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Heterophase Radical Polymerisation

V.A.Popov and G.P.Gladyshev

The review deals with the characteristics of the heterophase polymerisation of various monomers, the effect of the transition from a homogeneous to a heterogeneous system, and certain physical factors on the rate of polymerisation, the molecular weight of polymers, and the composition of copolymers. A general account is given of published data for the morphological structure of the polymer phase formed. The views of various investigators on the mechanism of the heterophase polymerisation are discussed and the kinetic mechanisms and models of heterophase polymerisation are examined critically.

The bibliography includes 164 references.

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I. INTRODUCTION

One of the thoroughly investigated chemical reactions is radical polymerisation, a quantitative theory of which was developed as early as the 1940s and the 1950s. However, there are many processes in this field which deviate from the laws of ideal radical polymerisation and their rigorous kinetic analysis constitutes a difficult problem.

Such processes include radical heterophase polymerisation, characterised by the segregation of the polymer formed in a new phase with simultaneous occurrence of elementary chain propagation and termination stages in the solid phases, which are separated in space but can communicate via liquid or gaseous phases. The polymerisation of vinyl compounds such as acrylonitrile, acrylic and methacrylic acids, ethylene, and its halogeno-derivatives (vinyl chloride, vinylidene chloride, vinyl bromide, tetrafluoroethylene, chlorotrifluoroethylene, etc.) have all the properties characteristic of heterophase polymerisation. The appearance of a new phase is a characteristic of ω-polymerisation, the copolymerisation of certain monomers (for example styrene and maleic anhydride, methyl methacrylate, and methacrylic acid), and also the polymerisation of the usual monomers (styrene, methyl methacrylate, vinyl acetate, etc.) in media which do not dissolve the polymers.

A number of technically important polymers and copolymers have been obtained by heterophase polymerisation. Recently a method for the synthesis of poly(vinyl chloride) in bulk, with improved mechanical properties, high purity, and resistance to the atmosphere, has been developed and applied in industry[1-5]. However, the difficulty of temperature control at later stages of the reaction owing to the low thermal conductivity of the solid polymer phase hinders the application of this method to other monomers.

The study of heterophase radical polymerisation is of considerable theoretical as well as purely practical interest. Consequently many studies have been made of heterophase polymerisation, some of which have been described in a series of monographs and reviews[6-10]. However, since these reviews are concerned solely with the polymerisation of individual monomers and only give a general account of the results of earlier studies, we thought it desirable to give a systematic account of the extensive data which have now accumulated. Moreover, in recent years, certain definite advances have been achieved in the interpretation of the kinetic data and in studies on the morphology of the polymer phase, which have made possible considerable progress towards understanding of the mechanism of the heterophase polymerisation and have yielded qualitative and semiquantitative theories which give a generally satisfactory description of its characteristics.

This review also describes the results of certain earlier studies which were not considered in the above reviews, but which are of considerable interest in the light of modern ideas. Problems involving ω-polymerisation have been excluded from consideration, since they have been described fairly completely in a number of monographs[6,11].

II. KINETIC AND CERTAIN OTHER CHARACTERISTICS OF POLYMERISATION WITH FORMATION OF A NEW PHASE

1. Effect of Transition from a Homogeneous to a Heterogeneous System on the Rate and Degree of Polymerisation

Early studies[6,12,13] on the kinetics of the polymerisation of acrylonitrile and vinyl chloride in bulk already revealed their significant difference from the kinetics of the homogeneous polymerisation of the usual vinyl monomers: in the first case, the reaction takes place with self acceleration from the beginning, has higher average velocities, and gives higher molecular weights of the polymers formed. It has been shown that these anomalous properties are due to the formation of an insoluble polymer during the reaction. In the studies of recent years, the autocatalytic nature of the kinetic curves was noted for many monomers undergoing heterophase polymerisation in bulk or in precipitating media -vinylidene chloride[14], ethylene[15,16], tetrafluoroethylene[17,18], acrylic[19] and methacrylic acids[20], styrene[21], acrylamide[22], and others[23,24]. For example, Ryska et al.[25] observed the acceleration of the reaction from the instant of transition from a homogeneous to a heterogeneous polymerisation system comprising vinyl chloride in diethyl oxalate. The acceleration period depends on the physical and chemical properties of the medium and can continue up to conversions of 2—3% (as for acrylic and methacrylic acids) or much higher values (40% and above, as in the case of vinyl chloride).

Heterophase polymerisation is also distinguished by the formation of polymers with higher molecular weights. Fig. 1 shows the variation of the degree of polymerisation of vinyl chloride in tetrahydrofuran (THF) with the initial concentration of the monomer in solution[26]. At a monomer concentration in excess of 9 M, the polymer formed is segregated from the solution and its molecular weight increases sharply on further increase of the amount of monomer in THF. If the rate constant for chain transfer to the monomer is low, the degree of polymerisation usually increases with conversion[15,16,27-29].

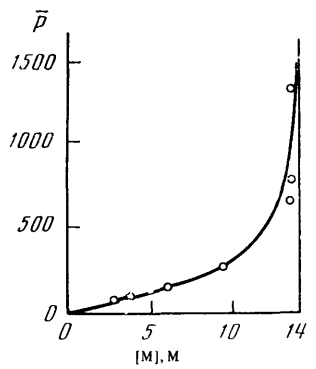


Figure 1. Variation of the degree of polymerisation of vinyl chloride with the initial monomer concentration [M] in THF.

The above anomalous phenomena in heterophase polymerisation (self acceleration, high average reaction rates and molecular weights of the polymers) are usually explained by a decrease of the rate of termination of the growing chains owing to the low mobility of the macroradicals in the solid phase. According to the theory of solutions of high-molecular-weight compounds[30], a macromolecule, in which there is an appreciable degree of freedom of rotation of the individual units relative to one another, coils up in solution. The structure of the coil depends on the solvent power of the medium. In "good" solvents, the coil has a very loose structure and is filled with solvent molecules to the extent of 95—99%.[9,31] In media which do not dissolve the polymer, the macromolecule and the macroradical becomes segregated from the solution in the form of a dense coil, access to the active radical of which is greatly hindered (the macroradical is occluded). Subsequent aggregation of the macromolecules into polymeric particles causes further blocking of the macroradicals and reduces the rate of chain termination—according to certain data[32], the rate constant for chain termination may decrease by 5—6 powers of ten. If one assumes that the rate of chain propagation does not change or changes insignificantly, because of the high mobility of the small monomer molecules, it becomes understandable why the rate of polymerisation increases following the appearance of the solid phase.

