polymerisation, i.e., initial irradiation of the polymer in the absence of air followed by contact of the monomer with the irradiated polymer; 3) the peroxide method, i.e., initial irradiation of the polymer in an atmosphere of air or oxygen followed by treatment of the irradiated polymer with the monomer under conditions where the peroxides and hydroperoxides formed by irradiation decompose; 4) cross-linking of polymer mixtures. The last of these methods has not been developed to any significant extent. In the development of the first three methods, however, there have been a number of new results in recent years that have considerable significance for synthetic radiation chemistry.

The direct method has become the most widely used method for radiation graft polymerisation. Most frequently the polymer is in contact during irradiation with an excess of monomer, which can be used in liquid form (including in solution) or gaseous form. Sometimes use is made of the initial impregnation method, in which the polymer is first impregnated with the monomer and then irradiated. The method is non-stationary since there is no additional supply of monomer when it is consumed. The advantage of the direct method is that it occurs in a single stage, and the main disadvantage is the possibility of homopolymerisation of the monomer used for grafting occurring at the same time as a side-reaction; this is particularly significant in liquid-phase processes.

The methods for suppressing homopolymerisation during direct grafting have been examined in detail.[24]

One of these methods involves the introduction of transition metal ions into the system. This method is used particularly often in liquid-phase grafting. Recently a number of studies have been published on the kinetics of direct radiation liquid-phase grafting in a system of such practical importance as polyethylene (PE)–acrylic acid (AA)–water–Mohr's salt.[64–66] By comparing the effect of the dose rate, concentrations of monomer and ferrous ions on the kinetics of graft polymerisation of AA on to PE and the kinetics of homopolymerisation of AA, it was possible to optimise the conditions for grafting of AA on to PE in an aqueous solution of monomer.[66]

There is a certain interest in introducing organic compounds that are polymerisation inhibitors into the system. By using the difference in the ability of inhibitor and monomer molecules to diffuse to the active sites that initiate polymerisation in the polymer matrix, it is possible not only to suppress the unwanted homopolymerisation process in the external solution but also to control the distribution of graft polymer with respect to the thickness of modified material.[67] The chemical addition of components to the chains of graft polymer is also possible, as a result of which a substantial increase in the stability of the material towards thermal stability and oxidation and also deformation strength properties is achieved.[68–70]

Out of the different variants of the direct method of radiation graft polymerisation, it is gas-phase grafting that has been successfully developed.[15,16,21,22] This method involves the irradiation of different solid supports, including mineral supports,[15,16,22,71] in the presence of monomers that are in the gas phase or in the form of unsaturated vapour. The energy of irradiation in this case is absorbed almost solely by the solid support, as a result of which active sites initiating polymerisation are essentially formed only in it. Consequently, homopolymerisation in the gas phase is almost completely suppressed and, moreover, there is the possibility of grafting in those systems which are characterised by a low radiochemical yield of active sites in the support compared to their yield in the monomer. For graft polymers obtained by gas-phase graft polymerisation, a layered macroheterogeneous structure with a distinct boundary between the grafted and ungrafted layers is typical as is the formation of ordered (crystalline and oriented) structures of the graft polymer when using polymers in an oriented state as supports.[72]

In studying the structure of radiation grafted polymer materials obtained by the direct method, attention has until recently mainly been focussed on the macrodistribution of the graft polymer and the characteristics of ordering of the macromolecules. Experimental methods for analysing non-uniformity in the distribution of a graft polymer on the surface and width of a modified polymer material have been developed further. Thus, for studying the surface of grafted polymer films and fibres, the use of a radioactive indicator method has been proposed[77] along with the traditional methods of optical[73–75] and electron[51,76] microscopy. According to the former method a radioactive label is introduced into grafted chains, after which an image is obtained on a photographic plate, characterising the irregularity of distribution of the graft polymer on the surface of the sample. For this purpose it has been proposed to utilise the different capacity of the chains of polymer matrix and grafted polymer to undergo radiothermoluminescence.[78] In order to study irregularity in the distribution of a grafted polymer along the cross-section of a modified sample, in addition to the known indirect methods that consist of an analysis of the dependence of the content of the grafted polymer on the thickness of the sample and changes in geometric dimensions on the material during grafting and the direct methods related to a study of lateral sections of grafted polymer materials, a method based on comparison of optical densities in IR transition and multiply attenuated internal reflection spectra has been put forward.[79] In addition to inteferrometry,[80] microprobe X-ray spectroscopic analysis[63,81,82] has started to be widely used for the analysis of sections of graft polymer materials. It was possible, in particular, to use this method to establish the broken, step-like nature of the edge of the graft in graft copolymers of PE with AA obtained by direct irradiation in an aqueous solution of AA in the presence of Mohr's salt.[82]

There has also been further development of theoretical methods for analysing the irregularity of distribution of a graft polymer along the cross-section of radiation grafted polymer materials; these are based on the equations of diffusion kinetics.[16,83,84] In one study,[85] in order to determine the characteristic parameter, $\alpha$, which can be used to determine the concentration distribution profile of a graft polymer along the cross-section of a sample, a transcendental equation has been obtained and solved, which contains only experimentally measured parameters of radiation graft polymerisation — the rate of grafting, the degree of equilibrium sorption of the monomer, the diffusion coefficient of the monomer in the polymer, and also the thickness of the modified material. Calculation of the width of a grafted layer from the value of the parameter $\alpha$ has been improved.[86]

In a study of the radiation grafted films and fibres of PE–polyacrylonitrile and chlorinated polyvinyl chloride–polyacrylonitrile synthesised by direct irradiation in monomer vapour with high dose rates, experimental confirmation has been obtained for the existence of "cut-off" layers on the surface of grafted materials,[87] whose possible occurrence had been considered previously.[15,16] Comparison of the strength and vapour permeability of samples with a "cut-off" layer, obtained at a high dose rate, and samples obtained at a low dose rate and not containing a "cut-off" layer showed that in the first case a considerable change in the properties of the material was achieved even with a small content of grafted polymer whereas in the second case there were only substantial changes in the properties for high degrees of grafting.[87]

