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The Radiation Polymerisation of Monomers Adsorbed on Solid Surfaces

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The present state of the study of the processes involved in the polymerisation, initiated by radiation, of monomers adsorbed on solid surfaces has been examined. Particular attention has been paid to the results of work on the quantitative description of the elementary stages of polymerisation on a surface.
The bibliography contains 97 references.

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I. INTRODUCTION

The processes involved in the polymerisation of monomers adsorbed on solid surfaces have attracted considerable and increasing attention from research workers in the last 20 years. Interest in these reactions is due chiefly to their possible use for the solution of a number of practical problems. These processes are potentially convenient for modifying the surface properties of various solids (in particular mineral fillers, pigments, and chromatographic sorbents) and obtaining new materials (graft polymer fibres, films, and membranes, organic and mineral–organic ion-exchange materials, textile materials of various kinds, etc.).[1-4] In recent years there has been considerable interest in these reactions in connection with the problems of obtaining composite materials by polymerisation filling[5-7] and encapsulation.[8,9] The investigation of the characteristic features of the elementary stages of the polymerisation of monomers on a surface, and their relationship to the nature of the adsorption interaction of the monomers and polymers and the nature and actual structure of the solid support, is undoubtedly of independent scientific importance.

These reactions are initiated using special initiators,[10-14] ultraviolet radiation,[15,16] the mechanochemical method,[17] or an electric discharge.[18] Forms of ionising radiation, namely gamma-rays, X-rays, and fast electrons, are extremely convenient and are widely used in research practice. The processes of radiation-initiated polymerisation on a surface have now probably been most extensively studied. The examination of these processes is the main subject of the present review, which deals chiefly with the reactions involved in the radiation polymerisation of monomers on the surface of inorganic solids in adsorption systems of the "open" type. Polymerisation in clathrate complexes and inclusion compounds, which may be called adsorption systems of the "closed" type, was examined in Refs.19–22.

The topics examined in the present review have been dealt with to some extent in a number of review papers.[1,5,23,24] They have been examined most systematically (from data published up to 1972) in Ref.1; a fairly extensive bibliography is given in Ref.23. All these papers analyse chiefly the overall kinetic relationships for the processes involved in polymerisation on a surface. This is mainly due to the fact that studies of the mechanism and characteristics of the elementary stages in these reactions have been carried out only in recent years. In the present review, particular attention is paid to the results of studies of the elementary stages of the polymerisation. It may be noted that many of the conclusions about the characteristics of the elementary stages of radiation polymerisation on a surface, in particular the reactions of chain growth, transfer, and termination, also apply when other methods of initiation are used.

The reactions examined in the present review are described in the literature in different ways: polymerisation at a "gaseous monomer–solid" interface, grafting from the vapour phase or gas-phase graft polymerisation, polymerisation in adsorption layers, thin-layer polymerisation, etc. All these terms essentially refer to systems consisting of a solid, a monomer adsorbed on its surface (at different degrees of surface coverage, from fractions of a monolayer to tens and hundreds of monolayers), and the vapour of the monomer, present in equilibrium. The present review deals chiefly with systems in which a strong specific interaction between the polymerising group (the C=C bond) of the monomer and the solid (characteristic, in particular, of heterogeneous-catalytic polymerisation) does not take place. In most systems the main contribution to the adsorption interaction with the surface is made by the substituent at the double bond.

II. GENERAL REGULAR FEATURES OF POLYMERISATION ON A SURFACE

1. The Nature of the Active Centres of Polymerisation

The processes involved in radiation polymerisation on a surface have been studied chiefly in the temperature range from −50 °C to +100 °C. Under these conditions, both ionic and radical polymerisation chains may develop.

a) Ionic polymerisation

The irradiation of solids may lead to the production on their surface of various ionic active centres, whose lifetime is usually much greater than that of the ionic active centres in liquid monomers. This fact increases the probability of the development of ionic polymerisation chains on the surface. Unfortunately, there have been comparatively few studies of the processes involved in ionic radiation polymerisation on a surface.

It has been established[25-29] that in the polymerisation of styrene (ST) on various silicon dioxide specimens, the process takes place by cationic and radical mechanisms simultaneously. The polymerisation was carried out at temperatures close to room temperature, in comparatively thick adsorption layers (5–7 monolayers). The proportion of polymer formed by the cationic mechanism increases with increase in the quantity of aluminium impurity in the SiO_2. In specimens containing 10^{-2}–10^{-3}% aluminium, this proportion is 60–80%; at an aluminium concentration of ~1%, practically all the polymer is formed by the cationic mechanism, and, other conditions being equal, the rate of the process is several times that in the absence of impurity.[28] The mechanism of polymerisation in these systems was established by analysing the molecular mass distribution (MMD) of polystyrene (PST) formed under different conditions, including the use of inhibitors of different kinds. The molecular masses (MM) of the PST obtained by the radical mechanism are 10^5–10^6, and those for the cationic mechanism 10^3–10^4. In agreement with this, the gel-chromatograms of the PST show clearly defined bimodal character. The formation of low-molecular-weight PST is inhibited by ammonia, and that of high-molecular-weight PST is inhibited by benzoquinone.[26] The total activation energy of the cationic polymerisation of ST on silica gel is close to zero, and the kinetic order of the reaction with respect to the dose rate is ~0.7 (in the range 0.03–3 Gy s^{-1}).[27] Most of the cationic PST (~90%) is not grafted to the silicon dioxide surface. The radiation-chemical yield of the cationic polymerisation is ~10^4.

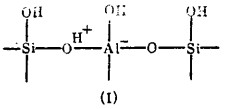
Similar results on the polymerisation of ST on SiO_2 were obtained in Refs. 30–32. In an earlier paper,[33] however, a radical mechanism was proposed for the radiation polymerisation of ST on Degussa aerosil.

The low molecular masses of the cationic PST quoted in Refs. 25–29 are attributed chiefly to non-degenerate chain transfer to the silicon dioxide surface, and in Refs. 30–32 chiefly to effective chain transfer to the monomer. The two factors can apparently play a definitive role. It should be borne in mind, however, that the relative constant for chain transfer to the monomer in the cationic polymerisation of ST in the liquid phase is extremely high ($C_m \cong 2 \times 10^{-2}$ [34]); thus in polymerisation on a surface, chain transfer to the monomer alone may lower the MM of the cationic PST to the values observed experimentally.

In the analysis of the probability of the development of ionic chains in the polymerisation of a given monomer on a surface, it is necessary to take into account, in addition to other factors, the possible drying action of the solid on the system, due to the strong adsorption bonding of water.

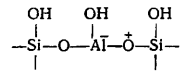
The low-temperature radiation polymerisation of isobutene (IB) on silica gel (SG) has been studied.[35-37] The EPR spectrum of the IB–SG system, irradiated at −196 °C and −78 °C, indicates the presence of terminal polymer radicals $\sim\!-CH_2-\dot{C}(CH_3)_2$, showing that polymerisation takes place directly at the temperature of irradiation. The inhibiting influence of added methylamine on the yield of the terminal polymer radicals and the polymer indicates a cationic polymerisation mechanism. It is suggested that the terminal polymer radicals are formed as a result of the recombination of the growing cationic polymer chains with an electron liberated from a trap. The yield of these radicals depends on the IB concentration on the SG surface, and this dependence correlates with the concentration dependence of the yield of the polymer, determined gravimetrically after the temperature of the irradiated specimens had risen. In the region of the maxima on the two curves, corresponding to monolayer covering of the surface, the radiation-chemical yield of terminal polymer radicals at −196 °C is 1.5; the radiation-chemical yield of the inhibition of the polymerisation G_{in} was estimated by assuming that the number of these radicals is equal to the number of initiated polymerisation chains. It is important to note that the average number of polyisobutene macromolecules formed, determined from the values of the viscosity-average molecular masses ($M_\eta \cong 5000$), was found to be appreciably greater than the number of polymer radicals (by a factor of ~30), from which the authors correctly conclude that chain transfer reactions take place effectively during the polymerisation.

The following views were put forward[35-37] regarding the mechanism of chain initiation and transfer in the polymerisation of isobutene on silica gel. It is assumed that both processes are associated with the existence on the SG surface of Bronsted acidic centres, localised close to impurity aluminium atoms in tetrahedral configuration



(I)

The protons of these centres cannot initiate polymerisation in the absence of irradiation, since they compensate the negative charge of the aluminium atoms. On γ-irradiation, paramagnetic centres are formed in SG,[38] of the type



in which the hole is localised on an oxygen atom adjoining an aluminium atom. The proton of this centre is liberated, and can either capture an electron and be stabilised as a hydrogen atom, or add on to an IB molecule and form the carbonium ion $(CH_3)_3C^+$, which brings about polymerisation. The probable participation of the acidic surface centres of SG in the initiation of polymerisation is indicated by the fact that decrease in the acidity of the SG by preliminary treatment with alkali leads to a marked decrease in the yield of polyisobutene.[36]

It is suggested that the main contribution to the mechanism of chain transfer is made by the reaction of the growing macro-cations with the acidic centres of the SG surface of type (I), as a result of which the macro-cation neutralises the charge on the aluminium, and the liberated proton, by reacting with a monomer molecule, starts a new polymer chain. In the opinion of the authors,[35-37] the polyisobutene macromolecules are also formed as a result of the mutual recombination of terminal polymer radicals.