On decrease of the molecular weight of the polymer and after the introduction of active chain transfer agents, the self acceleration diminishes owing to the lower degree of occlusion of the macroradicals, the escape of small radicals (formed as a result of chain transfer) from the polymer particles to the liquid phase, and the increase of the rate of chain termination reaction[6,33,34].

One should recall that in certain studies[35] the above view on the nature of the self acceleration of heterophase polymerisation (occlusion of the active ends of macroradicals) is used also as a qualitative explanation of the "gel effect" in the polymerisation of certain vinyl monomers at advanced stages of the reaction.

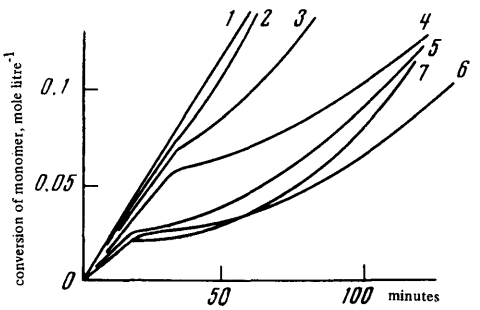


Figure 2. Polymerisation of vinyl chloride in diethyl oxalate at 25°C. The monomer concentration increases from 9.81 M (curve *1*) to 13.05 M (curve *6*). The breaks in the curves correspond to the formation of the polymer phase.

However, studies in recent years showed that, when the medium becomes heterogeneous, the morphological structure of the polymer phase, its swellability, the permeability of the polymer aggregates, the physical adsorption of monomer molecules on the solid phase, etc. have a marked influence on the rate of polymerisation. In many cases, at the instant when the medium becomes heterogeneous the polymerisation reaction is not accelerated but actually retarded, which indicates the influence of these physical factors not only on the chain termination reaction but also on the chain propagation reaction. Thus Ryska et al.[25], who studied the polymerisation of vinyl chloride in diethyl oxalate and 2,4-dichloropentane solutions, observed, on transition of the reaction from the homogeneous to the heterogeneous region, a stage with a sudden decrease of the rate followed by a rapid increase with conversion (Fig. 2). In the presence of an effective chain transfer agent (carbon tetrabromide), an increase of the ratio of the rates of chain transfer to carbon tetrabromide and of chain propagation was noted under heterogeneous conditions. On this basis, it was concluded[25] that transition to the heterogeneous region is accompanied by a decrease of the rate of chain propagation owing to the coiling up of insoluble macroradicals and their subsequent association, which hinders the access of the monomer molecules to the polymeric aggregates and reduces their local concentration in the vicinity of the active radical centres. According to approximate calculations of Bamford et al.[36], this local concentration of acrylonitrile is 1/180 of the macroconcentration of the monomer in the system. On the other hand, it is believed[25] that the rate of chain termination at the instant when the medium becomes heterogeneous changes less than might be

expected owing to the mutual approach of the active ends on association. However, as the amount of polymer increases, the rate of reaction rises with conversion, i.e. there is an acceleration effect owing to the further blocking of the macroradicals and a more marked effect of the solid phase on chain termination than on chain propagation.

Talamini and coworkers[37] observed a decrease of the initial rate of heterophase polymerisation of vinyl chloride in THF and in 1,2-dichloroethane with increase of monomer concentration. On the other hand, the average rate of reaction, measured at a specified degree of conversion, was always higher than in a homogeneous medium, owing to autocatalysis.

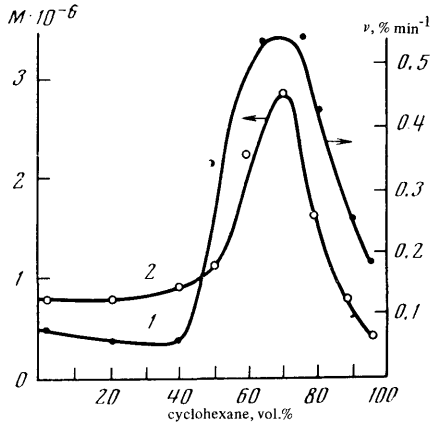


Figure 3. Variation of the maximum rate of polymerisation of methyl methacrylate (curve *1*) and the molecular weight of the polymer (curve *2*) with dilution of the monomer by cyclohexane at 55°C.

A decrease of the initial rate when the medium became heterogeneous was noted in the polymerisation of acrylonitrile in dimethylformamide (DMF) and ethylene carbonate[38] and of acrylic acid in methanol[39]. The variation of the maximum rate of polymerisation with the amount of precipitant in the methyl methacrylate system in cyclohexane was found to pass through a maximum[40,41] (Fig. 3). The authors explain these results by the influence of the swellability of the polymer phase, the permeability of the polymer aggregates, and the accessibility of the active centres on the elementary reactions. Since these factors depend on the type of polymer and solvent (or precipitant), the type of relation between the rate of polymerisation and monomer (or precipitant) concentration is different for specific monomers (vinyl chloride, acrylic acid, acrylonitrile, methyl methacrylate)[37-41]. When the precipitant content is high, the polymer phase is weakly swollen and the chain propagation reaction in it is retarded owing to the decrease of the local concentration of the monomer and its mobility in the relatively impermeable aggregate. The addition of solvent increases the swelling of the aggregate, which accelerates the diffusion of monomer molecules and increases the rate of polymerisation within the swollen particles. However, in the presence of a high content of the solvent, the increase of the mobility of the macroradicals and of the rate of termination of the growing chains plays a dominant role. Accordingly, the molecular weight of the polymers varies in parallel with the rate of polymerisation[37,38,40] (Fig. 3).