In recent times, starting with the studies of Kurilenko et al.,[88–90] for radiation grafted polymer materials there has been considerable development of ideas about the heterogeneous nature of graft polymerisation and the microdistribution of components in graft copolymers, as proposed by Kargin and Platé in the 1950s. In addition to low-angle X-ray dispersion and electron microscopy,[23,75,87–90] low-angle neutron has been successfully used to obtain distribution curves of the dimensions of the particles of the microphase of a graft polymer for an analysis of the microheterogeneous structure of radiation grafted polymer materials.[91,92] Ideas about the microheterogeneous structure of radiation grafted polymer materials and the effect of the particles of the microphase of a grafted polymer on the molecular mobility and interchain interaction in amorphous microregions of a modified polymer have been used to analyse the causes of the change in thermal and deformation strength properties of polymer materials from radiation grafting.[23]

Out of the studies on direct radiation grafting which have undergone considerable development, mention should be made of radiation grafting on to latex particles from emulsions.[24] Radiation emulsion polymerisation is one of the most promising developments

in radiochemical technology.[93] It combines the advantages of emulsion polymerisation and radiation initiation. Several examples of radiation emulsion graft polymerisation are reported in the literature.[94-105] Thus, the radiation emulsion grafting of styrene, vinyl acetate, butyl methacrylate, and methyl methacrylate (MMA) on to lattices of polyvinyl acetate, polybutyl acrylate, and polymethyl methacrylate (PMMA) occurs in high yield (up to 80%).[94] The radiation grafting of styrene, vinyl acetate, ethyl acrylate, and MMA on to polytetrafluoroethylene (PTFE) in a latex has been studied.[95] Grafting did not occur at all with chemical initiation whereas with radiation grafting the quantity of graft polymer reached 6–8% of the weight of PTFE. Grafting by irradiation of lattices in the systems polyvinyl acetate–acrylonitrile (AN) and polyethyl acrylate–MMA was also studied.[95] The content of graft copolymer in the final product reached 40–50%. The radiation graft polymerisation of MMA on to polybutyl acrylate in an emulsion has been established,[96] and the radiation graft polymerisation of styrene in a polybutadiene latex has been studied.[97-99] The results were compared with those obtained by chemical initiation under the same conditions. No significant difference in the degree of grafting was observed for both methods of initiation; this was attributed to the ease of transfer of a growing polystyrene chain to polybutadiene with removal of a hydrogen atom at a α-position relative to the double bond.[24] The resulting polymer radical is one of the main sites of grafting. Therefore, the additional formation of polymer radicals on polybutadiene during irradiation does not make a significant contribution to the overall degree of grafting.

The radiation grafting of styrene and AN on to a polybutyl acrylate latex has been reported.[100] The quantities of graft copolymer amount to double-figure percentages, the yield of graft increasing as the ratio of water to polymer in the initial latex increases, which is related to the preferential participation of the radiolysis products of water in graft polymerisation rather than homopolymerisation. The process of obtaining an atmospherically stable, high-impact plastic which is based on the radiation grafting of a styrene copolymer and AN on to a rubber latex has been reported.[101-105] The plastic obtained has physicomechanical properties which are not inferior to ternary copolymers of AN, butadiene, and styrene (ABS plastic) and are frequently superior to them in terms of atmosphere stability. This extends their range of application.

The combined literature data provide an indication of the high efficiency of radiation graft emulsion polymerisation compared to other forms of radiation grafting due to the more extensive surface of the matrix. In materials obtained by radiation emulsion graft polymerisation there is a sufficiently uniform distribution of macromolecules of a different chemical nature throughout the bulk of the sample.

The advantages of the radiation method for initiation in emulsion graft polymerisation are particularly obvious in grafting on to polymers that do not tend to undergo chain-transfer reactions. We should note that there is virtually no information about the physicochemical properties of polymer materials obtained by radiation emulsion graft polymerisation.

## III. Low-temperature post-radiation graft polymerisation

Low-temperature post-radiation grafting with devitrification of the polymer matrix is one of the relatively new methods used to carry out graft polymerisation. This method has been discussed in two reviews.[106,107] and in a study published later.[108] In essence the method involves the introduction of a monomer into the polymer being modified by sorption from a liquid or gas phase, the system is cooled to a temperature below the glass-transition temperature of the polymer, exposed to ionising radiation at this temperature, and then devitrified. Direct grafting of a monomer in solution does not occur in a vitrified polymer. Radiation graft post-polymerisation is only achieved by devitrification of the polymer matrix, and it occurs at a high rate with virtually no formation of homopolymer. Acceleration of grafting at temperatures corresponding to transition of the matrix from a vitreous form to a hyperelastic form had previously been recorded.[109,110] A significant shortcoming of these studies was the use of the traditional gravimetric method for determining the yield of polymer, the yield of graft polymer being determined at room temperature and not at the temperature corresponding to the maximum rate of graft polymerisation. For low-temperature processes the yield of graft polymer was actually determined after decomposition of the vitreous matrix. For quantitative kinetic studies necessary for an understanding of the processes that occur during devitrification of the matrix, methods were needed which would allow a process to be monitored directly as it occurred and not after its completion and decomposition of the surrounding matrix. It was also necessary to analyse in each particular case the two-component system "monomer–vitrifying matrix", to determine the limits of mutual solubility at the glass-transition temperatures of the system, and finally the temperature itself in the region of vitrification. All these methodological problems were successfully resolved by the use of a calorimetric technique.[107]

It was shown that most monomers introduced into a polymer matrix by sorption are preserved in the form of a solution in the pores of the matrix on freezing. A characteristic crystalline phase of monomer is formed when it is in excess, but this occurs in far from every case for all of the monomers. In the devitrification of a polymer mtrix an intense evolution of heat occurred, related to the process of polymerisation, which in a number of cases was confirmed by IR spectra to be grafted in nature.[108,111-115] Studies were also carried out on systems such as polyisobutylene–AN, polyisobutylene–divinylbenzene, polyisobutylene–methyl acrylate, polyisobutylene–MMA,[111] polyisobutylene–tetrafluoroethylene (TFE),[108] PE–TFE,[112] ethylene–propylene rubber (EPR)–TFE,[108,113-115] polydimethylsiloxane–AN, polydimethylsiloxane–MMA, polydimethylsiloxane–methyl acrylate, polydimethylsiloxane–vinyl acetate,[114] polydimethylsiloxane–TFE,[108,114,115] polydimethylsiloxane–styrene, polydimethylsiloxane–butadiene, polydimethylsiloxane–vinyl fluoride,[114] polydimethylvinylsiloxane–TFE, polydimethylphenylmethylvinylsiloxane–TFE, polydimethylmethylphenylsiloxane–TFE, polystyrene–TFE, PMMA–TFE, fluororubber SF-26–TFE, polybutadiene–TFA, butyl rubber–TFE, polyvinyl chloride–TFE.[108] In all systems, with the exception of polydimethylsiloxane–styrene, polydimethylsiloxane–butadiene, polydimethylsiloxane–vinyl fluoride, polymerisation of the introduced monomer occurred at about the temperatures corresponding to devitrification of the polymer matrix. High values of the yield graft of polymer were achieved in the rubber matrices, especially those of silicones. Graft polymerisation occurred

throughout the whole volume of the matrix and yielded materials with a uniform distribution of graft polymer along their cross-section.