The results of studies of the radiation polymerisation of liquid monomers in the presence of various solid oxides,[39-44] examined in detail in Ref. 39, are relevant to the subject of the present review. These studies were generally carried out under conditions in which the liquid monomer was poured over a layer of solid oxide powder; the concentration of the monomer was 40–80 mass %. In these studies, chiefly in work carried out in the Karpov Physicochemical Scientific

Research Institute,[39-41] the idea of a correlation between the semiconducting character of the oxides and the mechanism of polymerisation was put forward. It was shown that the *n*-type (electronic) semiconductors ZnO, TiO_2, and Cr_2O_3 facilitate the development of cationic chains, and the *p*-type (hole) semiconductors MgO, Cu_2O, and NiO the develpment of anionic polymerisation chains.

b) Radical polymerisation

Most studies carried out up to the present have dealt with monomer–support systems in which radiation polymerisation on the surface develops chiefly by a radical mechanism.[1,9,45,46] A radical mechanism of polymerisation is proved using data on the influence on the process of typical radical inhibitors (diphenylpicrylhydrazyl, O_2, benzoquinone) [33,45]† and data on the compositions of the copolymers and the kinetics of copolymerisation on a surface,[47,49] and on the micro-structure of the polymer chains formed.[47] Thus the processes involved in radical polymerisation on a surface have been studied in most detail. Subsequently, unless otherwise stated, radiation polymerisation by a radical mechanism is discussed.

2. The Adsorption Mechanism of Polymerisation

One of the first questions arising in the analysis of the mechanism of polymerisation on a surface, as in the analysis of other surface reactions, is the question of whether this reaction takes place by an "adsorption" mechanism or by a "collision" mechanism. In the first mechanism, the monomer molecules are adsorbed, migrate over the surface, and finally are added on to the active centre situated on the surface (the active terminal unit of the growing chain); the "working" concentration of the monomer is its concentration in the adsorption layer. In the second mechanism, the acts of chain growth take place when monomer molecules from the vapour phase collide directly with the active centre; here, the "working" concentration is the monomer concentration in the vapour phase.

The mechanism of polymerisation was a subject of discussion in the mid-sixties. In Refs.33, 45, and 46 it was concluded from overall kinetic data that polymerisation on a surface takes place by an adsorption mechanism. The main evidence was the decrease in the rate of polymerisation with increase in temperature at a constant monomer vapour pressure. The collision mechanism of polymerisation was developed in Refs.16, 50, and 51. In the opinion of these authors, this temperature dependence of the rate of polymerisation may be due to the destruction of active centres with increase in temperature, and a corresponding decrease in the rate of initiation of polymerisation.[50]

The results in Refs.9, 47, and 53–55 apparently prove that polymerisation takes place by an adsorption mechanism in the systems studied. The dependence of the rate constants of chain growth k_g on the mechanism of adsorption and on the nature of the adsorption bonding between the monomer and the support, observed in these studies, can be understood only by assuming an adsorption mechanism of polymerisation. For example, as established in Refs.47 and 54, the change in the heat of adsorption of vinyl acetate (VA) on AS/400# in the range of coverage of about half a monolayer is accompanied by a fairly sharp (several-fold) change in k_g. An important feature is that this change in k_g at different temperatures (20 °C and 50 °C) takes place in approximately the same range of coverage, whereas the pressures in the vapour phase, corresponding to this range of coverage, differ by a factor of more than 20.

If the calculations are carried out using as working concentration the surface concentration of adsorbed monomer σ, the temperature dependence of the value of k_g for radical polymerisation is described by the Arrhenius equation with "normal" values of the activation energy of growth E_g.§ Similar calculations using the concentration of the monomer in the vapour phase give negative or anomalously low values of E_g.

In later papers on polymerisation on a surface from the vapour phase,[16,50,51] the authors conclude that polymerisation takes place by an adsorption mechanism.[52]

3. Thermal and Diffusion Processes Accompanying Polymerisation on a Support

For a correct analysis of the kinetics of polymerisation on a surface, it is necessary to estimate correctly the role of macrokinetic factors, such as, in particular, the possible non-isothermal nature of the process and the diffusion retardation in the transport of the monomers in real adsorbent specimens (porous granules, tablets, layers of powder, etc.). Unfortunately, in many papers these factors are not properly analysed.

When the dose rate is not too high, the heating of the specimens in the radiation field, not associated with polymerisation, is usually insignificant. At dose rates of 1–10 Gy s^{-1}, it generally does not exceed fractions of a degree. In the analysis of the possible non-isothermal nature of the system resulting from the heat liberated on polymerisation, it must be borne in mind that although the reaction zone usually makes up only a small fraction of the total volume of the specimen, a significant increase in temperature is possible, because of the low thermal conductivity of the specimens. For specimens of silicon dioxide in the form of tablets or powder with a specific surface of ~200 m^2 g^{-1}, a layer porosity of 80–90%, and characteristic layer dimensions of 0.5–1 cm, the increase in temperature as a result of the polymerisation of MMA and VA for monolayer coverage of the surface and dose rates of the order of 1 Gy s^{-1} is 1–10 K.[56] The increase in temperature increases considerably with increase in the degree of coverage of the surface by the monomer.

The correction to the stationary rate of polymerisation v_{st}, taking account of the increase in temperature, in the case of experiments in a closed system with a small vapour phase volume ("without maintenance") can be calculated from the expression[57]

$$v_{st}/v_{st,0} = \exp\left[-\frac{E}{R}\left(\frac{1}{T_0+\Delta T_\infty}-\frac{1}{T_0}\right)\right] \simeq 1+\frac{E}{RT_0^2}\Delta T_\infty$$

†Because of the decrease in the "activity" of most inhibitors on a surface,[48] the quantities of inhibitor which are effective are much greater than the stoichiometric quantities.

#Here and subsequently, AS/200, AS/400, etc. denote aerosils treated in a vacuum at 200 °C, 400 °C, etc.

§Thus for example the values of E_g for the polymerisation of VA and methyl methacrylate (MMA) on an aerosil at a monolayer coverage of the surface by monomers are 17 kJ $mole^{-1}$ and 32 kJ $mole^{-1}$ respectively.[55]

where T_0 is the temperature of the thermostat, ΔT_∞ the stationary increase in temperature, E the total activation energy of the process, and $v_{st,0}$ the stationary rate under isothermal conditions. The quantity ΔT_∞ is related to the effective heat of polymerisation $-\Delta H_{eff}$ by the expression

$$\Delta T_\infty = \frac{-\Delta H_{eff}}{c} \frac{v_{st}}{a}$$

where c is the heat capacity of the system, and a an experimentally determined parameter characterising the rate of removal of heat from the specimen.

It is more difficult to take account of possible non-isothermal character in experiments in an open system "with maintenance", when an increase in the temperature of the specimen leads to a decrease in the equilibrium concentration of the monomer on the adsorbent; it is then necessary to solve simultaneously the equations for the kinetics of polymerisation, adsorption, diffusion, and thermal conductivity.

The influence of diffusion retardation in the layer of adsorbent on the stationary kinetics of polymerisation can be examined further. When the polymerisation is carried out under conditions in which the formation of the polymer produces a diffusion flux of the monomer in the specimen, the influence of diffusion retardation on the observed stationary rate of polymerisation (v_{st}) is revealed by a deviation of the distribution of the monomer concentration $\sigma(x)$ along the cross-section of the specimen from the equilibrium distribution, leading to a decrease in the observed rate of polymerisation, which starts to depend on the specimen thickness L. In those cases where the average decrease in the monomer concentration $\overline{\Delta\sigma}$ in the specimen is small compared with the equilibrium adsorption σ^*, the rate of polymerisation can be taken as approximately constant over the cross-section of the specimen. $\sigma(x)$ is then described by a simple parabolic law, and $\overline{\Delta\sigma}$ is given[56] by the expression:

$$\overline{\Delta\sigma} = v_{st}L^2/12D_{eff}$$

where D_{eff} is the effective diffusion coefficient of the monomer in the specimen. The coordinate x is measured from the centre of the specimen. The magnitude of the deviation has been analysed,[56] and it was shown, in particular, that in the polymerisation of VA, MMA, and ST on aerosil tablets with a thickness of ~2 mm, compressed at a pressure of 300 kg cm^{-2}, for degrees of coverage by the monomer of about one monolayer, a temperature of 50 °C, and a radiation dose rate of 0.35 Gy s^{-1}, the value of $\overline{\Delta\sigma}$ does not exceed 10% of σ^*.

In the case of polymerisation at low concentrations of adsorbed monomer, however, when it is necessary to carry out the reaction to degrees of conversion close to or greater than σ^*, the influence of diffusion retardation on the observed rate of polymerisation may be considerable. Decrease in the monomer concentration leads to a marked decrease in the value of D_{eff}, and this in turn also increases the influence of diffusion on the rate of polymerisation at low concentrations. Under these conditions, the dependence of the rate on the coordinate x cannot be neglected, and the distribution of the monomer concentration over the cross-section of the specimen for linear termination of the kinetic chains is described by the expression:[58]

$$\sigma(x) = \sigma^* \frac{\mathrm{ch}\{[(k_g/k_x)(v_i/D_{eff})]^{1/2}x\}}{\mathrm{ch}\{[(k_g/k_x)(v_i/D_{eff})]^{1/2}(L/2)\}}$$

where v_i is the rate of initiation, k_g the chain growth rate constant, and k_x the rate constant for linear termination. The observed rate of polymerisation is proportional to $1/L$.

4. Overall Kinetics of Polymerisation

The influence of the support on the rate of polymerisation of monomers on a surface can be examined first. Table 1 gives the values of the radiation-chemical yields for polymerisation in various systems, calculated from published data.[32,47,56] A noteworthy feature is the high values of the polymerisation yields calculated per unit of energy absorbed by the adsorbed monomer, G^*_{pol}; they are much greater than the values for the polymerisation of the same monomers in the bulk.¶ Similar results were obtained in other studies (see Ref. 1). Thus for a number of systems, the supports have an appreciable accelerating action on polymerisation. The mechanism of this action will be examined below.