Somewhat different kinetic relation are observed in the polymerisation in a precipitant (cyclohexane) of acrylonitrile and acrylic and methacrylic acids, the polymers of which are incompatible with their monomers, in contrast to poly(methyl methacrylate)[41,42]. In this case, the rate of reaction decreases monotonically with dilution by cyclohexane, since access by monomer molecules to the occluded macroradicals is difficult owing to the incompatibility of the polymer and monomer and the low swellability of the polymer in the reaction medium. The unusual variation, involving a maximum in the dependence of the degree of polymerisation of acrylonitrile on temperature for the chemically initiated reaction, which was observed for the first time by Bamford and Jenkins[13] and Thomas and Pellon[12], is explained by the effect of swellability and mobility of the macrochains on the chain propagation and termination reactions:

Temperature, °C	30	40	50	60	70	80	90	100
Average molecular weight × 10^{-5}	4.3	6.25	8.64	10.73	6.36	3.76	2.17	1.38

Later similar results were obtained for the γ-initiated polymerisation of acrylonitrile[43] and ethylene[44].

An anomalous temperature effect was not noted[45] for vinyl chloride in the range 33–85°C owing to the high rate constant for chain transfer to the monomer. However, Talamini and Vidotto[46], who investigated its polymerisation at lower temperatures, found that the maximum molecular weight is reached at −30°C. According to another paper by the same investigators[47], the reason for this type of temperature variation is different degrees of crystallinity of the specimens obtained.

Bamford and Jenkins[48] examined certain cases of the secondary polymerisation of monomers initiated by macroradicals formed in the polymerisation of acrylonitrile (PAN) in bulk. The wide variety of kinetic curves obtained is due to the complex mutual relation between the swellability of PAN, the rate of diffusion of macroradicals and monomer molecules, and the kinetic characteristics of the process.

The rate of polymerisation of vinyl chloride in bulk at conversions less than 1% was found to be discontinuous by precise dilatometric measurements[49]. The study of the morphological structure of the solid phase formed made it possible to explain this decrease in the rate of polymerisation by the effect of the aggregation of macromolecules, which occurs on reaching the above conversions, on the elementary chain propagation and termination reactions.

Talamini and coworkers[37,38] examined the quantitative aspect of the decrease of the initial rate of polymerisation when the medium becomes heterogeneous. The reaction begins and continues in solution until the polymer concentration reaches a value such that the system separates into two phases. One of these is enriched and the other depleted in the polymer (we shall call these phases concentrated and liquid respectively). Using the steady-state hypothesis, the following expression was obtained for the ratio of the radical concentrations in the heterogeneous

and homogeneous systems before separation into different phases (Y):

$$Y = f_1^{1/2} \cdot v_1^{1/2} + \left(\frac{k_{tl}}{k_{tc}}\right)^{1/2} \cdot (1 - f_1)^{1/2} \cdot (1 - v_1)^{1/2} \quad (1)$$

where k_{tl} and k_{tc} are the rate constants for chain termination in the liquid and condensed phases respectively, v_1 is the volume fraction of the liquid phase, and f_1 the fraction of radicals formed per unit time in the liquid phase.

Eqn. (1) is valid also for the ratio of the rates of polymerisation in the heterogeneous and homogeneous systems on the assumption that the chain propagation rate constants remain unchanged. If $f_1 < v_1$ (the growing radicals and the polymeric molecules are more soluble in the concentrated phase) and $k_{tc} < k_{tl}$, the macroradicals pass to the concentrated phase at the instant of phase separation, y is less than unity, and the rate of polymerisation falls. The addition of a solvent accelerates polymerisation owing to the decreased probability of finding the growing chains in the precipitated phase. However, with increased conversion, Y becomes greater than unity faster the lower the value of k_{tc} compared with k_{tl}, i.e. phase separation gives rise to autocatalysis. For very high values of k_{tl}/k_{tc} (for example above 100), a decrease of the rate of polymerisation is observed only at low conversions (less than 1%). Autocatalysis becomes more pronounced with increasing conversion the more the growth of radicals in the concentrated phase predominates, i.e. the lower the solvent power of the medium.

An interesting effect of the presence of different phases on the conformation of polymethacrylic acid molecules was observed by Japanese workers[50]: in media precipitating polymers, the content of a syndiotactic polymer decreases owing to the active influence of the polymer phase on the addition of monomer molecules to the growing chain.

Thus the overall data presented above definitely demonstrate an active influence by the polymer formed not only on chain termination but also on chain propagation. It was shown that the apparent chain propagation rate constant decreases owing to the low swellability of the polymer (for example by 2—3 powers of ten in the polymerisation of acrylonitrile in bulk[32] compared with homogeneous conditions). Comparative analysis of the diffusion coefficients of low-molecular-weight substances in polymeric materials and of the rate constants for elementary reactions also demonstrates that, when the swellability of the polymer is low, the rate of chain propagation with $k_p > 10^2$—10^3 litre mole^{-1} s^{-1} is limited by diffusional parameters and not by kinetic parameters[51-55]. By altering the reaction medium and its interaction with the polymer, it is possible to influence actively the heterophase radical processes. For example, the rate of polymerisation of methyl methacrylate in methanol is much lower than in a methanol—water mixture owing to the greater swellability of the polymer and the higher mobility of macroradicals in the swollen solid phase in the first case[52].

The effect of pressure on the rate of heterophase polymerisation was studied by Gonikberg and coworkers[56-58], who observed an unusually marked acceleration of the polymerisation of butyraldehyde and isobutyraldehyde[56], α-methylacrolein[57], acrylonitrile[58], and methacrylic acid[20] at high pressures. This finding can be explained either by an increased rate of diffusion of the monomer in the polymer aggregates or by an increase of the degree of occlusion of the radicals (a decrease of the rate of chain termination).

When a chain transfer is introduced, the usual type of pressure variation of the rate and molecular weight is observed[58], which supports the second hypothesis. From this standpoint, one can understand the absence of anomalous phenomena in the polymerisation of vinyl chloride in bulk at high pressures[59,60].

2. The Role of the Polymer Phase in Heterophase Copolymerisation

The theory of homogeneous radical copolymerisation (in which the reactions are considered without considering the phase state of the system) makes it possible to calculate readily the composition of the copolymers when the relative activities of the monomers r_1 and r_2 are known. The study of the effect of heterogeneity on the composition of the copolymers led to the conclusion that the Mayo—Walling equation is inapplicable to heterophase copolymerisation. The majority of investigators[61-64] noted differences between the relative activities of the monomers of a particular binary system in different media. At present, the characteristics of heterophase copolymerisation can be accounted for solely on the basis of qualitative assumptions of different kinds.