The main advantage of low-temperature post-radiation graft polymerisation over other methods of radiation grafting lies in the possibility of obtaining graft copolymers with such readily polymerising and difficult to graft monomers as fluoroolefins, in particular, TFE. There is future potential in the low-temperature post-radiation grafting of TFE to by-products of the processing of PTFE, which would make it possible to obtain monolithic blocks of PTFE from the by-products, similar in properties to the initial polymer,[116,117] as is the low-temperature grafting of vinyl fluoride and vinylidene fluoride to by-products of the production of PTFE, PE, and polyvinyl chloride.[118-122]

The physicochemical properties of the materials obtained by low-temperature post-radiation graft polymerisation have been insufficiently studied. In one review[106] it was pointed out that graft copolymers with TFE have improved thermal and chemical stability and a lower coefficient of friction compared to the initial polymers. The improved heat stability of a graft polymer of PE with vinyl fluoride compared to the initial PE has also been recorded.[119] The properties of graft polymer materials obtained by low-temperature post-radiation grafting and their structures have not been studied in detail.

## IV. Plasma-initiated grafting

Initiation of graft polymerisation with a non-equilibrium plasma from a gaseous discharge is regarded at the present time as a novel method of radiation graft polymerisation.[22] Although plasma-initiated graft polymerisation, as was mentioned by Tsetlin et al.,[22] can be achieved using the direct method, most of the published articles relate to plasma-initiated graft post-polymerisation.

The first studies on the effect of a high-frequency gas discharge plasma on solid organic compounds, including monomers in a vitrified state, were carried out at the beginning of the 1960s.[123] At that time the possibility of using radicals formed by discharge on the surface layer of a polymer for the synthesis of graft copolymers was suggested.[124] The preparation of graft copolymers of cellulose with ethyl acrylate by initiating the process with a corona discharge was reported.[125]

In recent years the processes which occur in PE on exposure to a non-equilibrium gas discharge plasma have been studied in detail,[126,127] and methods have been developed from this for plasma-initiated graft polymerisation of MMA, AA, methacrylic acid on to PE powder.[128,129] In essence the methods involve PE powders being evacuated, and then at a small residual pressure of oxygen (10–260 Pa) or in an atmosphere of an inert gas they undergo treatment with a high-frequency gas discharge plasma, after which the PE is again evacuated and brought into contact with monomer vapour, resulting in plasma-initiated post-polymerisation. It has been shown that neither a wide variation in pressure of the inert gas nor in specific power of discharge has an effect on the initial rate of grafting of MMA on to PE, which, however, depends on the time of treatment of PE in the plasma. Thus, for the first 3–5 min of treatment with the plasma, the rate of grafting of MMA on to PE increases substantially and then remains virtually unchanged, which is due to the attainment of a given limiting concentration of active sites or products initiating the reaction.[129] Plasma-initiated grafting of methacrylic acid on to PE occurs at a higher rate than grafting with AA.[128] Grafting of water-soluble monomers on to PE films, polypropylene (PP), and polyethylene terephthalate, treated with a high-frequency discharge plasma, from aqueous solutions of AA, 2-hydroxyethyl methacrylate, 2-dimethylaminoethyl methacrylate, vinylpyridine, acrylamide, and 2-acrylamide-2-methyl-1-propanesulphonic acid has been reported.[130] Comparison of the kinetics of plasma-initiated grafting of AA on to PE powder with γ-initiated graft post-polymerisation (Fig. 1) showed that a similarity of the kinetic curves for formation of graft polyacrylic acid (PAA) is achieved at a dose of 40 kGy.[23,128] Consequently, in certain cases plasma-initiated grafting in terms of both energy and process equipment design may be preferable than that initiated by γ-irradiation or accelerated electrons.

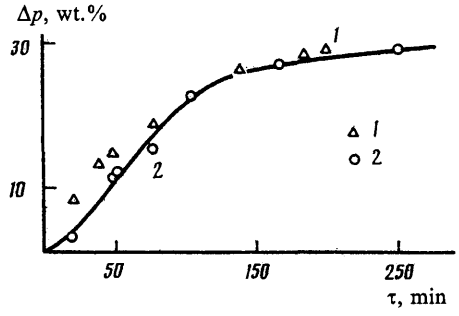



**Figure 1.** Dependence of the degree of grafting ($\Delta P$) of AA on to PE on the time of the process for plasma-initiated post-polymerisation after initial treatment of PE for 10 min in a helium plasma at a pressure of $9.3 \times 10^2$ (*1*) and for γ-initiated post-polymerisation with an irradiation dose of 40 kGy (*2*); temperature of grafting was 323 K.[128]

A characteristic of plasma-initiated graft polymerisation is the occurrence of the process on the surface layer of the modified material with thickness of several μm, where the active sites that initiate grafting are primarily located. The nature of these sites and their relative efficiency in initiating the process of graft polymerisation is not yet completely clear. It has been noted[24] that plasma-initiated grafting may be a convenient method for modifying the surface properties of polymer materials, but these properties have also been sufficiently studied. There is future potential in the use of PE powder grafted by plasma chemical initiation for immobilisation of supported polymerisation catalysts[128] and PE films for adsorption of metal ions.[130] The mechanical properties of films that are grafted by plasma chemical means have hardly been studied at all.