Table 1. Some overall kinetic characteristics of the radiation polymerisation of monomers on a surface (coverage of the surface by monomers about one monolayer, temperature 50 °C, dose rate 0.35 Gy s^{-1}).[32,47,56]

Monomer	Adsorbent	n_i^*	$10^{-4}\,G_{pol}$	$10^{-4}\,G^*_{pol}$	$10^{-4}\,G^b_{pol}$
VA	AS/400	1	0.7	12	3.5**
VA	AS/700	1	0.6	10	3.5**
VA	AS/900	0.8	—	—	3.5**
VA	MAS***	0.5	2.0	120	3.5**
MMA	AS/400	1	0.6	10	0.9
MMA	AS/200	1	1.0	15	0.9
MA	AS/400	1	2.6	43	7**
BMA***	AS/400	0.8	0.3	5	0.6
ST	AS/400	0.7	0.3	10	0.04**

Notes. The specific surface of the adsorbents is ~200 m^2 g^{-1}. The polymerisation of all the monomers except ST takes place by a radical mechanism; the polymerisation of ST takes place by caticnic and radical mechanisms simultaneously on an aerosil surface, and by a radical mechanism in the bulk. Notation: G_{pol} and G^*_{pol} are the radiation-chemical yields of polymerisation on a surface, calculated per 100 eV of energy adsorbed by the entire system and by the monomer respectively; G^b_{pol} the radiation-chemical yield of polymerisation in the bulk ("in the mass") in the initial stages; MA = methyl acrylate; BMA = butyl methacrylate.

*Dose rate range studied 0.05–5 Gy s^{-1}.
**Calculated from published data.[95]
***Methylated aerosil; specific surface ~60 m^2 g^{-1}.
****Temperature 25 °C.

Analysis of the available data shows (see for example Table 1) that in polymerisation on a surface, in contrast to processes in the liquid phase, linear termination of the kinetic chains is observed extremely frequently (the order for the dependence of the reaction rate on the irradiation dose rate, $n_i = 1$); the reasons for this will be examined below.

¶ The values of G^*_{pol} are proportional to the relative or reduced rate of polymerisation v/σ, expressed as fractions of the original quantity of the monomer on the surface in unit time (for example in s^{-1}).

The specific mechanisms of linear termination may be different in different systems. For the polymerisation on an aerosil of vinyl acetate and various other monomers with highly active growing radicals, the mechanism apparently involves degenerate chain transfer to the hydroxide groups of the surface and the formation of radicals whose activity is much lower than that of the growing macro-radicals; kinetically, this appears as chain termination.[47,59] This mechanism is confirmed, in particular, by the fact that with decrease in the concentration of hydroxide groups on the aerosil surface, for example as a result of an increase in the temperature of treatment to 900 °C, the rate of termination in the polymerisation of VA decreases, and n_i deviates from 1 towards lower values.[56] On a methylated aerosil not containing hydroxide groups, $n_i = 0.5$, that is quadratic termination of the kinetic chains takes place.[47] A similar mechanism of termination has been assumed[33] for the polymerisation of MMA on an aerosil; with increase in the quantity of polymer formed on the surface, n_i decreased from 1 to 0.5.

Chain termination associated with the occlusion of the growing macro-radicals is apparently fairly common. Complete "burial" of the growing active centre is not essential. A sufficiently marked decrease in the specific growth rate, due to a decrease in the local concentration of the monomer close to the active centre, will appear kinetically as chain termination. As an experimental indication of the role of occlusion phenomena in chain termination, data[60] on the radiation polymerisation of acrylonitrile (AN) on alumina fibres can be considered. n_i changes from 0.5 to 1 on going from the non-porous to the fine-porous fibre. An occlusion mechanism has been proposed for the deactivation of the growing macro-radicals in the polymerisation of acrylic acid on kaolin.[61] An occlusion mechanism of chain termination in the polymerisation of AN on KSK-2 silica gel was established by EPR.[62] Post-polymerisation and EPR methods have shown that in the polymerisation of MMA on an aerosil at a temperature of 25 °C, kinetic termination of all the growing radical chains is not accompanied by chemical destruction of the macro-radicals; for reasons which are not yet completely clear, the growing macro-radicals at a definite moment undergo occlusion immobilisation, as a result of which the specific growth rate decreases by a factor of ~300; with increase in the temperature of the system (for example to 70 °C), "reanimation" of the kinetic chains is observed.†

There are probably several forms of occlusion, for example: 1) self-occlusion of the chains in the fine pores as a result of the covering of the transport "windows" of the pores as chain growth proceeds; 2) occlusion in pores with small windows (particularly in dead-end pores), taking place as a result of the growth of other chains, which prevent the transport of the monomer into the pore; in this case, as noted by Kabanov (see Ref.1), n_i may be less than 1. It is more difficult to picture the occlusion immobilisation of a macro-radical growing on an open surface. In some systems with extremely weak adsorption interaction of the units of the macromolecule with the surface, deactivation of the macro-radical may take place as a result of a conformational change ("collapse") from an unfolded chain to a compact globule with localisation of the active centre inside the globule. The actual mechanism of the occlusion termination of the growing chains in polymerisation on the surface of solids has not been established for any system.

†See E.Ya.Yunitskaya, Candidate's Thesis, Karpov Physicochemical Scientific Research Institute, Moscow, 1986.

Linear termination of the growing radical chains on impurities, for example iron ions, is also possible. As far as the mechanism of the quadratic termination of polymerisation chains on a surface is concerned, it is possible that, because of the obvious retardation of the thermal diffusion of the macro-radicals on the surface (see also section V), in some systems a "reactive" or "chemical" mechanism of diffusion will predominate, where the meeting of the growing active centres and their disappearance take place as a result of their movement over the surface during the actual growth reaction.

Study of the temperature dependence of the rate of polymerisation has shown that the corresponding activation energy E_{tot} in different systems varies from 0 to 40 kJ mole^{-1}, and usually decreases with increase in the degree of covering of the surface by the monomer.[55,63] The latter is related[55] to the corresponding decrease in the activation energy of polymerisation chain growth E_g (see section V and Table 3).

High kinetic orders of the polymerisation with respect to the concentration of the adsorbed monomer have been noted.[1,64] The authors cited relate these results to the formation of associates of the monomers on the surface of the support. These results, however, are fully covered by the general concept based on the dependence of the chain propagation rate constant on the nature of the adsorption bonding and also on the degree of covering of the surface by the monomer and the thickness of the adsorption layer; this concept is developed below (see sections V and VI).

III. MOLECULAR AND STRUCTURAL CHARACTERISTICS OF THE POLYMERS FORMED

1. Structural and Conformational Characteristics of the Macromolecules and Their Distribution on the Surface

The structure of the macromolecules formed and their distribution on the support in relation to the processes of radiation polymerisation on a surface has been the subject of special study only in recent years. The molecular mass distribution of the polymers formed in the polymerisation of ST and MMA on silica gels has been studied[25–29,65,66] by gel-permeation chromatography (GPC). The polymerisation was carried out at extremely high monomer concentrations and degrees of conversion. The results were used chiefly for the separate determination of the yields of radical and ionic, grafted and non-grafted polymers. The fraction of grafted PST is very low (15–20%), whereas for polymethyl methacrylate (PMMA) this fraction is 70–80%. Under the conditions studied, ST was polymerised chiefly by a cationic mechanism, and MMA by a radical mechanism. The proportion of grafted PST is higher if the polymerisation is carried out as a result of the post-effect after preliminary irradiation of the silica gel in a vacuum.[29] The influence of the monomer concentration on the MMD of polystyrene obtained by the radiation polymerisation of ST on silica gel has been examined.[31] GPC has been used[67] to study the molecular characteristics of PST formed by the radiation polymerisation of ST in the porous structure of wood.

In the initial stage of the polymerisation of vinyl acetate on aerosil (at degrees of conversion up to one third of an effective monolayer), linear macromolecules are formed, and $\overline{M}_w/\overline{M}_n \cong 2$.[68] On further polymerisation, effective branching of the macromolecules and marked broadening of the MMD take place. In the range of degrees of conversion from one third

to two thirds of a monolayer (irradiation dose 0.3–0.6 kGy), the width of the MMD increases by a factor of ~3, and the degree of branching by a factor of 2.5. It is suggested that these changes are related to radiolysis of the polymer and chain transfer to the polymer.

Infrared spectroscopy has been used to study the conformational characteristics of the polymers formed in the polymerisation of VA and MMA on aerosil (AS/400 and AS/200), before their separation from the surface.[47,56] It was shown that a fairly high proportion of the units of the PVA and PMMA formed are joined to the aerosil surface by hydrogen bonds (between the CO groups of the polymers and the OH groups of the surface). The proportion of units bonded to the surface increases, in particular, with decrease in the monomer concentration σ at which the synthesis is carried out, and is 70–80% at a concentration lower than one quarter of a monolayer. This indicates that the macromolecules formed under the given conditions have unfolded conformations. If the polymerisation is carried out at high concentrations of the adsorbed monomer (several monolayers or more), the PMMA molecules on the surface apparently have the form of a non-planar coil.

The micro-structure of the macromolecules formed by polymerisation on a surface has been studied by high-resolution ^1H and ^{13}C NMR spectroscopy.[47,56] It was established, in particular, that PVA and PMMA synthesised on an aerosil have an atactic structure, similar to that of the polymers obtained by radical polymerisation in the liquid phase. At the same time, the PMMA obtained at low degrees of covering of the surface by the monomer (approximately one quarter of a monolayer) contains a higher proportion of isotactic triads.[56] This is apparently due to the stronger adsorption bonding of both the monomer and the polymer to the surface, and to the more rigid stereochemical control of the acts of chain growth at low values of σ. Poly-n-butyl methacrylate synthesised on an aerosil also contains a higher proportion of the isotactic structure than the liquid-phase radical polymer.[9]

The nature of the distribution of the resulting polymer on the surface is of considerable interest, particularly from the practical viewpoint. A number of authors report that this distribution is markedly non-uniform. In a study of the polymerisation of MMA and ST on MgO and an aerosil, it was concluded from kinetic data that more or less complete "overgrowth" of the surface of the support by the polymers takes place on the formation of 3–6 effective monolayers of the polymers on the aerosil, and 10–20 on MgO.[1,33]

The nature of the distribution of the macromolecules of PST, PMMA, and polyacrylonitrile (PAN) grafted to an MgO surface as a result of radiation polymerisation of the monomers from the vapour phase has been studied.[69,70] The size distribution of the MgO particles was studied by sedimentation in a hydrocarbon medium; the adsorption on the magnesium oxide powders of stearic acid, which can undergo irreversible adsorption on the non-modified regions of the MgO surface, and other characteristics, were also studied. The measurements showed that with increase in the quantity of grafted PST (from 1 to 25 effective monolayers), the aggregates of MgO particles in toluene gradually break down, since the surface of individual MgO particles becomes organophilic. The characteristic size of the aggregates changes from 20 μm to 0.5 μm; the size of an individual MgO particle is 0.01–0.1 μm, that is breakdown of the aggregates is still not complete. Even for the maximum quantity of grafted PST, approximately one third of the MgO surface is not covered by the polymer and retains its ability to absorb stearic acid. A similar picture is observed in the grafting of PMMA and PAN.