Since the activity of comonomers is understood as the ratio of the chain propagation rate constants k_{11}/k_{12}, the deviations associated with the presence of the solid polymer can be explained by postulating that the rate of chain propagation reactions is determined by the rate of diffusion of the monomers to the active centres, or by a change in the elementary rate constants k_{11} and k_{12} owing to the specific features of the solid, or, finally, by the selective sorption of the monomers on the polymer phase, which leads to a change in the composition of the mixture of comonomers in the vicinity of the macroradical. Evidently the last factor has a major influence in the case of comonomers with markedly different polarities.

We shall consider certain experimental data using the sorption hypothesis. In this connection one must note the work of Brandrup[61,62] concerning the dependence of the composition of the copolymers of acrylonitrile and acrylic esters on the solvent. It has been shown that, on passing from a homogeneous to a heterogeneous system, the copolymer always becomes depleted in acrylonitrile as a result of a change in the water content in the solvent (DMF).

If the copolymerisation is carried out in water alone, then the copolymer is also always enriched in acrylic esters compared with homogeneous conditions. The lower the solubility of the acrylic ester in water the greater the probability of its incorporation in the copolymer. These findings can be readily explained if one assumes the preferential sorption of the less soluble acrylic esters by the polymer.

The above conclusion is confirmed also by the composition of the copolymers obtained in other precipitants (heptane, cyclohexane), where the opposite situation obtains, the copolymers being enriched in acrylonitrile relative to the initial mixture (Fig. 4). Since Brandrup's data show that acrylonitrile is less soluble in heptane and cyclohexane than acrylic esters, it is sorbed preferentially and its content in the copolymer increases.

Ryabov, Semchikov, and coworkers[40,42,65] found that, with increased concentration of the non-polar precipitant (cyclohexane) in the heterophase copolymerisation of methyl methacrylate with acrylonitrile, acrylic acid, or methacrylic acid, and also of vinylidene chloride with

acrylonitrile, the content of the more polar component in the copolymer increases. Since chain propagation occurs mainly within and on the surface of the polymer particles, i.e. in the zone of enhanced concentration of the sorbed polar monomer, this is responsible for its increased content in the copolymer. A definite piece of evidence supporting the selective sorption of one of the monomers is the decrease of the content of acrylic and methacrylic acids in the copolymers when the hydrogenated monomers (propionic and isobutyric acids) are added, which is due to the displacement of the unsaturated acids by the saturated acids from the sorption layers[66].

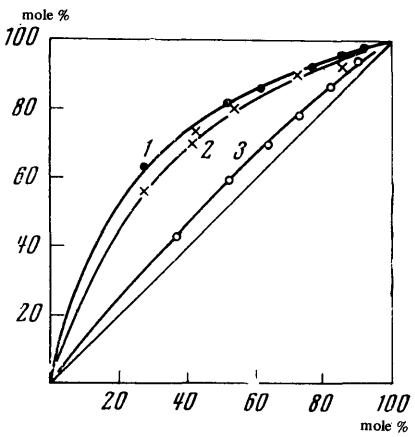


Figure 4. Composition curves for the acrylonitrile—ethyl acrylate copolymer in different media. The content of acrylonitrile in the copolymer is plotted against its content in the initial mixture: 1) heptane; 2) cyclohexane; 3) dimethylformamide (homogeneous media).

Graft copolymers of styrene with acrylonitrile or methyl methacrylate on polyethylene or Teflon are also enriched in the more polar monomer[67].

The local concentrations of the comonomers in the polymer phase $[M_i]_a$ may be related to their volume concentrations in the liquid phase $[M_i]$ by the Langmuir equation

$$[M_i]_a = \frac{k_{ad.\,i}[M_i]}{1 + k_{ad.\,i}[M_i]}; \quad i = 1.\,2 \qquad (2)$$

where $k_{ad.i}$ is the constant of the adsorption isotherm of the monomer in the polymer particles. Hence it follows that, when $k_{ad.1} \neq k_{ad.2}$, the composition of the copolymer formed in the solid phase $\{[M_1]_a/[M_2]_a\}$ will be different from the composition of the copolymer in the liquid phase $\{[M_1]/[M_2]\}$. The greater the difference between the constants k_{ad} the more pronounced is the inhomogeneity of the composition.

Moreover one should also expect a change in the rate constants for the elementary reactions. Thus copolymers with the same average composition (24% of potassium acrylate and 76% of acrylamide) obtained under homogeneous and heterogeneous conditions had different microstructures, i.e. different distributions of units in the chain, which indicates an effect of the solid phase on the elementary chain propagation reactions[64].

The curves describing the distribution of the compositions of the copolymers of acrylamide with maleic acid[68,69] and of methyl methacrylate with methacrylic acid[70] also form an anomalously broad peak compared with the theoretical curves, owing to the effect of phase heterogeneity on the chain propagation and macroradical recombination reactions.

Compared with sorption and the changes in rate constants, diffusion factors should have a smaller influence on the composition of the copolymers in view of the insignificant differences between the diffusion coefficients of the comonomers in such heterophase systems. For example, in the copolymerisation of acrylonitrile with methyl and propyl acrylates in bulk (heterophase conditions) and in the presence of an excess of acrylonitrile, the composition of the copolymers differs little from that obtained in the polymerisation in DMF solution. In this case, the rate of diffusion of monomers is so high that selective sorption is prevented[61].

If there is no preferential sorption of one of the monomers or if the added substance is a solvent for the copolymer causing its swelling and an increase of the rate of diffusion of the monomer molecules in the solid phase, phase heterogeneity has no effect whatever on the composition of the copolymer (provided that the chain-propagation rate constants remain unchanged); in this case the process has all the characteristics of homogeneous copolymerisation.