## V. Effect of matrix structure on post-radiation grafting

A series of studies by Nikol'skii et al.[75,131-134] is concerned with the dependence of the rate of gas-phase graft post-polymerisation of vinyl monomers (mainly styrene) to polyolefins on the characteristics of their hypermolecular structure. The structure of PE and PP films was modified by changing the rate of cooling the polymer melt and also by annealing. The dependence of the radiochemical yield of the

radicals, stable at 77 K and quasi-stable at room temperature, was studied. The yield of radiation graft copolymer was studied in parallel. It was shown[131] that the radiochemical yield of the free radicals in low-density PE at 77 K did not depend on the rate of cooling the polymer melt when it was changed from 1.5 to 2000 K $min^{-1}$ and constituted 3 sp/100 eV. The magnitude of the radiochemical yield of radicals that were quasi-stable at room temperature increased by 25–30% on reducing the rate of cooling from 2000 to 1.5 K $min^{-1}$. At the same time the yield of polystyrene and polyacrylonitrile, grafted on to PE by gas-phase graft post-polymerisation on alkyl radicals that were quasi-stable at room temperature and also by liquid-phase grafting on alkoxyl radicals formed by the thermal decomposition of hydroperoxide groups in PE irradiated in air, increased several times on reducing the rate of cooling by a factor of 10–100. Hence, reduction in the rate of cooling a PE film by a factor of 10–100 during its preparation makes it possible to reduce the dose necessary for grafting by a considerable amount.

Studies carried out with low- and high-density PE films obtained with rapid cooling (cooling rate 2000 K $min^{-1}$) and annealed for 7 h under vacuum at 313–393 K showed that the radiochemical yield of free radicals at 77 K, equal to 3 sp/100 eV for annealed films, increases on annealing by only 10–20% whereas the radiochemical yield of radicals that are quasi-stable at 295 K increases more markedly.[133] The yield of polystyrene grafted on to PE using gas-phase graft polymerisation increases to a greater degree than the yield of radicals that are quasi-stable at room temperature. A study of the structure of annealed films showed that as the temperature of annealing increases the density of polymer and its crystallinity increase. The initial rate of sorption of styrene increases on annealing by 20–30% while the maximum sorption, on the other hand, is slightly reduced. The increase in yield of graft polystyrene correlates with the increase in concentration of free radicals that are quasi-stable at room temperature.

Rapidly cooled low-density PE films were compared[132] with slowly cooled high-density PE films. The rapidly cooled (quenched) low-density PE films did not contain spherulites, but when they were annealed spherulites of diameter 6–9 μm appeared. At the same time the density and (X-ray) crystallinity of the polymer increased and there was a reduction in the adsorption of styrene. The slowly cooled high-density PE films had a spherulite structure with spherulites of average diameter 3–6 μm. On annealing the diameter of the spherulites increased to 15–20 μm. At the same time the density and crystallinity of the polymer increased. The radiochemical yield of free radicals at 77 K in all of the samples was 3 sp/100 eV. The concentration of radicals that were quasi-stable at room temperature in the slowly cooled high-density PE films was 2–3 times higher than in the rapidly cooled low-density PE films. Annealing led to an increase in concentration of these radicals, this being exhibited most distinctly for high-density PE. Gas-phase graft post-polymerisation of styrene on slowly cooled films on the whole occurred at a higher rate than on rapidly cooled films.

Similar characteristics of the effect of the rate of cooling and annealing temperature on the yield of graft polystyrene were determined in the system PP–styrene.[134] A spherulite structure formed in PP on slow cooling of the melt, and on rapid cooling a smectic structure occurred. Annealing led to an increase in crystallinity and a sharp increase in the yield of graft polystyrene, which was due to an increase in concentration of radicals that were quasi-stable at room temperature as well as an improvement in conditions for sorption and diffusion of the monomer.

It was also shown[132–134] that the dependence of the degree of grafting on the thickness of the initial polyolefin film is extremal in nature, the position of the maximum being determined by the conditions of crystallisation and the annealing of the sample and also by parameters of the grafting process such as reaction time and radiation dose. On the basis of the kinetic data, it was suggested[132–134] that the maximum in the dependence of the degree of grafting on the thickness of the sample corresponds to the start of a gradual change from "bulk" grafting, characterised by a comparatively uniform distribution of graft component, to "surface" grafting, where the graft polymer is localised in the layer of material near the surface.

## VI. Complexation as a method of controlling graft polymerisation

Complexation which achieves stabilisation of the macroradicals growing during polymerisation is used to control radiation graft post-polymerisation processes.[135–138] Thus, the polymerisation of acrylic and methacrylic monomers in the presence of orthophosphoric acid occurs in apparently homogeneous solutions and after the incorporation of an initiation source.[139] The cause of the suppression of bimolecular termination is the cross-linking of the polymerisation system through the formation of macromolecular and radical associates that are stabilised by hydrogen bonding. By using radicals bound on to cellulose for initiation of polymerisation in the system $H_3PO_4$–acrylic or methacrylic monomer, it was possible to obtain graft copolymers.[135] We should mention that complexation has also been used in direct radiation grafting, making it possible to obtain graft copolymers with allyl monomers in good yield.[140] The γ-initiated graft post-polymerisation of MMA and methyl α-chloroacrylate on to cellophane film in the presence of $H_3PO_4$ has been studied in detail.[135] Irradiation of the film was carried out at 77 K with grafting at room temperature. Grafting did not occur in the absence of $H_3PO_4$. When the complexing agent was added, grafting occurred, and in the initial stages of the process a linear increase in the content of graft polymer and its molecular weight with time was observed when there was a constant number of graft chains. Consequently, in the presence of $H_3PO_4$ graft post-polymerisation of MMA to γ-irradiated cellulose occurred virtually without termination or chain transfer, so that it was possible to obtain by a "living" mechanism grafted block copolymers of cellulose–(graft)(MMA–block methyl α-chloroacrylate). Graft copolymers of cellulose triacetate with a regularly varying number and length of PMMA chains were synthesised by means of continuous irradiation post-polymerisation of MMA in the presence of $H_3PO_4$.[136] A characteristic of this system was the increase in the number of grafted chains with grafting, which Akrabov et al.[136] attributed to the progressive involvement in graft polymerisation of macroradicals of cellulose triacetate that accumulated during γ-irradiation. It was observed[135] that the materials obtained using continuous irradiation graft polymerisation are characterised by a uniform distribution of graft polymer along their cross-section. For graft copolymers of cellulose triacetate with PMMA synthesised in the presence of $H_3PO_4$, the thermodynamic properties of their solutions were studied.[141] The dependence of the physicochemical properties of graft copolymers of PE synthesised using material initiators on the length and frequency of the graft chains has previously been recorded.[142,143] Hence there would be considerable interest in research into the properties of graft copolymers obtained

by means of continuous irradiation polymerisation in the presence of a complexing agent; this could help to determine the dependence of the physicochemical properties of radiation grafted polymer materials on the parameters of their molecular structure.