It was concluded[69,70] that the radiation grafting of the macromolecules on the surface of mineral carriers is "mosaic" in character. This was attributed to non-uniformity of the original surface; it was assumed that on the surface there are regions on which adsorption and hence polymerisation of the monomers does not take place. In Ref.1, the non-uniformity of the distribution of a grafted copolymer is related to the higher rate of initiation of grafting to the polymer already formed on the surface, compared with the original support. Further studies are required to obtain a more definite answer to the question of the reasons for the non-uniform distribution of polymers on a surface. In all cases, however, in the analysis of this question it is necessary, in particular, to take account of the actual conformation of the macromolecules on the surface.

2. The Efficiency of the Grafting of Macromolecules to a Surface

Even in the earliest papers on the "approach" radiation grafting of polymers from the vapour phase (see Ref.1), attention was drawn to the fact that this method, unlike grafting from the liquid phase, usually gives a very small quantity of homopolymer, indicating that the grafting of the macromolecules has a high efficiency. According to these data, the quantity of non-grafted polymer usually did not exceed 5% of the total concentration of polymer. These results were related to the fact that under the experimental conditions used in these studies (at a fairly low concentration of monomer on the surface), most of the active centres initiating polymerisation are produced from the material of the support, and this may lead to the production of a covalent bond between the macromolecules formed and the support at the initiation stage. It has also been suggested[1,45] that the low-molecular-weight radicals formed in the system on irradiation are unable to initiate polymerisation before their transfer to the vapour phase and disappearance, since the time for which they are present in the adsorbed state τ_a is small compared with the characteristic time of the act of polymerisation chain growth τ_g

$$\tau_a \ll \tau_g \qquad (1)$$

It was subsequently established,[26,65,71] however, that the quantity of non-grafted polymer is usually much greater than indicated in the early studies, although it is sufficiently less than that for grafting from the liquid phase. In the polymerisation of VA, AN, and MMA on an aerosil it amounts to 10–50% of the total quantity.[71] In the analysis of these results it must be borne in mind that in most experiments, relationship (1) apparently is not fulfilled. Because of the porosity of real adsorbent specimens (layer of powder, porous tablet, etc.), the total time for which the low-molecular-weight radical is present in the adsorbed state during its diffusion over the specimen to the point of possible disappearance (τ_a^{Σ}), because of repeated re-adsorption on the pore walls, is usually greater than τ_g. Thus most of the low-molecular-weight radicals are able to take part in the polymerisation on the surface.[71]

The total time for which the diffusion species is present in a real specimen can be described by the relationship:[72]

$$\tau_D = l^2/3D_{eff}$$

where l is half the thickness of the specimen. In typical systems with weak bonding, D_{eff} for the monomer molecules is 10^{-3}–10^{-5} cm^2 s^{-1}.[73] For low-molecular-weight radicals such as the radicals of chain transfer to the monomer and similar radicals, D_{eff} is usually of the same order of

magnitude. In most experiments on polymerisation, the fraction of the surface diffusion flux of the monomer in the specimen is fairly high relative to the total,[73] so that τ_a^{Σ} is close to τ_D. Estimation of τ_a^{Σ} for the low-molecular-weight radicals which chain transfer to the monomer in the polymerisation of vinyl acetate on an aerosil (specimen in the form of a tablet with thickness 2 mm and porosity ~80%) gives the value ~10 s (for $\tau_a \cong 10^{-4}$ s), whereas $\tau_g \cong 10^{-2}$ to 10^{-1} s.[55,73] Naturally, the situation must be evaluated separately in each specific case with allowance for the above considerations.

In the analysis of experimental results from the viewpoint of the efficiency of grafting, account must be taken of a number of additional features. Thus the efficiency of grafting is determined by treating the specimens, after polymerisation, with solvents to extract the non-grafted polymer from the surface. To obtain correct results it is necessary to make the correct choice of solvent. On the one hand, it is necessary to take account of the fact that the compound used should not only be a good solvent for the polymer but also displaces it effectively from the adsorbent surface.[71] On the other hand, it is necessary to bear in mind the possibility of the hydrolysis, under the influence of the solvent, of the covalent bond between the macromolecule and the support, or hydrolytic rupture of the main chain of the macromolecule.[65,71,74] The hydrolytic instability of the $\geqslant$Si–O–C bond and the stability of the $\geqslant$Si–C bond have been noted.[74]

3. Secondary Reactions in the Polymer Chains Formed. The Radiolysis of Polymers on a Surface

An important characteristic feature of the processes involved in radiation polymerisation is that the macromolecules are subjected to the action of radiation for some time after their formation. Attention has been drawn[65,57,68] to the fact that in polymerisation on a surface, various manifestations of the radiolysis of the polymers are observed for very small radiation doses (less than 1 kGy). In polymerisation in the bulk, secondary radiation reactions in the polymers are usually not observed at such low doses. It has been established[68] that there is effective branching of PVA macromolecules on an aerosil, and marked broadening of the MMD in the dose range ~0.5 kGy. A decrease in the number-average values of the molecular mass was observed for PVA with increase in the polymerisation time at doses of ~1 kGy; it was suggested that this effect is due to the sensitising influence of the support on the radiolysis of the macromolecules. Attention has been drawn[65] to the radiation degradation of PMMA on silica gel at doses of 1.2–5 kGy; it was also concluded that this process is accelerated by the support, although the experimental data obtained by comparing the results of the irradiation of PMMA on a silica gel surface and in a "block", on the basis of which this conclusion was reached, are not completely correct, because of the marked differences in the molecular masses of the PMMA specimens compared. The accelerating action of the support on the radiation degradation of PST in the grafting of ST on wood has been reported.[67]

The special study of the radiolysis of polymers on solid surfaces, including the study of model systems in the absence of monomer, is of considerable interest. The action of radiation on PST deposited and grafted on silica gel has been studied.[75] It was shown, in particular, that radiation degradation of the grafted polymer takes place; the radiation-chemical yield of the ruptures is 2. The presence of the homopolymer suppresses the degradation. When PST is irradiated in a "block", cross-linking of the polymer takes place; $G_{c-l} \cong 0.17$.

Various characteristic features of the radiolysis of polymers deposited on an aerosil and undergoing degradation (PMMA) or mainly cross-linking (polymethyl acrylate, PMA), have been studied.[32]# The polymers were deposited on the aerosil by polymerising the monomers on the surface. The radiation-chemical yield of the ruptures of the main chains of PMMA, G_r^*, determined by measuring the molecular mass of the polymers viscosimetrically and recalculating to unit energy absorbed by the polymer, was much greater for irradiation on the aerosil, compared with the yield of ruptures for the irradiation of PMMA in a "block". When the quantity of polymer deposited on the aerosil is close to an effective monolayer, the value of G_r^* is 5–10 (depending on the conditions of synthesis and hence on the conformation of the macromolecules), whereas for the irradiation of PMMA in a "block", this yield is close to 1. G_r^* decreases regularly with increase in the quantity of polymer on the surface.

The radiation-chemical yield of polymer radicals G_R^* is also much higher for the irradiation of PMMA on a surface. At concentrations of PMMA on the aerosil of ~0.05 and ~0.5 effective monolayer, the initial yield of terminal radicals G_R^*, determined by EPR, has the values ~350 and ~70 respectively, whereas for irradiation of the specimen in a "block", this yield is 3–4. This is due chiefly to the effective transfer of the energy of the radiation, absorbed by the silicon dioxide particles, to their surface and to the polymer adsorbed on it. Similar effects were previously noted in a study of the radiolysis of adsorbed low-molecular-weight hydrocarbons.[76–79]

Another noteworthy feature is that under comparable conditions, G_R^* is much greater than $2G_r^*$. An appreciable proportion of the ruptures of the main chains is apparently localised close to the ends of the macromolecules, and are not detected by measuring the average molecular mass viscosimetrically.

The radiolysis of PMA on an aerosil surface has been studied for specimens containing ~2 and ~4 effective monolayers of the polymer.[32] The original molecular mass of the polymers ($\bar{M}_\eta$) was ~10^7. Irradiation of the specimen in a block leads to effective cross-linking of the PMA; for a dose of 1–1.5 kGy, the concentration of the gel fraction was ~50%. On irradiation on a surface with doses up to 10 kGy, gel formation is not observed, but effective degradation of the macromolecules takes place, and the initial yield is $G_r^* \cong 5–10$. On subsequent irradiation, a gel fraction gradually appears. The dose required for the formation of 50% gel fraction in the polymer on the support is 20–50 times that for the "block". It is suggested that this marked suppression of gel formation when PMA is irradiated on a surface is due to a change in the ratio of the yields of ruptures and cross-linkages in favour of the first process, and also to the characteristic topological features of the specimen (the small thickness of the polymer layer, and its distribution in "islets").