3. The Molecular Weight Distribution (MWD) of Polymers

Polymerisation involving the precipitation of the polymer formed is known to give rise to a broad or "irregular" molecular weight distribution with several maxima. Thus MWD of polyacrylonitrile obtained in dimethyl sulphoxide (homogeneous conditions) is much narrower than in the polymerisation of acrylonitrile in water (a heterogeneous system)[71]. A trimodal MWD was obtained by Pyrkov[72] in the polymerisation of acrylonitrile and by Eriksson[73] in the polymerisation of methyl methacrylate in water. Krozer and Czlonkowska[74] observed a distinct bimodal distribution for poly(vinyl chloride) polymerised in bulk at all conversions ranging from 18—78%. The MWD curves obtained by the fractional precipitation method for poly(vinyl chloride) polymerised in bulk also have two maxima[75]. Frenkel'[35] demonstrated for numerous instances of the polymerisation of acrylonitrile and vinyl acetate in water, vinyl acetate in heptane, ethylene under critical conditions, etc. that multimodal MWD is inevitably obtained in heterophase polymerisation. The multimodality arises as a result of the simultaneous occurrence of the elementary reactions in different phases (liquid and solid), each of which has its own characteristic monomer, radical, and initiator concentrations. In this case several distributions are superimposed. Part of the polymer is formed in solution and chain termination takes place in the liquid phase ($R^{\cdot} + R^{\cdot} \rightarrow P$); part of the growing macroradicals $P^{\cdot}$, trapped by the solid polymer particles, are deactivated either by the interaction of the dissolved macroradicals ($P^{\cdot} + R^{\cdot} \rightarrow P$) or by collision with another similar active polymer species ($P^{\cdot} + P^{\cdot} \rightarrow P$). This should result in a tri- or bimodal distribution function depending on whether chains are terminated by recombination or disproportionation. Fig. 5 presents trimodal

MWD for polyacrylonitrile obtained by polymerisation under heterogeneous conditions[35]. Evidently the distribution function is very broad and the ratio of the weight-average molecular weight of the polymer to the number-average molecular weight (P_w/P_n) is more than 10.

It has been shown[35] that detailed analysis of MWD and also of the variation of MWD with conversion may yield additional information about the mechanism of heterophase polymerisation, i.e. about the sites where chain propagation reactions occur, about the type of chain termination reaction, etc.

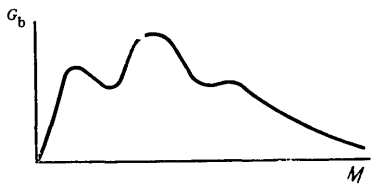


Figure 5. Molecular weight distribution of polyacrylonitrile obtained by the polymerisation of acrylonitrile in an aqueous medium; G_b—weight distribution function.

4. Post-polymerisation

The retardation of the rate of termination of macroradicals on formation of the solid phase leads to appreciable post-polymerisation. According to Magat's data[76], the rate of polymerisation of acrylonitrile in bulk decreased on switching off the radiation source to 1% of the initial value after 100 days and the conversion increased from 7 to 11%. The magnitude of the after effect depends on the duration of the initiated reaction[77].

Lyubetskii et al.[29] investigated the polymerisation of ethylene initiated by azobisisobutyronitrile at 70°C and a pressure of 100—600 atm. After cooling the system to 20°C ($v_{init} = 0$), the yield of polymer in 7 h increased from 125 to 156 g and the intrinsic viscosity increased from 1.10 to 1.70. Analogous results were obtained by Machi and coworkers[16,78,79].

Volkova and coworkers[17,18,80] observed an appreciable post-polymerisation of tetrafluoroethylene, vinyl fluoride, and vinylidene fluoride. Over a period of 60 min, the post-conversion of tetrafluoroethylene increased from 2 to 3.5% at 17.5°C. Fig. 6 illustrates the course of the post-polymerisation of acrylic acid in bulk at 20°C.[19]

Similar kinetic curves are characteristic of the post-polymerisation of acrylonitrile and vinyl chloride[32]. The after effect is appreciably suppressed with increase of temperature or when active chain transfer agents are introduced[32,43]. Analysis of the after effect can yield valuable information about the mechanism of the destruction of macroradicals, their lifetime, and kinetic constants.

If one assumes that in post-polymerisation macroradicals are destroyed as a result of bimolecular termination, it is easy to obtain the equations

$$\frac{1}{v_c} = \frac{k_t t}{k_p [M]} + \frac{1}{v_i}. \qquad (3)$$

and

$$\frac{\Delta [M]}{[M]} = \frac{k_p}{k_t} \ln ([R^\cdot] k_t t + 1), \qquad (3a)$$

where v_c and v_i are the rates of reaction at times t and $t = 0$ respectively. If chain termination proceeds via a mixed mechanism (bi- and mono-molecular)

$$-\frac{d[R]^\cdot}{dt} = k_t [R^\cdot]^2 + k_t' [R^\cdot], \qquad (4)$$

the following equation should hold:

$$\frac{\Delta [M]}{[M]} = \frac{k_p}{k_t} \ln \left(1 + \frac{k_p}{k_t'} [R^\cdot]\right) (1 - e^{-k_t' t}), \qquad (5)$$

where k_t' is the monomolecular chain termination rate constant.

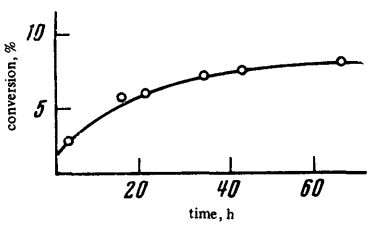


Figure 6. Post-polymerisation of acrylic acid at 20°C. The duration of polymerisation initiated by γ-irradiation was 20 min.

It has been found in a number of studies[32,43] that the post-polymerisation of acrylonitrile at 20—100°C and of vinyl chloride at −20°C is described by Eqns. (3) and (3a). However, in radiochemical polymerisation the linear relation $1/v_c = f(t)$ or $\Delta[M]/[M] = f(\ln t)$ has different proportionality coefficients at different conversions, which conflicts with the hypothesis that bimolecular chain termination with invariant k_t takes place. The authors attribute this to the occlusion of macroradicals. It has been shown that Eqn. (5) does not agree with the experimental data.

Markevich and coworkers[81] showed that Eqn. (3) holds for the dark polymerisation of tetrafluoroethylene in a precipitant (perfluorotriethylamine) and calculated k_t/k_p at 25°C. With increase of conversion, k_t/k_p decreases from 30 to 4 owing to the change in k_t. Under homogeneous conditions, the ratio k_t/k_p is constant at 70. k_p = 770 litre mole^{-1} s^{-1} has been determined by the method of inhibitors.