## VII. The peroxide method and grafting of metal-containing monomers

The peroxide method of radiation graft polymerisation has been widely used since the 1950s,[3] but its mechanism cannot yet be regarded as established conclusively. A series of studies relating to both the mechanism of grafting conventional monomers (AA, acrylamide) on to PE and an investigation of the features of graft polymerisation of metal-containing monomers on to PE is of prime importance for the development of research on radiation graft polymerisation using the peroxide method.[144,148,149,151-153]

The nature of the active sites that initate grafting using the peroxide method is still the subject of controversy. The results of experiments on the grafting of AA on to irradiated PE powder and on to the same powder after iodometric titration resulting in decomposition of the hydroperoxides have been compared.[144] In the latter case grafting did not occur at all, from which it was concluded that hydroperoxides had higher activity than dialkylperoxides in graft polymerisation.

Transition metal salts are used to accelerate graft polymerisation by the peroxide method. The addition of small quantities of these leads to a more efficient decomposition of the peroxides.[145-147] It was shown[148] that on increasing the concentration of cobalt palmitate from 0 to 0.8%, the initial rate of radiation grafting of AA on to irradiated PE powder in a solution of monomer in heptane increased by a factor of two. In contrast to the grafting of AA on to PE,[148] there was no detectable accelerating action of cobalt salts on the grafting of acrylamide on to PE. A possible reason for this phenomenon, in the opinion of Savost'yanov et al.,[149] could be the formation of complexes between the cobalt compounds and acrylamide.[150]

In a study of graft polymerisation of Co(II), Ni(II), and Cu(II) acrylates on to PE powder that had previously been irradiated in air, it was shown[152] that this process occurs at lower rates than grafting with AA. In the grafting of acrylamide complexes of Co(II), Ni(II), and Cu(II) [composition of the complex was $MX_2 \cdot 4AA$, where M = Cu(II), Ni(II), Cu(II), X = Cl or $NO_3$, AA = acrylamide) to PE powder that had previously been irradiated in air, homopolymerisation was completely suppressed and the initial rate of grafting and yield of graft polymer were similar to those values that were observed in grafting of pure acrylamide.[153] The only exception to this was the $CuCl_4 \cdot 4AA$ complex, which underwent virtually no grafting on to irradiated PE.

There is also virtually no grafting of allyl alcohol on to PE previously irradiated in air, whereas complex compounds of allyl alcohol with transition metal salts [particularly with $Co(NO_3)_2 \cdot 6H_2O$, $CoCl_2$, and $CoCl_2 \cdot 6H_2O$] are grafted at a high rate.[151]

Thus, by using metal-containing monomers in the modification of polymer materials by radiation graft polymerisation with the peroxide method, it is possible in certain cases to carry out the grafting of monomers that are usually grafted with difficulty. Metal-containing graft copolymers are of interest in the treatment of polymerisation catalysts.[128] Moreover, they could most probably be used as materials with increased heat stability by analogy with ionomers.[154] However, the physicochemical properties of materials obtained by extrusion of PE with graft metal-containing polymers have hardly been studied at all.

## VIII. The mechanism of radiation graft polymerisation

In the 1970s there was considerable progress in studies relating to radiation graft polymerisation.[155-169] For a long time it was thought that radiation graft polymerisation at room temperature and higher temperatures occurred solely by a radical mechanism. Direct evidence for such a graft mechanism was obtained for certain systems. Thus, in a study of radiation gas-phase graft copolymerisation of AA and styrene on to PP fibres there was agreement between the values of the relative activities $r_1$ and $r_2$ obtained during radiation copolymerisation from the gas phase and the corresponding values of $r_1$ and $r_2$ relating to copolymerisation of the same monomers in bulk form, which was known to occur by a radical mechanism.[170] It was concluded from this that radiation graft polymerisation from the gas phase occurs by a radical mechanism. Most authors accepted this mechanism without further question for all cases of radiation grafting with the exception of grafting in swollen polymer systems at low temperatures.[171-173]

In a series of studies carried out mainly in the 1970s it was shown that radiation graft polymerisation could occur at room temperature even for those monomers which polymerise by an ionic mechanism.[155-169]

The development of these studies resulted from the known fact that certain carefully dried monomers which did not polymerise by a radical mechanism could undergo radiation polymerisation at room temperature by an ionic mechanism.[174,175] These monomers (α-methylstyrene, vinyl n-butyl ether, isobutylene, propylene oxide, acrolein) were also used in the first studies on radiation ionic grafting on to PE, PTFE, and polyvinyl chloride.[155,160,162,165] These monomers, which were dried by the usual methods, including drying over calcium hydride, underwent virtually no grafting on to the above-mentioned polymers during direct liquid-phase grafting at room temperature, whereas after special drying graft polymerisation occurred effectively, the yield of homopolymer at the initial stages of the process being extremely low for radiation liquid-phase graft polymerisation ($\leqslant 1\%$).