Thus the results indicate that there is a marked increase in the rate of radiation degradation and a change in the direction of the processes involved in the radiolysis of the polymers on the surface of silicon dioxide particles. These

#See also M.A.Bruk, G.G.Isaeva, E.Ya.Yunitskaya, S.A.Pavlov, and A.D.Abkin, Radiat.Phys.Chem., 1986, 27, 79.

results are extremely important, not only for the investigation of the details of polymerisation on a surface but also for the study of the radiation stability of filled polymer materials and their modification by radiation.

IV. THE ADSORPTION AND MOLECULAR TRANSPORT OF MONOMERS ON A SURFACE. SYSTEMS WITH STRONG AND WEAK ADSORPTION BONDING

As noted in section II, radiation polymerisation on a surface usually takes place by an adsorption mechanism. The relation of the characteristic features of the elementary stages of the polymerisation, in particular the reactions of chain growth, to the nature of the adsorption and the surface mobility of the monomers and polymers is therefore a central question in the area being discussed. The analysis of adsorption equilibria and the molecular transport of the monomers in the specimens is also necessary to determine the true concentration of the monomers in the reaction zone.

The equilibrium adsorption of MMA and ST on an aerosil and on magnesium oxide has been studied on a McBain balance.[1] The published conclusion that the adsorption is monomolecular in these systems does not appear fully justified. The heats of adsorption of various monomers on KSK-2 silica gel have been determined calorimetrically.[80,81] The heats of adsorption decrease considerably with increase in the degree of covering of the surface (at degrees of covering less than a monolayer). The equilibrium adsorption of acrylic and methacrylic acids on kaolin has been studied.[61]

The adsorption equilibria, mechanism, and dynamics of the adsorption of a wide range of monomers on silicon dioxide specimens (chiefly aerosil and its modified forms) have been studied in detail.[47,56,73,82] On the basis of the results obtained, the authors cited divide the systems studied into two main groups. In the systems of the first group, the values of the heats of adsorption $-\Delta H_a$ are 30–90 kJ mole^{-1}, and the adsorption is non-localised, reversible, and characterised by a high surface mobility of the monomers. This type of adsorption on SiO_2 is shown by most of the vinyl monomers studied (VA, AN, ST, MMA, tetrafluoroethylene, etc.). These systems were called systems "with weak bonding".

The main adsorption centres on the silicon dioxide surface in these systems are surface hydroxide groups, which form hydrogen bonds with the polar functional groups of the monomer molecules (MMA, AN, VA, etc.) or weak π-complexes with a system of conjugated double bonds (ST). The strength of these adsorption bonds can be characterised to some extent by the magnitude of the displacement of the absorption band of the hydroxide groups of the surface in the region of 3750 cm^{-1} ($\Delta\nu_{OH}$) on adsorption.

In some systems (for example in the adsorption of VA and AN on AS/400), there is a change in the nature of the adsorption of the monomers at a coverage of about half an effective monolayer. In particular, at this degree of coverage there is a decrease in the heat of adsorption, the decrease being particularly marked for VA (~17 kJ mole^{-1}), a marked decrease in the width of the absorption bands in the ^{1}H NMR spectra of the adsorbates, and a displacement of the absorption band of the carbonyl groups of VA in the infrared spectra.[82]

The systems of the second group are characterised by localised activated adsorption, irreversible at room temperature.[56,73] In these systems the strength of the bonds between the monomer molecules and the surface is close to that of chemical bonds. These systems have been called systems "with strong bonding". Of the systems studied by the authors cited above, the following, in particular, are of this type: acrylic acid on an aminated aerosil, 4-vinylpyridine (4-VP) on a carboxylated aerosil, and 4-VP on an aerosil in the presence of water (in these, ionic bonds are formed). When 4-VP and N-vinylpyrrolidone (N-VP) are adsorbed on an aerosil, ionic bonds are not formed, but the stability of the adsorption complexes and the nature of the adsorption differ considerably from those for systems with weak bonding. Systems with strong bonding are characterised by values of the heats of adsorption of 100 to 200 kJ mole^{-1} and an extremely low surface mobility of the monomers.

The above separation of systems with strong and weak adsorption bonding is to some extent arbitrary. A particular system may "move" from one group to the other, for example when there is a marked change in the surface coverage or the temperature. The characteristics of a number of systems have intermediate values. Nevertheless, the proposed classification is useful, chiefly because of the marked differences in the nature of the processes of monomer polymerisation in the systems of the two groups.

The study of the processes involved in the surface molecular transport of monomers is of considerable interest. Here, the analysis of the possible influence of the surface diffusion of the monomers on the observed rate constant for the growth of the polymerisation chains is of fundamental importance. The coefficients of surface diffusion of the monomers D_S have been determined[56,73] for a number of systems with weak bonding (VA–AS/400, MMA–AS/200, MMA–AS/400, ST–AS/200, and VA–MAS). In these systems at temperatures of about 50 °C and degrees of covering of about one monolayer, $D_S = 10^{-5}$–10^{-3} cm^2 s^{-1}. The values of D_S increase rapidly with increase in temperature (the activation energy of surface diffusion decreases with increase in the concentration of adsorbed monomer σ). Within the monolayer, the values of D_S increase significantly with increase in σ, and in some systems (for example VA–MAS) they pass through a maximum.

Thus systems with weak bonding are characterised by high values of D_S for the monomers, close to the diffusion coefficients in non-viscous liquids. In systems with strong bonding, the values of D_S are much lower; for example, for 4-VP on an aerosil, $D_S = 10^{-8}$–10^{-9} cm^2 s^{-1}.

V. THE QUANTITATIVE STUDY OF THE ELEMENTARY STAGES OF RADICAL POLYMERISATION IN SYSTEMS WITH WEAK BONDING

An extremely important step in the determination of the characteristic features of polymerisation reactions on solid surfaces is the measurement of the rate constants for the elementary stages of these reactions. Considerable progress has been made in this field in the last few years. It has been possible to determine the rates of initiation v_i, the lifetimes of the kinetic chains τ, the growth rate constants k_g, and various other kinetic parameters of the radical polymerisation of a number of monomers on a silicon dioxide surface, initiated by radiation.[48,53–56,73]

Isolated attempts to estimate the growth rate constants for radiation polymerisation on a surface had been made earlier. The values of k_g had been calculated[50,51] for the grafted polymerisation of acrylonitrile on nylon fibre from the vapour phase using the post-effect. In these calculations the authors assume a "collision" mechanism of polymerisation, although in fact the mechanism is one of adsorption. Moreover, the estimation of the concentration of initiating radicals in the surface layer of the fibre was extremely arbitrary.

The authors cited concluded that the values of k_g on the surface are close to those observed in the radical polymerisation of AN in the liquid phase, and at the same time obtained for the activation energy of chain growth E_g a value of zero, which is unlikely for this reaction and which differs considerably from the values established for the radical polymerisation of AN and other monomers in the liquid phase. An attempt was made[81] to estimate the growth rate constant k_g for the radiation polymerisation of MMA on KSK-2 silica gel. The lifetimes of the kinetic chains were determined calorimetrically. In Ref.81, the rate of initiation of the polymerisation was not determined experimentally;[81] it was assumed, somewhat arbitrarily, to be equal to the yield of paramagnetic centres stabilised in irradiated silica gel at 77 K, determined in Ref.43. Moreover, it should be borne in mind that the yields of radicals in silica gels irradiated in the presence and absence of adsorbates usually differ considerably. They also depend on the concentration of impurities in the specimens. It was concluded[81] that k_g for MMA for monolayer coverage of the surface by the monomer is close to that for the liquid phase. For the above reasons, this conclusion does not appear completely reliable. The idea that k_g depends on the heat of adsorption and the degree of covering of the surface by the monomer was developed in Ref.81.

The principal results[48,53–56,73] of the determination of the rate constants and other parameters of the elementary stages of the radiation polymerisation of VA and MMA on an aerosil and a methylated aerosil in the initial stage of the reaction can be considered.§ The kinetic parameters were determined using the usual equations of the theory of radical polymerisation which describe the stationary stage of the process:

$$v_{st} = v_i k_g [M]\tau$$

$$v_{t,sp} = 1/\tau;\ \nu_p = k_g[M]\tau;\ k_t = 1/v_i\tau^2 \qquad (2)$$

Here, v_{st} is the stationary rate of polymerisation, $v_{t,sp}$ the specific (calculated for one growing chain) rate of termination, ν_p the length of the polymerisation kinetic chains, and k_t the rate constant for quadratic chain termination. The growth rate constants k_g were determined from Eqn.(2); here, the main difficulties are associated with the reliable measurement of the rates of polymerisation initiation v_i and the lifetimes of the polymerisation kinetic chains τ.

1. Determination of the Rate of the Radiation Initiation of Polymerisation

As shown below, the initiation of radiation polymerisation on a surface when the concentrations of adsorbed monomers are not too high (up to 1–2 monolayers) is due chiefly to the active centres produced as a result of the absorption of the energy of the radiation by the solid. It should be noted that a sufficiently complete mechanism has not yet been reliably established for the radiolysis processes leading to the initiation of radical polymerisation on a surface, even for the most widely studied adsorbent silicon dioxide. It has been shown[35–38,84,85] by various methods (EPR, ultraviolet spectroscopy, etc.) that the γ-irradiation of finely dispersed silicon dioxide may lead to the production of hole, electronic, and radical centres on its surface. The hole centres may be localised on an oxygen atom of a hydroxide group or on an oxygen atom situated next to an impurity aluminium or boron atom.[36] Impurity atoms usually play an extremely important role in the localisation of electron or hole active centres and to a large extent determine the EPR and ultraviolet spectra of these centres. When an adsorbate is present on the surface of the irradiated specimens, transformation of these centres to radical-ions of the adsorbed molecules, or the formation of their donor–acceptor complexes with the adsorbate, is observed, depending on the relationship between the ionisation potential (or electron affinity) of the adsorbed molecules and the "depth" of the hole or electron traps. The radical-ions formed may take part in the initiation of surface ionic and radical reactions.