Using Eqn. (3a), Dainton and coworkers[82,83] found τ = 300 s for the polymerisation of acrylonitrile in water at 15°C, where $\tau = 1/k_t[R^\cdot]$. With increase of temperature to 30°C, τ falls to 150 s. The authors also concluded that the radicals in polymer particles are destroyed as a result of quadratic chain termination.

According to the data of Machi and coworkers[16,78,79], the rate of post-polymerisation of ethylene at a pressure of 250—400 atm increases with temperature in the range between 20° and 80°C, but remains constant for several hours at a specified temperature, which indicates the absence of chain termination reactions. However, at a

high temperature (140°C), the after effect is shown during a very brief period owing to the intense destruction of macroradicals.

Popov and Gladyshev[52] investigated the post-polymerisation of acrylonitrile in bulk at 17°C in the presence and absence of weak inhibitors of the type of diphenylamine (Fig. 7). It was shown that, when a solid phase is formed, the destruction of macroradicals takes place virtually at the instant of their interaction with the molecules of the weak inhibitor owing to the occlusion of active radical centres and the decrease of the rate of the R$^{\cdot}$ + R$^{\cdot}$ chain termination reaction; post-polymerisation is described by the equation

$$\ln \frac{v_{\text{нп}}}{v_c} = k_Z[Z](t - t_1) , \qquad (6)$$

where v_i and v_c are the rates of post-polymerisation at the initial instant t_1 and at any time t respectively, k_Z is the inhibition constant, and [Z] the concentration of the weak inhibitor.

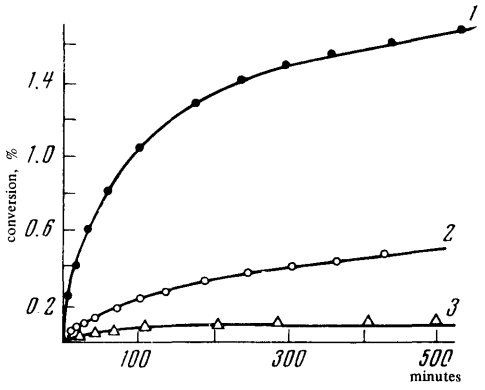


Figure 7. Post-polymerisation of acrylonitrile in bulk in the presence and absence of diphenylamine at 17°C; diphenylamine concentration (M): 1) 0; 2) 0.48×10^{-3}; 3) 1.21×10^{-2}. The polymerisation initiated by azobisisobutyronitrile (0.245×10^{-2} M) was continued up to a conversion of 3—3.5% at 60°C.

The constant k_Z was calculated from the linear relation between $\ln(v_i/v_c)$ and $t - t_1$ and was found to be 1.61×10^{-2} litre mole^{-1} s^{-1} for diphenylamine at 17°C. Thus the after effect method in heterophase polymerisation can yield valuable information about the reactivity of weak inhibitors of this kind, which previously could not be achieved in principle by the earlier Kise—Bagdasar'yan methods[11,84].

5. Quantitative Data

In heterophase polymerisation, the exponent n in the equation $v = k[M][I]^n$ is usually greater than 0.5. Thus, regardless of the method of initiation, $n = 0.8$ for acrylonitrile[7,85-87] and $n = 0.6$ for vinyl chloride[46,47]. An increased reaction order with respect to the initiator, which is characteristic also of other monomers undergoing heterophase polymerisation[6,16], is due to the occlusion of macroradicals and the catalytic effect of the polymer.

With increase of temperature, the degree of occlusion of active centres falls, the rate of termination rises, and n decreases to 0.5.[43,88]

The activation energy E_a for the polymerisation of acrylonitrile (thermochemical initiation) in bulk is fairly high, amounting to 35—37 kcal mole^{-1}.[12,89] With increase of temperature, E_a for radiation-induced polymerisation of acrylonitrile initially increases and then falls[43,90]:

Temperature, °C	0—20	20—60	60—70	70—90
E_a, kcal mole^{-1}	5	13.5—15	7.4	1.7

A similar relation between the apparent E_a and temperature was also found for methacrylic acid[88,91]: $E_a = 18.3$ kcal mole^{-1} at $T < 40°$, $E_a = 38.8$ kcal mole^{-1} at 40—75°C, and $E_a = 5.9$ kcal mole^{-1} at $T > 75$°C.

In the course of radiation-induced polymerisation of acrylonitrile, E_a increases up to a 20% conversion, then remains constant, and increases again at very advanced stages[92]:

Conversion, %	0	20—90	100
E_a (0-20°C), kcal mole^{-1}	4.65	6	10.4

The overall activation energy for the polymerisation reaction is defined as $E_a = E_p + nE_{init} - mE_t$, where $0.5 < n < 1.0$ and $m = 0.5$. Since E_t enters into this equation with a negative sign, the high value of E_a is evidently due to the diffusional component of the activation energy for chain propagation E_p and, in the case of thermochemical initiation, to the contribution of E_{init} owing to the increased value of n compared with homogeneous polymerisation. This equation also shows that E_t cannot be large. Indeed, according to certain experimental data, the chain termination activation energy for polyacrylonitrile[82,93,94] and poly(vinyl chloride)[95] under heterophase conditions is ~5—10 kcal mole^{-1} at $T < 100$°C.

The activation energy for the diffusion of macrochains in polymeric materials has been estimated as 25 ± 10 kcal mole^{-1}.[96,97] Since, as shown above, the active centres are deactivated by a bimolecular mechanism in heterophase polymerisation, the destruction of macroradicals is evidently not due solely to diffusion factors. Possibly, apart from quadratic chain termination, termination of the "relay" type as a result of chain transfer to the monomer and polymer, occurring by segmental and translational diffusion of macroradicals, plays an extremely significant role in this case.

This hypothesis is confirmed by a study of the heterophase polymerisation of certain monomers in the presence of weak inhibitors (inhibition constant $k_Z < 1$ litre mole^{-1} s^{-1}),[52] which are known not to affect the kinetics of homogeneous polymerisation. However, the sharp limitation of the rate of mutual termination of the growing chains when a solid phase is formed gives rise to a specific effect of relatively unreactive compounds of this kind owing to the increased importance of chain termination by the inhibitor. If the quadratic chain termination reaction may be neglected under certain conditions, it follows from the simplified mechanism that

$$v = \frac{k_p[M]}{k_Z[Z]} v_{in} , \qquad (7)$$

and

$$\bar{P} = \frac{k_p[M]}{k_Z[Z]} \qquad (8)$$

where [Z] is the concentration of the weak inhibitor. It has been shown that the rate of polymerisation of acrylonitrile in bulk decreases sharply from the very beginning

when small amounts of diphenylamine are added (Fig. 8). The reaction proceeds at a constant rate at least up to 50—60% conversion. In this case Eqns. (7) and (8) are valid and were used to calculate the ratio $k_Z/k_p = 0.151$ at 60°C.