In view of its particular importance, the question of the method of drying deserves special consideration. On the basis of a calculation using the value of the radiochemical yields and kinetic polymerisation constants, the upper limit of the water content at which grafting usually occurred was determined. This constituted $\sim 10^{-6}\%$ ($\sim 10^{-8}$ mol litre$^{-1}$).[158,169] Such a high degree of drying a monomer is a complex technical problem, the more so that such concentrations of traces of moisture in organic liquids cannot even be measured experimentally.[169] It is recommended that all drying operations in grafting from the start to sealing the tubes with modified polymer should be carried out in a completely sealed vacuum system, excluding completely contact with air.[169] The prime importance of careful heating of the glass apparatus at a temperature close to the softening temperature of the glass has been demonstrated.[169] In the choice of suitable drying agents it is necessary to consider not only their ability to absorb water but also the unwanted possibility of initiating on their surface the polymerisation of monomers that are in contact with them. Thus, metallic sodium is a good drying agent, but monomers placed over it

gradually polymerise. Styrene polymerises particularly readily, giving a thin film of polystyrene, which reduces the efficiency of drying, and this occurs not only on the surface of metallic sodium but also on the surface of such efficient drying agents as molecular sieves and barium oxide.[159] For grafting of monomers which only polymerise by an ionic mechanism, drying initially with calcium hydride followed by two or three batches of barium oxide that have been calculated for 6–12 h at 773 K under high vacuum ($\sim 10^{-5}$ mmHg) has proved effective.[155–157, 160] Calcined zeolites of the type CaA and NaA are not very effective. A good drying agent for many monomers, including styrene, is silica gel (KSM-6P grade) with a specific surface area of $\sim 500$ m$^2$ g$^{-1}$ and average pore radius of 11.2 Å, which has been activated under vacuum ($\sim 10^{-5}$ mmHg) for 20 h at 773 K.[159,160,162,163,165]

The fact that graft copolymers are obtained at room temperature by radiation graft polymerisation of monomers that do not polymerise by a radical mechanism is evidence for an ionic mechanism.[155–157] In a study of the kinetics of radiation graft polymerisation of vinyl n-butyl ether on to PE, additional evidence for an ionic mechanism was obtained. The initial rate of grafting on a fixed portion proved to be proportional to the dose rate at the first stage and the temperature coefficient of grafting was negative.[157] It was also shown that grafting of vinyl n-butyl ether on to PE by initial irradiation in a "dry", i.e., specially purified, system as opposed to the usual free-radical process on to a "wet" system, i.e., one purified in the normal way, did not occur.[157] It was established using IR spectroscopy in the system PE–acrolein that graft polymerisation in a "dry" system does not occur via a C = C bond as occurs in radical polymerisation but via a C=O bond as in ionic polymerisation.[165]

The nature of the effect of organic solvents on the rate of radiation graft polymerisation in "dry" systems is also confirmation of an ionic mechanism for the process.[162,167] For example, in the system PE–vinyl n-butyl ether grafting is suppressed in electron-donating solvents but is accelerated in electron-withdrawing solvents, which is typical for processes that occur via a cationic mechanism. In this case, for example, in the presence of such a strong electron-withdrawing solvent as 1,2-dichloroethane, grafting of vinyl n-butyl ether, which does not polymerise by a radical mechanism, even takes place in a "wet" system.[162]

The ionic nature of graft polymerisation in "dry" systems has also been confirmed by the direct detection of active sites of an ionic nature in irradiated monomer–polymer systems using low-temperature UV spectroscopy.[164]

Together with monomers that polymerise solely by an ionic mechanism, monomers such as styrene, AN, 4-vinylpyridine, 2-methyl-5-vinylpyridine, phenylacetylene, which can polymerise by both an ionic and a radical mechanism, have also been studied.[159–161,163,166,167,169] When the monomer and the complete system were dried, higher values of the yield of graft polymer were generally obtained compared to "wet" systems. This provided the basis for the proposal of a possible mixed mechanism for grafting, i.e., that it takes place simultaneously by a free-radical and an ionic mechanism.

The fraction of ionic process θ is given by the following equation:[169]

$$\theta = \frac{V_{ion}}{V_{ion}+V_{rad}} = \frac{k_{ig}V_{in}^{ion}k_{rt}^{1/2}}{k_{rg}(V_{in}^{rad})^{1/2}\{(k_{ig}V_{in}^{ion})^{1/2}+k_{ox}[H_2O]\}+k_{rt}^{1/2}k_{it}v_{in}^{ion}}$$

where $V_{ion}$ and $V_{rad}$ are the initial rates for ionic and radical graft polymerisation respectively; $k_{rg}$, $k_{rt}$, $k_{ig}$, $k_{it}$, and $k_{ox}$ are the growth and termination constants of radical ($k_{rg}$ and $k_{rt}$) and ionic ($k_{ig}$, $k_{it}$, $k_{ox}$) chains, $V_{in}^{rad}$ and $V_{in}^{ion}$ are the rates of initiation of radical initiation of radical and ionic graft polymerisation.

For monomers with known constants (styrene, for example), figures show the dependence of θ on the dose rate $I$ (Fig. 2) and on the water content (Fig. 3) in the case of grafting on to PE without taking into account chain transfer.[169] It is clear from Fig. 2 that the fraction of the ionic process increases with an increase in dose rate. The complete process can be divided into three bands: a purely radical process, a mixed process, and purely ionic grafting. To achieve ionic grafting over a wide range of dose rates, it is necessary that the water content (or other impurities on which an ionic process can be terminated) should not exceed $10^{-8}$ mol litre$^{-1}$. When the concentration of water is $\sim 10^{-4}$ mol litre$^{-1}$, the transition to a purely ionic grafting only occurs at dose rates exceeding $10^4$ Gy s$^{-1}$.

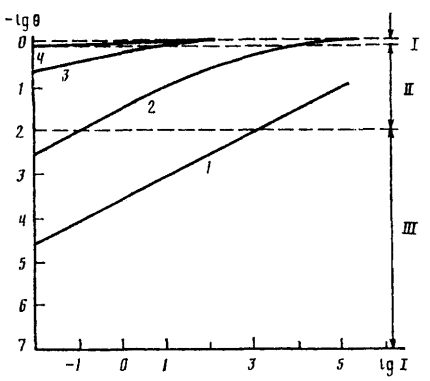



**Figure 2.** Dependence of the fraction of ionic process on the dose rate ($I$) with a varying content of water in the system (mol litre$^{-1}$): *1*, $10^{-2}$; *2*, $10^{-4}$; *3*, $10^{-6}$, *4*, $10^{-8}$; $G = 1$; $k_{it} = 10^{11}$; $k_{ig} = 3.5 \times 10^6$; $k_{ox} = 10^{10}$; *I*, purely ionic grafting; *II*, mixed grafting; *III*, radical grafting.[169]