The initiation of radical reactions can also take place as a result of the transfer to the adsorbate molecules of the energy of recombination of the electron–hole pair, which is often sufficient for bond rupture in the adsorbed molecule. The energy of recombination of the ion pair may also bring about bond rupture in the surface silanol groups and the formation of $\geqslant$SiO$^\bullet$ and $\geqslant$Si$^\bullet$ radicals, and also the low-molecular-weight radicals H$^\bullet$ and HO$^\bullet$, which can also initiate radical reactions involving the adsorbate. It has been suggested[86,87] that an appreciable proportion of radical centres are formed by a homolytic mechanism.

The reliable determination of the rate of initiation of polymerisation v_i on a surface is fairly complicated. The use of the usual methods for determining v_i in the liquid phase, involving the measurement of the induction periods of inhibited polymerisation or the rate of consumption of radical acceptors,[89] in the case of polymerisation on a surface is complicated by the lowered diffusion mobility of the inhibitors and acceptors usually employed. As a result, their reactions with the active centres of the polymerisation are diffusion-controlled, and the efficiency of these reactions is lowered, making quantitative analysis of the results difficult.

Three different methods for determining v_i, whose results show fairly good agreement with one another, have been developed and used: 1) the determination of the duration of the induction period of the polymerisation when an effective non-adsorbed inhibitor, namely gaseous oxygen, is used; 2) a kinetic method, based on the use of expressions, familiar from the theory of radical polymerisation, relating the average degree of polymerisation to the kinetic parameters of the process; and 3) a method based on the determination of the number of polymeric molecules formed in systems with a low effective constant for non-degenerate chain transfer. The characteristic features and limits of applicability of each method were discussed.[48]

Table 2 gives the values found by averaging the results obtained by different methods for v_i and the radiation-chemical yields of the initiation calculated per unit of energy absorbed by the entire system G_i and by the adsorbed monomer G_i^* for the radiation polymerisation of MMA and VA on an aerosil. It is significant that the values of v_i were found to be practically the same for the two monomers. Table 2 shows, in particular, that the values of G_i^* are anomalously high. This indicates directly that there is effective migration of the energy absorbed in the bulk of the aerosil particles to their surface. Table 2 also shows that the values of v_i in the range of degrees of coverage from 0.4 to 1.5 monolayer depend little on the degree of coverage. In the temperature range studied, from −20 °C to +50 °C, the values of v_i are practically independent of temperature.[48] The values of v_i may differ significantly for a given monomer

§See also M.A.Bruk, S.A.Pavlov, G.G.Isaeva, and E.Ya.Yunitskaya, Europ.Polym.J., 1986, **22**, 169.

on different adsorbents. For example, the values of ν_i for VA on AS/400 and on MAS are ~10^7 molecule cm^{-2} s^{-1} and ~6×10^7 molecule cm^{-2} s^{-1} respectively.

Table 2. Average values of ν_i, G_i, and G_i^* for the radiation polymerisation of MMA and VA (dose rate 0.35 Gy s^{-1}).[48]

m*	$10^{-7}\nu_i$, molecule $cm^{-2}s^{-1}$	G_i, 1/100 eV	G_i^*, 1/100 eV	m*	$10^{-7}\nu_i$, molecule $cm^{-2}s^{-1}$	G_i, 1/100 eV	G_i^*, 1/100 eV
Adsorbent AS/400				Adsorbent AS/200			
0.4	1.1	1.0	30	0.4	1.3	1.2	47
1.0	1.2	1.1	17	1.0	1.4	1.3	20
1.5	1.3	1.2	12	1.5	1.6	1.5	15

*The number of effective monolayers of monomer on the surface in the polymerisation.

2. Determination of the Lifetimes and Rate Constants for the Growth of the Kinetic Chains

The lifetimes of the polymerisation kinetic chains τ have been determined from the measured durations of the initial non-stationary period of the polymerisation. Analysis of the relationship between τ and the extrapolated non-stationary time t_{ns} showed that for systems with linear termination of the kinetic chains $t_{ns} = \tau$,[56,83] and for systems with mixed termination $t_{ns} = z\tau$, where z lies in the range 0.7–1, depending on the ratio of the rates of linear and quadratic termination.[91] For systems with quadratic termination, $t_{ns} = \tau \ln 2$.[89] Thus in all cases, it is possible with sufficient accuracy to use the relationship $\tau \cong t_{ns}$.

The initial non-stationary stage of the polymerisation has been studied by two methods: vacuum gravimetry (VG) and adiabatic increase in temperature (AIT). The determination of t_{ns} by VG under real experimental conditions requires the introduction of a correction, associated chiefly with retardation in the diffusion transfer of the monomer in the specimen, and has a low accuracy.[56,73] The conclusion[83] that there is no diffusion retardation is apparently erroneous. The fact that the observed values of t_{ns} are independent of the thickness of the aerosil tablets on which the polymerisation was carried out, which provided the experimental basis for this conclusion, is probably related to the influence of the non-isothermal character of the specimen on the dynamics of the adsorption of the monomer.[56,73] Thus the values of k_g obtained in Ref.83 are several times too low.

The AIT method is more convenient for determining t_{ns}. The method involves essentially the measurement of the increase in the temperature of the specimen as a result of the heat liberated on polymerisation under pseudo-adiabatic conditions, when heat exchange between the specimen and the surrounding medium can be neglected. The measurements were made in a cell with an adiabaticity time from 5 min to 9 min; particular attention was paid to the analysis of the possible errors of the method.[56] The method used makes it possible to determine t_{ns} in the range 5 to 100 s with a relative error ≤30%. In Refs.53–56 the rate constants were calculated using the values of t_{ns} obtained by the AIT method.

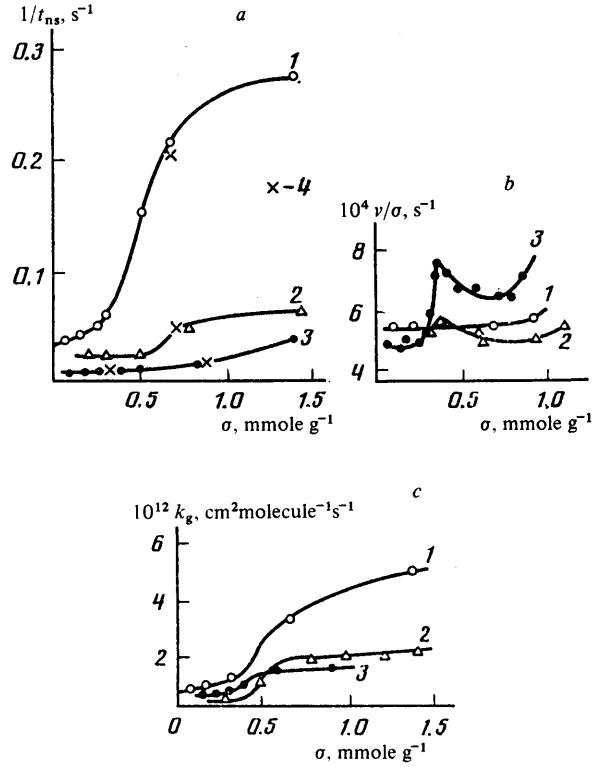


Figure 1. Dependence of $1/t_{ns}$ (*a*), the reduced stationary rate of polymerisation (*b*), and the chain growth rate constant (*c*) on the concentration of adsorbed monomer σ: *1*) VA on AS/400; *2*) MMA on AS/400; *3*) MMA on AS/200. Temperature 50 °C, dose rate 0.35 Gy s^{-1} (points *4* were obtained at 1.7 Gy s^{-1}).[9,55]

Fig.1*a* gives the results of the experimental determination of the values of $\nu_{t,sp} = 1/t_{ns}$ for various systems studied. The values of $\nu_{t,sp}$ are much lower than those for polymerisation in the liquid phase in the initial stages; these values increase with increase in the monomer concentration σ. These data, the values of ν_i given above, the values of ν_{st} given in Fig.1*b*, and Eqn.(2) were used to calculate the growth rate constants k_g for different values of σ. Fig.1*c* shows that the values of k_g are of the order of 10^{-12} cm^2 $molecule^{-1}$ s^{-1}, and that they increase with increase in σ. A significant feature is that k_g increases abruptly in the range of degrees of coverage corresponding to approximately half a monolayer (0.3–0.4 mmole g^{-1}), where an abrupt decrease in the heat of adsorption takes place (see section IV). Calculation shows that for VA molecules, which are adsorbed "more weakly" (filling the second half of an effective monolayer), the values of k_g on the average are ~4 times those for the monomer adsorbed "more strongly" (at degrees of covering of 0.2–0.3 monolayer).

Interesting results have been obtained in experiments on polymerisation in adsorbed solutions.[53,54] If two thirds of a monolayer of ethyl acetate (EA) are added to one third of a monolayer of VA, there is a sharp increase in the effective value of k_g (by a factor of ~4). It is suggested that this effect is related to the fact that in the presence of VA, whose adsorption properties on the aerosil are practically completely analogous to those of VA, an appreciable proportion of the VA molecules are displaced from strong to weak adsorption centres. When additives such as chloroform, which are adsorbed on the aerosil much more weakly than VA and EA, and which cannot displace the monomer from the strong centres, are introduced into the adsorption layer instead of EA, k_g remains practically unchanged.[54]

The question of whether the values of E_g are different for the monomer adsorbed on strong and weak centres are different is extremely important. Table 3 gives the results of a study of the temperature dependence of the rates of the overall process (E_{tot}), the termination reactions (E_t), and the growth (E_g) of the polymerisation chains of various monomers on AS/400 for different values of σ. As already noted, $E_i \cong 0$. It can be seen that E_g is much higher at low than at high degrees of covering. This difference corresponds approximately to the differences in k_g.