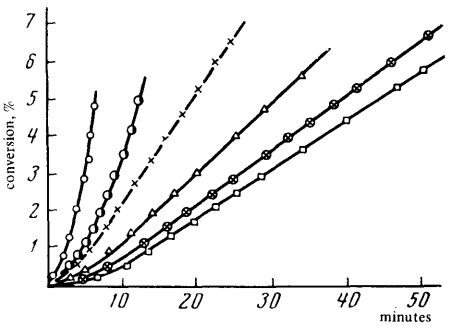


Figure 8. Polymerisation of acrylonitrile in bulk in the presence of diphenylamine at 60°C; concentration of azobisisobutyronitrile initiator 0.245×10^{-2} M; concentration of diphenylamine (M): 1) 0; 2) 0.12×10^{-2}; 3) 0.48×10^{-2}; 4) 1.21×10^{-2}; 5) 2.42×10^{-2}; 6) 3.64×10^{-2}.

In the polymerisation of methyl methacrylate in decane (a precipitant), diphenylamine has almost no effect on the reaction kinetics[52]. Evidently the degree of swelling of the polymer is in this case sufficiently high for chain termination by the recombination of macroradicals. However, the rate of polymerisation falls appreciably in methanol as a precipitant and even more so in a methanol—water mixture[52]. In the latter case, Eqns. (1) and (8) are also valid. The calculated k_Z are of the order of 10^{-1}—10^{-2} litre mole^{-1} s^{-1}. Thus the apparent reactivity of relatively inactive compounds increases sharply in heterophase polymerisation.

The constant for chain transfer to the monomer $C_M = k_{tr}/k_p$ is of the order of 10^{-5} for acrylonitrile[85,98]; $k_{tr} \simeq 10^{-2}$ litre mole^{-1} s^{-1} when $k_p \simeq 10^3$ litre mole^{-1} s^{-1}. Consequently, when one considers the mechanism of polymerisation with formation of a new phase, one must take into account reactions of this type. On the other hand, with increase of temperature the importance of physical factors (swellability of the polymer, diffusion of the monomer, occlusion of macroradicals) decreases, which leads to normal values of E_a.[88,90] If the polymer can undergo appreciable swelling, the overall activation energy is also close to the usual value, which has been noted, for example, for vinyl chloride (according to Gerren's data[99] the solubility of vinyl chloride in its polymer is 29% at 50°C and the constant for chain transfer to the monomer $C_m = 10^{-3}$).[26,100-102]

Some investigators[32,81,103] attempted to determine the rate constants for the elementary reactions. Thus Bawn et al.[32] found by the method of post-polymerisation that $k_p = 0.35$ and $k_t = 51$ litre mole^{-1} s^{-1} for acrylonitrile at 60°C and $k_p = 0.05$ and $k_t = 5$ litre mole^{-1} s^{-1} for vinyl chloride at −20°C. $k_p/k_t^{1/2}$ for acrylonitrile has a maximum at 50°C, which correlates satisfactorily with the temperature variation of the molecular weight[104]:

Temperature, °C	25	35	40	45	50	55
$k_p/k_t^{1/2}$	0.077	0.134	0.176	0.180	0.670	0.070

The values of k_p and k_t for ethylene calculated by different investigators show marked discrepancies[105-108].

Certain kinetic data may be obtained by studying heterophase polymerisation in the presence of inhibitors[52]. Then it is easy to calculate the ratio k_Z/k_p from Eqns. (7) and (8) and hence k_p if k_Z is known. On the other hand, k_p may be determined from the relation $v = k_p[M][R^\cdot]$ by measuring the concentration of macroradicals by the ESR method, since in the presence of an inhibitor the reaction proceeds under steady-state conditions. The values calculated for the polymerisation of acrylonitrile in bulk at 40°C are $k_p = 1.2$ and $k_t = 340$ litre mole^{-1} s^{-1}.

However, the observed rate constants for the elementary reactions are apparent values, since it was shown above that the rate of heterophase polymerisation depends on many factors and, moreover, there are not yet any quantitative data on the ratio of the monomer concentrations in the liquid and solid phases. However, first studies on these lines have been made[40,109,110].

III. MORPHOLOGY OF THE POLYMER PHASE

The first systematic studies on the morphology of the precipitated polymer were those of Thomas[10,12,111] on the polymerisation of acrylonitrile in bulk and in aqueous solution. At the beginning of the reaction (polymerisation in bulk), an opalescence appears with subsequent transition to a light turbidity. After 0.2—0.3% of the monomer has been converted into the polymer, the fine suspension of the polymer coagulates, forming a curd-like precipitate which fills the entire volume. When about 50% of the monomer has been converted, the reaction mixture consists of a white solid. Electron microscope studies showed that in the early stages the particles formed are dense globular, and identical in size. When the monomer conversion is about 1%, the particle diameter reaches 1000—2500 Å. The number of particles remains almost constant during the polymerisation process, and amounts to 10^{12}—10^{14} per cm^3 depending on the reaction conditions.

At high conversions (70—80%), a monolithic transparent solid is formed[112]. Kinetic studies on the polymerisation of acrylonitrile[89,112,113] and vinyl chloride[114] in bulk up to high conversions showed that the formation of a transparent polymer requires a correspondence between the rate of reaction and the rate of diffusion of the monomer molecules into the pores of the polymer particles. Under these conditions, the growth of the particles leads to close contact between them and to the disappearance of interfaces.

A series of studies dealing with the morphology of poly(vinyl chloride) polymerised in bulk and allowing a considerable understanding of the mechanism of the formation of the polymer phase were published in recent years[49,114-119]. In the initial stages of the process, the macromolecules are in a molecularly dispersed state in the monomer medium. When the degree of polymerisation of vinyl chloride exceeds 25—32, the macromolecules are no longer soluble in the monomer[49]. After the attainment of the critical concentration, the particles of a new polymer phase (possibly a polymer-monomer phase) are segregated. Their dimensions are determined by the

critical dimensions for nucleus formation. Bort[116] called these growing nuclei microglobules. Microglobules can grow both owing to the formation of the polymer within the particles and as a result of the adsorption of the polymer formed in the bulk of the monomer.