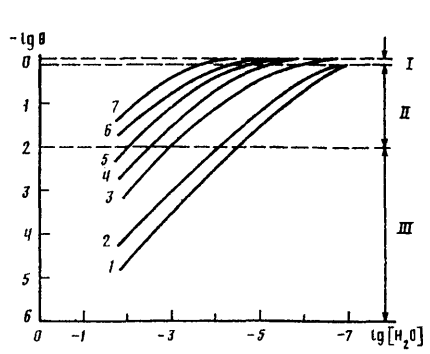



**Figure 3.** Dependence of the fraction of ionic process on the water content in the system at different dose rates, Gy s$^{-1}$: *1*, $10^{-2}$; *2*, $10^{-1}$; *3*, 10; *4*, $10^2$; *5*, $10^3$; *6*, $10^4$; *7*, $10^5$; $G = 1$; $k_{it} = 10^{11}$; $k_{ig} = 3.5 \times 10^6$; $k_{ox} = 10^{10}$ (concentration of water, mol litre$^{-1}$); *I*, purely ionic grafting; *II*, mixed grafting; *III*, radical grafting.[169]

The theoretical dependence of θ on the water content at different dose rates (see Fig. 3) indicates that in order to achieve purely ionic grafting at dose rates of $10^{-2}-10^{0}$ Gy $s^{-1}$, the water content in the system must be lowered to $10^{-8}-10^{-9}$ mol $litre^{-1}$. With the normal content of water in styrene ($10^{-3}-10^{-1}$ mol $litre^{-1}$) grafting by an ionic mechanism occurs at dose rates of $10-10^{3}$ Gy $s^{-1}$.

Not only water molecules but also other molecules which accept a positive charge (amines, etc.) act as impurities on which termination of the ionic chains can occur. However, the content of these impurities in the monomers used is negligible.

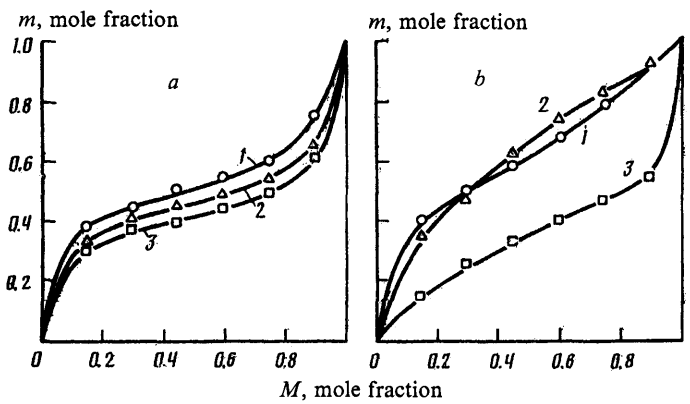



**Figure 4.** Dependence of the composition of graft copolymer of styrene and acrylonitrile ($m$) on the composition of the initial mixture of monomers ($M$); dose rates were $8 \times 10^{-2}$ Gy $s^{-1}$ (*a*), $(1 \pm 0.2) \times 10^{3}$ Gy $s^{-1}$ (*b*); *1*, without using a solvent; *2*, in methylene dichloride; *3*, in HMPT.[168,169]

**Table 1.** Constants for graft copolymerisation of styrene and acrylonitrile.[168,169]

| Solvent | Dose rate, Gy $s^{-1}$ | Copolymerisation constant | |
|---|---|---|---|
| | | $r_1$ | $r_2$ |
| No solvent | $8 \cdot 10^{-2}$ | 0.18±0.03 | 0.16±0.03 |
| $CH_2Cl_2$ | $8 \cdot 10^{-2}$ | 0.07±0.02 | 0.22±0.04 |
| HMPT | $8 \cdot 10^{-2}$ | 0.06±0.02 | 0.55±0.06 |
| No solvent | $(1 \pm 0.2) \cdot 10^{3}$ | 0.94±0.08 | 0.20±0.04 |
| $CH_2Cl_2$ | $(1 \pm 0.2) \cdot 10^{3}$ | 1.55±0.13 | 0.26±0.04 |
| HMPT | $(1 \pm 0.2) \cdot 10^{3}$ | 0.04±0.01 | 0.83±0.07 |

In order to confirm the conclusion that the contribution of the ionic process increases with an increase in dose rate, the radiation graft copolymerisation of styrene with AN on to PE was studied under the same conditions at dose rates of $8 \times 10^{-2}$ and $(1 \pm 0.2) \times 10^{3}$ Gy $s^{-1}$. The results of determining the composition of the copolymer (Fig. 4) and the copolymerisation constants $r_1$ and $r_2$ (Table 1) show that the effect of the solvents differs considerably at low and high dose rates. When a dose rate of $(1 \pm 0.2) \times 10^{3}$ Gy $s^{-1}$ is used, the copolymer is enriched with the styrene component when grafting is carried out in bulk or in the electron-withdrawing methylene dichloride but is enriched with the nitrile component from grafting in the electron-donating hexamethylphosphorotriamide (HMPT). The copolymerisation constants also differ considerably. These results indicate that the radiation graft copolymerisation of styrene with AN on PE takes place at high dose rates with a significant contribution from the ionic mechanism.

The mechanism of initiation or radiation ionic graft polymerisation (cationic and anionic) has been studied insufficiently. It has been suggested[169] that the active sites of cationic graft polymerisation may be radical cations or carbocations that are formed both directly by radiolysis of PE and by the reaction of a monomer radical ion with a radical of the polymer matrix:

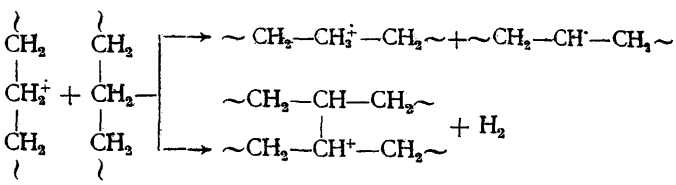
$$R^{\cdot} + M^{\dot{+}} \rightarrow RM^{+}.$$

The first stage in the radiolysis of PE is formation of a radical cation:[169]

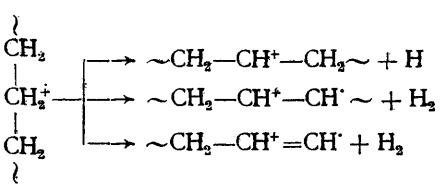
$$\sim CH_2-CH_2-CH_2 \sim \xrightarrow{\gamma} \sim CH_2-\dot{C}H_2-CH_2 \sim + e^{-}.$$

The electron undergoes partial thermolysis and can be captured by structural traps in PE. In adding on the monomer, the radical cation forms an active site for cationic graft polymerisation.