Table 3. Activation energies of the overall process (E_{tot}) and the reactions of chain growth (E_g) and termination (E_t) in the polymerisation of monomers on AS/400 (dose rate 0.35 Gy s^{-1}).[53,55]

Monomer	σ, mmole g^{-1}	Activation energies, kJ $mole^{-1}$		
		E_{tot}	E_t	E_g
VA	0.25	8.4	14.2	22.6
VA	0.7	6.3	10.9	17.2
MMA	0.25	28.5	9.7	38.2
MMA	0.65	21.8	9.7	31.5
MA	0.25	23.4	—	—
MA	0.7	10.5	—	—

Table 4. Kinetic parameters of the polymerisation of VA and MMA on an aerosil and on MAS (monolayer coverage, temperature 50 °C, dose rate 0.35 Gy s^{-1}).[9,55]

Parameter	VA-AS/400	VA-MAS	MMA-AS/400	MMA-AS/200
k_g, $cm^2 molecule^{-1} s^{-1}$	$3.6 \cdot 10^{-12}$	$7.1 \cdot 10^{-12}$	$1.0 \cdot 10^{-12}$	$0.67 \cdot 10^{-12}$
k_t, $cm^2 molecule^{-1} s^{-1}$	—	$2.4 \cdot 10^{-20}$	—	—
k_m, $cm^2 molecule^{-1} s^{-1}$	$1.8 \cdot 10^{-15}$	—	$1.6 \cdot 10^{-17}$	$1.1 \cdot 10^{-17}$
$10^{-8} n_{st}$, cm^{-2}	0.72	4.9	3	8.4
$10^{-3} \bar{P}_n$	1.3	0.45	4	4.4
$10^{-4} \nu_p$	0.44	1.2	0.5	0.8
τ, s	6	8.5	25	60

Notation: n_{st} is the stationary concentration of growing radicals; $\bar{P}_n$ the number-average degree of polymerisation; and k_m the rate constant for chain transfer to the monomer.

Table 4 gives the values of the principal kinetic parameters of polymerisation for some systems with weak bonding. Table 4 shows, in particular, that k_g for VA on MAS is ~2 times that on AS/400. This is apparently due to the weaker adsorption bonding of VA on the MAS surface.

3. Comparison of the Kinetic Parameters of Polymerisation on a Surface and in the Liquid Phase[9,55]

It is of considerable interest to compare the rate constants for the growth and termination of the chains in the polymerisation of monomers in the adsorbed state and in the liquid phase in the initial stages of the reaction (Table 5). The values of the surface constants were recalculated to the bulk values using a model in which the adsorbed monolayer is regarded as a reaction volume of thickness 4 Å, which is approximately equal to the gas-kinetic diameter of the monomer molecules. Table 5 shows, in particular, that the values of k_g, recalculated to bulk values, correlate well with the values of the specific rates of chain growth $\nu_{g,sp}$, which are independent of the concentration dimensions and are not related to the model adopted.¶ This indicates that the model adopted for the recalculation is correct.

Table 5. Kinetic parameters of the polymerisation of VA and MMA on the surface of AS/400 and MAS (monolayer coverage)[9,55] and in the liquid phase (in the bulk)[89,90] (temperature 50 °C).

Parameter	Vinyl acetate			Methyl methacrylate		
	on AS/400	on MAS	in the liquid phase	on AS/400	on AS/200	in the liquid phase
k_g, litre $mole^{-1} s^{-1}$	84	160	1500—2600	22	15.4	350—410
$10^{19} k_g$, $cm^3 molecule^{-1} s^{-1}$	1.4	2.7	25—43	0.39	0.26	5.8—6.8
k_t, litre $mole^{-1} s^{-1}$	—	$5.4 \cdot 10^3$	$2,5 \cdot 10^7$	—	—	$2 \cdot 10^7$
$10^{17} k_t$, $cm^3 molecule^{-1} s^{-1}$	—	0.9	$4.2 \cdot 10^3$	—	—	$3.3 \cdot 10^3$
$\nu_{g,st}$, s^{-1}	$0.73 \cdot 10^3$	$1.4 \cdot 10^3$	$(1.6—2.8) \cdot 10^4$	$0.2 \cdot 10^3$	$0.15 \cdot 10^3$	$3.5 \cdot 10^3$
$\nu_{t,st}$, s^{-1}	0.16	0.12	—	0.04	0.017	1*

*For the radiation polymerisation of MMA in the bulk in the initial stage; dose rate 0.35 Gy s^{-1}.[32]

Table 5 shows that the rate constant of the quadratic termination k_t for the polymerisation of VA on MAS is lower by ~3.5 orders of magnitude than that in the liquid phase. This result is due to the diffusion character of k_t and the fact that the translational mobility of the macro-radicals on the surface is much lower than that in the liquid phase. The suppression of the quadratic termination of the chains on the surface is responsible for the low rates of termination and

¶ Thus Table 5 shows that the ratio of the bulk and surface specific growth rates for each of the systems studied is close to the ratio of the bulk and surface growth rate constants.

for the fact that the lifetimes of the polymerisation kinetic chains are much longer than those in the liquid phase. The same factor increases the role of linear chain termination in polymerisation on a surface and the occurrence of systems with linear and mixed termination. An analysis of the initial non-stationary stage in systems with mixed termination kinetics has been carried out.[91]

The data in Table 5 also show that for the systems studied, the values of k_g in an adsorbed monolayer are 15–20 times lower than those in the liquid phase.

The possible influence of processes of molecular transport of the monomers on the surface on the observed values of k_g has been analysed.[92] The analysis was carried out using the concepts of the theory of diffusion processes in an adsorbed layer, and also the experimentally determined values of D_S and data on the equilibrium adsorption of monomers. The authors obtained mathematical expressions which give the conditions for replacement of the limiting stage of the chain growth process (and also any other bimolecular reaction) on a surface, that is the conditions corresponding to the change from kinetic to diffusion conditions, and which make it possible to calculate the values of the effective rate constants of polymerisation under purely diffusion conditions and under intermediate conditions. The analysis showed that for values $D_S \cong 10^{-5}$ cm^2 s^{-1}, appreciable deviations of the concentration of the reagent close to the reaction centre from the equilibrium concentration for a bimolecular reaction on a surface are possible only for values of the chemical rate constant of this reaction greater than 10^{-6} cm^2 molecule^{-1} s^{-1}. This value corresponds to a bulk rate constant of ~10^{-13} cm^3 molecule^{-1} s^{-1} or 10^8 litre mole^{-1} s^{-1}; it is greater by ~5 orders of magnitude than the experimental values of k_g for the radical polymerisation of monomers in the liquid phase. Such high values of k_g obviously cannot be realised for non-catalytic reactions of radical polymerisation on a surface. Thus in the systems with weak bonding studied, as in the polymerisation of monomers in the liquid phase in the initial stages, kinetic conditions of chain growth are established.

With allowance for this, it is possible to examine the nature of the observed differences in the values of k_g on a surface (k_g^{surf}) and in the bulk (k_g^{bulk}). When examining the reactions of the chain growth of VA or MMA in an adsorbed monolayer on an aerosil, it is necessary to bear in mind that, according to adsorption measurements,[82] the monolayer can be regarded as a "compact" monolayer, in which the average area corresponding to one monomer molecule is close to the corresponding value for the liquid monomer. On the other hand, it is necessary to take account of the probable difference in the number of monomer molecules close to the reaction centre, in the reaction "cage" (n_c). The value of n_c is apparently 2–3 times lower for polymerisation in an adsorption monolayer than for polymerisation in the bulk of the liquid monomer. With allowance for this essentially concentration factor, however, the values of k_g^{surf} for the systems studied are appreciably lower than those for polymerisation in the bulk, by a factor of 6–8 for monolayer coverage, and by a factor of ~20 for a coverage corresponding to one third of a monolayer. These differences are due to corresponding differences in the nature of the elementary act of chain growth, related to the characteristic features of the structure of the intermediate complex and the form of the potential surface. A definite role may be played by both the energy and the entropy factors.[9,32,55] In the polymerisation of MMA, the energy factor, associated with the need for a decrease in the strength of the adsorption bond of the monomer, predominates; in the polymerisation of VA, a greater role is played by the entropy factor.

4. Various Thermodynamic Characteristics of Polymerisation on a Surface

The enthalpy and entropy of adsorbed monomers and polymers formed on a surface usually differ considerably from the corresponding parameters in the liquid and gas phases. Thus polymerisation on a surface should show definite thermodynamic characteristics. A general analysis of this question[32] leads to the conclusion that in polymerisation on a surface at degrees of covering up to one monolayer, the heat of polymerisation Q_{pol} may be appreciably lower (by ~10–50 kJ mole^{-1}) than that for the polymerisation of the corresponding monomers in the liquid phase. The examination of this question in Ref.1, where the opposite conclusion was reached, is apparently not completely correct (see Ref.32).

Various problems of the thermodynamics of polymerisation on a surface have been studied experimentally.[80,81] According to the results of a calorimetric study of the polymerisation of a number of monomers (AN, MMA, tetrafluoroethylene) adsorbed on KSK-2 silica gel, the effective heats of polymerisation Q_{pol}^{surf} at low degrees of covering of the surface by the monomer differ considerably from the values of Q_{pol} for the polymerisation of the same monomers in the liquid phase. In some systems (for example for MMA and AN) at coverages of a quarter of a monolayer, the values of Q_{pol}^{surf} are only 5–10 kJ mole^{-1}. With increase in the degree of covering of the surface, Q_{pol}^{surf} increases (extremely sharply in the systems indicated), and in the range near one monolayer it reaches values characteristic of the liquid phase.

Some approximate thermodynamic estimates have also been made[32] using the results of a study of the polymerisation of VA and MMA on an AS/400 surface by the adiabatic increase in temperature method. These estimates showed that for both monomers, Q_{pol}^{surf} increase considerably with increase in the degree of coverage of the surface by the monomers up to a monolayer, but at a coverage corresponding to a monolayer they still remain slightly lower than the values for the liquid phase; in the range of degrees of coverage studied, Q_{pol}^{surf} for MMA is appreciably lower than that for VA.