The radical cation of PE can react with a neighbouring polymer molecule to form a cross-link or a carbocation:



Moreover, the radical cation can be converted by elimination of an H atom or $H_2$ molecule



The elimination of an H atom or $H_2$ molecule depends on the site of formation of the radical cation. The resulting $CH^{+}$ and $=CH^{+}$ carbocations can also act as initiators of cationic graft polymerisation.

Active sites of an anionic nature are mainly formed by capture of an electron by radicals from the matrix

$$R^{\cdot} + e \rightarrow R^{-}.$$

The second route for formation of active anionic sites is reaction of matrix radicals with monomer radical anions:

$$R^{\cdot} + M^{\dot{-}} \rightarrow RM^{-}.$$

All of the schemes shown above for the formation of active sites of ionic graft polymerisation are hypothetical in nature rather than based on experimental confirmation.

There is definite interest in the comparison of the physicochemical properties of radiation grafted copolymers of the same composition which are obtained by different mechanisms, namely free-radical and ionic. Studies of this nature have been carried out in the systems PE–4-vinylpyridine, PE–AN, and PE–styrene.[163] On the thermomechanical curves of PE with 4-vinylpyridine and AN grafted on by a radical mechanism, the flow temperature of the copolymer occurred 17–20 K below that in samples grafted on by an ionic mechanism. Kabanov et al.[163] relate this difference to the higher molecular weight of chains grafted by an ionic mechanism and hence to a stronger interaction between the graft chains. The differential thermal analysis curves of graft copolymers of PE–polystyrene and PE–polyacrylonitrile obtained by different mechanisms do not reveal any significant differences.

In recent years there has been an increase in studies relating a determination of the characteristic of the fundamental stages of radiation polymerisation of monomers adsorbed on the surface of solids, their relationship to the nature of the adsorption of the reactants, and also with the structural features of polymer chains that are formed on the surface of a solid.[71,176–188] A detailed survey of studies on this topic published up to 1984 is given in a review.[71] A considerable number of the studies were conducted on systems with a "weak bond", for which the heat of absorption values were 30–90 kJ $mol^{-1}$. The adsorption itself is non-localised and reversible in nature and is characterised by a high monomer mobility. Silica (different samples of Aerosil) was used most frequently as the solid matrix and vinyl acetate or MMA were used as monomers. The experiments were carried out at a low concentration of adsorbed monomer, corresponding to one or two monolayers. The initiation rates, the lifetimes of the kinetic curves, and other kinetic parameters of the radical polymerisation of monomers on the surface of silica during radiation initiation were successfully determined in a series of studies.[176–182] The main difficulty was to make a reliable measurement of the initiation rate values and the lifetimes of the kinetic polymerisation chains. Three different methods were used to determine the initiation rates; the results of these are in quite good agreement with each other: 1) determination of the duration of the induction period of polymerisation when an effective non-adsorbing inhibitor such as gaseous oxygen is used: 2) a kinetic method based on the use of expressions from the theory of radical polymerisation which relate the average degree of polymerisation to the kinetic parameters of the process; 3) a method based on the determination of the number of resulting polymer molecules in systems with a low efficiency constant for non-degenerate chain transfer. The lifetimes of the kinetic polymerisation chains were determined from measurements of the length of the initial non-stationary temperature gradient, with the adiabatic temperature gradient method, which essentially involves measurement of the degree of heating of a sample from the heat evolved during polymerisation, being used most frequently.[177–180] Comparison of the kinetic parameters of the radiation polymerisation of vinyl acetate and MMA on the surface of Aerosil and methylated Aerosil containing no hydroxyl groups with the kinetic parameters of radiation liquid-phase polymerisation as reported by Bruk[71] showed that the rate constant for growth decreases approximately by a factor or ten on going from liquid-phase polymerisation to polymerisation on the surface, whereas the rate constant for quadratic termination decreases by a factor of more than $10^3$. This results from the diffusion nature of the termination constant and the sharply reduced translational mobility of macroradicals on a surface compared with the gas phase.

On going to systems with a "strong bond", for which localised activated adsorption that is irreversible at room temperature is typical (for example, the adsorption of AA on aminated Aerosil, 4-vinylpyridine on carboxyethylated Aerosil and on Aerosil in the presence of water), as are values of the heat of adsorption of 100–200 kJ $mol^{-1}$ and a low surface mobility of the monomers, a decrease in the rate of growth of chains was recorded because of the strengthening of the adsorptive bond between monomer molecules and the surface of the solid.[183]

A study of the principal mechanisms of radiation adsorptive polymerisation with an increase in thickness of the adsorption layer[184,185] revealed an extremal dependence of the rate of polymerisation on the thickness with a maximum at about four monolayers. It was shown that the rate of initiation decreased with an increase in filling while the rate constant of growth increased rapidly, reaching values typical for mass polymerisation in the region of five to seven monolayers. In a layer of thickness 10–15 monolayers, the rate constant of linear termination was similar to the constant typical for a monolayer, while the rate constant for quadratic termination was approximately 500 times less than that for mass polymerisation.

The conformational features of macromolecules formed by radiation adsorptive polymerisation have been studied.[186–188] It was shown that in systems with a "weak bond" graft macromolecules are formed in conformations that are considerably extended along the surface and can be represented by a model of two-dimensional bundles on the surface. The proportion of units of chains directly synthesised on the surface that are bound to the surface is usually 10–20% higher than in macromolecules adsorbed from solution.

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In the summary of this review it may be concluded that definite progress has been achieved during recent years in the development of methods of radiation graft polymerisation, in studying the mechanism of the processes that occur, and also in the practical application of radiation grafting as a method for modifying polymer materials. At the same time the theoretical principles of improved properties of polymer graft materials have not been sufficiently developed. This mainly relates to the question of the dependence of the physicochemical properties of radiation grafted polymer materials on their structure, the most important component of which is the nature of the structural units formed by macromolecules of the graft polymer and the nature of their localisation in the matrix of the main polymer. In our opinion, in studying this question it is to be expected that fundamentally important new results relating to the solution of problems concerning the preparation of polymer materials with required physicochemical properties will be obtained.

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