VI. POLYMERISATION IN ADSORPTION POLY-LAYERS

The main regular features of polymerisation on a surface at comparatively low concentrations of the adsorbed monomers (up to 1–2 monolayers) were examined above. From the practical viewpoint, the examination of the characteristic features of polymerisation at higher monomer concentrations is also of considerable interest. These characteristics have been examined[93] for the radiation polymerisation of MMA and VA on AS/400. Specimens containing 50 mass % monomer relative to the aerosil were taken as model specimens with a "thick" adsorption layer. The layer thickness was ~10 to 15 effective monolayers. In the thick layer the order of the polymerisation reaction with respect to the dose rate is 0.8–0.85, whereas it is 1 in a monolayer, and 0.5 in the liquid phase. Thus in a thick adsorption layer, a mixed mechanism of chain termination, with linear termination predominating, is observed. The predominantly linear termination of the chains is confirmed by the weak dependence of the molecular mass of the PMMA, formed in the "thick" layer, on the radiation dose rate.

The dependence of the reduced rate of polymerisation (v/σ) on σ has been studied.[93] For both monomers (VA and MMA) this dependence shows extremal character

with a maximum in the range of coverage corresponding to 3–4 monolayers (Fig. 2). The dependence of the molecular mass of PMMA on σ is similar. This is probably due to a corresponding change in the effective rate constants of growth (k_g^{eff}) and termination (k_t^{eff}); k_g^{eff} increases more rapidly at coverages up to 3–4 monolayers, and k_t^{eff} increases more rapidly at higher concentrations. Moreover, the reduced rate of initiation v_i/σ decreases with increase in σ. For polymerisation in a model "thick" layer, the value of E_g^{eff} is close to E_g for the liquid phase. It is suggested that the constant k_g^{eff} for the "thick" layer is close to k_g for the liquid phase. The reaction of chain termination is specific, however; quadratic termination is suppressed to a considerable extent, and linear termination predominates. In the initial stages the value of $v_{t,sp}$ is appreciably lower than in the liquid phase. This is confirmed, in particular, by the fact that the molecular mass of PMMA formed by polymerisation in a "thick" layer is 6 times that for polymerisation in the bulk under comparable conditions.[93]

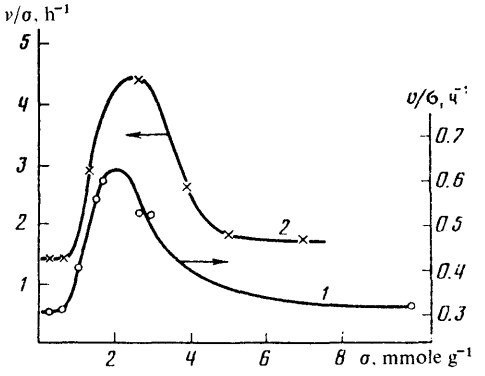


Figure 2. Dependence of the reduced rate of polymerisation v/σ for VA (*1*) and MMA (*2*) on AS/400 on the concentration of adsorbed monomer σ. Temperature 50 °C, irradiation dose rate 0.1 Gy s^{-1} (*1*) and 0.35 Gy s^{-1} (*2*).[93]

The ratio of the rates of radiation polymerisation on a surface at different values of σ and in the bulk is illustrated by the data in Table 6 for MMA and n-butyl methacrylate (BMA) on an aerosil. Table 6 shows, in particular, that in the region of the maximum (at a coverage of ~4 monolayers), the reduced rate of polymerisation on the surface is 30 to 50 times that in the bulk under comparable conditions. An important feature is that this difference should increase with increase in the dose rate, because of the difference in the dependence of the reaction rate on the dose rate. These results are apparently typical of a fairly wide range of monomer–support systems. The main channels of this accelerating influence of the support on the polymerisation are: 1) increase in the rate of initiation of polymerisation, firstly because of the "maintenance" of the adsorption layer by the active centres formed by the energy of the radiation absorbed by the solid particles (this "maintenance" is particularly significant in those systems in which there is effective transfer of energy from the bulk to the surface of the particles), and secondly as a result of the increase in the radiation dose rate for the layer of monomer situated at the interface with the solid with a high electron density[88] (this effect is not very great for an aerosil, but it should be considerable for heavy metal oxides); 2) decrease in the probability of termination and increase in the lifetime of the polymerisation kinetic chains.

Table 6. Rates and radiation-chemical yields of the polymerisation and the molecular masses of the polymers of MMA and BMA, formed on an AS/400 surface and in the bulk (in the volume) [temperature 50° (MMA) and 25° (BMA), dose rate 0.35 Gy s^{-1}].[32,93]

Parameter	Monomer	Adsorbed state*			Liquid phase (in the bulk)
		1 monolayer	4 monolayers	"thick" layer	
$10^4\,(v/\sigma)$, s^{-1}	MMA	4	12.5	6	0.4
	BMA	2.5	16	7	0.31
$10^{-4}\,G_{pol}$, 1/100 eV	MMA	0.61	6.5	6.0	0.94
	BMA	0.31	6.75	4.6	0.63
$10^{-4}\,G^*_{pol}$, 1/100 eV	MMA	10	31.2	18	0.94
	BMA	5	32.6	14	0.63
$10^{-6}\,\bar{M}_\eta$	MMA	0.6	4.8	2.9	0.5
	BMA	0.4	6.8	8.5	0.9

*Concentrations of adsorbed monomer for 1 monolayer, 4 monolayers, and the "thick" layer were 5 (? Ed. of trans.), 26, and 50 mass % respectively.

Various characteristics of radiation polymerisation in micron layers of monomers on solid surfaces† have been examined in general terms.[94] Attention is drawn to a possible change in the mechanism and rate of radiation-chemical transformations on a surface compared with polymerisation in the bulk. The "structure" of the monomer layer is examined with allowance for various characteristic features of the action of radiation on a heterogeneous system. In particular, a "range of molecular contact", which adjoins the support and in which higher rates of radiation polymerisation can be expected, is distinguished. The main factors responsible for this increase in the rate are considered[94] to be: 1) the increase in the dose rate in this range, due to the effect of radiation "reflected" from the solid; 2) the increased viscosity of the system, which hinders the termination of the growing radical chains; 3) the increase in the rate of chain growth, due to the ordered arrangement of the molecules relative to the substrate and one another. The effect of the first two factors appears indisputable. In the case of the last factor, however, the formation in the boundary layer on a solid surface of "prepared" monomer molecules whose relative arrangement would lead to an increase in the rate of polymerisation appears to be the exception rather than the rule. The formation of these "prepared" molecules requires at least strict complementarity between the support and the layer of adsorbed monomer.

†That is in extremely thick (thousands of monolayers) adsorption layers or thin liquid films of the monomers.

VII. POLYMERISATION IN SYSTEMS WITH STRONG BONDING

For a number of reasons, the study of polymerisation in systems with strong bonding is usually associated with considerable experimental difficulties. There are very few published papers on these systems.

Acrylic acid chemisorbed on an aminated aerosil undergoes practically no polymerisation. The monomer adsorbed physically above the chemisorbed layer is polymerised at an extremely high rate.[56,73]

The polymerisation of N-vinylpyrrolidone on Silochrome[9,96] takes place practically only at temperatures above 70 °C. The rate of polymerisation and the molecular mass of the polymer formed are low. The total activation energy of the process is 60–70 kJ mole^{-2}. The order for the dependence of the rate of polymerisation on the dose rate is $n_i \cong 1$. A study of the combined polymerisation on Silochrome of N-VP and the weakly-bonded monomer methacrylic acid gave an interesting result. At all compositions of the original mixtures studied, including mixtures containing 95 mole % N-VP, only pure polymethacrylic acid is formed, although the constants for the copolymerisation of these monomers in the liquid phase are similar. This shows that increase in the strength of the adsorption bonding decreases the effective reactivity of the monomer on the surface.

4-Vinylpyridine on AS/400 at 20–50 °C is polymerised at a rate which is 5–10 times lower than that for, for example, MMA under comparable experimental conditions. The molecular masses of the poly-4-VP formed are much lower.[9,73]

Thus the rates of polymerisation and the molecular masses of the polymers formed in typical systems with strong bonding are much lower than those in systems with weak bonding. These characteristic features are probably due chiefly to the much lower values of the effective growth rate constants. The values of k_g in systems with strong bonding are apparently 2–3 or more orders of magnitude lower than those for the polymerisation of the corresponding monomers in the liquid phase.

The polymerisation of 2-methyl-5-vinylpyridine on silica gel at high temperatures (90–150 °C) has been studied.[97] Under these conditions the rate of the process is fairly high. Judging from the kinetic data,[97] $G_{pol} \cong 10^4$ at 100 °C. At high temperatures this system apparently behaves like a typical system with weak bonding (see section IV).

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Thus in recent years considerable progress has been made in the study of the mechanism and characteristic features of the elementary stages of radiation polymerisation on a surface, providing a basis for the development of the theory of these reactions. Nevertheless, many unresolved problems remain in this field, primarily those related to the mechanism of the elementary stages of these processes. In the case of the initiation stage, it is necessary to study the influence of the electronic character, the actual structure, and the particle size of the solid on the rate of initiation and to determine the mechanism of the basic radiation reactions leading to the formation of the initiating centres. The more accurate determination of the conditions under which the surface exerts stereochemical control over the acts of chain growth is of particular interest; in this connection it is appropriate to study the characteristic features of the micro-structure of the polymer chains obtained in systems with strong adsorption bonding. Finally, it is necessary to carry out additional studies of the detailed mechanisms of linear and quadratic chain termination in real systems, including adsorption layers of different thickness. The study of this question should give new results of fundamental importance, related to the properties of the macromolecules and their solutions on solid surfaces. It is also extremely important to extend the range of systems in which the kinetic parameters of polymerisation are determined, to make detailed studies of the processes of ionic radiation polymerisation on a surface, and to study the characteristic features of polymerisation on regular supports and of oriented and matrix polymerisation on a surface.

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