Microglobules are unstable with respect to aggregation and coalesce into macroglobules. According to the data of Cotman et al.[49], this occurs at a conversion of 0.2—0.9%. The morphology and number of macroglobules are influenced by the average rate of polymerisation, an increase of which entails an increase in the number of particles up to a constant value of about 10^{12} per cm^3.

In the course of polymerisation, new particles are not formed and their number remains constant. The number of microglobules in the macroglobule varies from 1 to several tens, depending on the rate of polymerisation. With increase of the degree of conversion, the size of the macroglobules increases from 0.1 to 1—2 μm. The narrow unimodal distribution of the particles with respect to size is evidence that the rate of growth remains almost constant for all the particles.

Since the globular structure persists up to 30% conversion and the number of particles remains unchanged during polymerisation, Bort et al.[116] reached the unambiguous conclusion that the increase in the mass of the globules is due to the macromolecules growing within the globules themselves rather than to those formed in the bulk of the monomer. Since the termination of the growing chains in the globule is greatly hindered, the rate of polymerisation in the particle will be higher than in the bulk of the monomer.

In the polymerisation of methacrylic acid in bulk, the polymer is also formed from the early stages as globules whose size is about 0.1 μm, which are then aggregated into larger globules[120]. In the general case, one assumes that the formation of the solid phase is closely related to the topochemistry of the polymerisation process, which in turn is determined by the nature of the interaction between the polymer and its monomer[118,121]. If the solvent power of the medium is sufficiently high for the formation of a monomer-polymer phase, i.e. a solution of the polymer in the monomer, the accumulation of the solid monomer may occur partly owing to the adsorption of the macromolecules from the solution on the surface of the polymer particles. Then the surface of the growing particle becomes "grown over". Consequently the structure of the particles may be varied from very dense to loose by a suitable choice of solvent[10,122]. In the presence of a large amount of solvent, the particles cease to be globular and the polymer consists of a monolithic mass, as shown for the polymerisation of methyl methacrylate in cyclohexane[40].

If the polymer particles produced are incapable of swelling, then the appearance of comparatively dense and smooth globular structures, owing to the settling on the surface of a fine "fraction" of the polymer from the liquid phase, is also to be expected.

The solid phase is formed somewhat differently in the polymerisation of monomers capable of crystallising. For example, in the polymerisation of vinylidene chloride, a mixture of lamellar crystals and globules is formed[14]. The presence of two types of structures in the reaction medium is due to the simultaneous occurrence of two processes: polymerisation and crystallisation.

Thus the characteristics of the morphological structure of the polymer phase formed depend on the polymerisation kinetics (the average rate of polymerisation), the swelling of the polymer particles, and the capacity of macromolecules to form part of crystalline structures.

IV. THEORIES AND KINETIC MECHANISMS OF HETEROPHASE POLYMERISATION

Analysis of the existing models of heterophase polymerisation reveals two opposed views concerning the site of the reaction in the formation of the polymer phase. According to the immobilised surface theory[45], the increase of the rate of polymerisation with conversion is explained by the increase of the area of the polymer phase formed. According to the occlusion theory[6], the mass of the polymer determines the characteristics of the heterophase polymerisation. There exist also other theories—in particular the heterophase polymerisation of certain monomers in water is regarded as analogous to polymerisation in emulsion[111].

The majority of the kinetic mechanisms are bases on the invariance of the rate constants for the elementary reactions, which constitutes an appreciable simplification.

1. The Surface Theory

The kinetic mechanism of Bengough and Norrish[45] is based on the fact that the polymer exhibits a cocatalytic activity on the polymerisation of vinyl chloride. The ease of chain transfer to the polymer leads to the formation of immobilised radicals and polymer particles. These radicals are almost incapable of bimolecular chain termination but do retain their capacity for growth. Growth continues until small mobile radicals are formed as a result of chain transfer via the monomer. In consequence of these transfer reactions, the chain returns to the liquid phase where bimolecular termination ultimately takes place.

The equation derived by the authors,

$$v = k[\mathrm{I}]^{1/2}[\mathrm{M}]\left\{1 + \frac{k'[\mathrm{P}]^{2/3}}{[\mathrm{M}]}\right\} \qquad (9)$$

where k and k' are constants and [P] is the amount of polymer per unit volume, shows that the rate of polymerisation is proportional to the amount of polymer raised to a power of 2/3, i.e. to the surface area of the polymer phase. According to this theory, the number of branches arising by chain transfer to the polymer is also proportional to conversion raised to a power of 2/3.[123]

Bearing in mind Bamford's critical comments[6] concerning the variability of the kinetic constants, Mazurek[124] derived the equation

$$v = v_i\,(1 + b[\mathrm{P}]^{2/3}), \qquad (9a)$$

where v_i is the initial rate of polymerisation and b the phase heterogeneity constant defined as the ratio of the rates of propagation in the polymer particles and in the liquid phase at a conversion of 1%. The following additional reactions were included in the usual kinetic mechanism:

$$\text{Transfer of radicals to the solid phase } R^{\cdot} \xrightarrow{k_a[\mathrm{P}]^{2/3}} R_a^{\cdot}$$

$$\text{Chain propagation in the solid phase } R_a^{\cdot} + M \xrightarrow{k_{pa}} R_a^{\cdot}$$

$$\text{Chain transfer to the monomer } R_a^{\cdot} + M \xrightarrow{k_{tra}} P + R^{\cdot}$$

where k_a is the rate constant for the transfer of radicals to the polymer phase and R_a are the radicals in the polymer phase.

It is assumed that the constant k_{pa} and k_{tra} vary with conversion but their ratio remains constant: $k_{pa}/k_{tra} \simeq$ const. On the basis of this mechanism, taking into

account the chain termination by radicals from different phases, and the concept of "live" polymer chains in the solid phase, Lyuberetskii and Mazurek[125] obtained an equation for the polymerisation of ethylene, which agrees satisfactorily with experimental data.

A mechanism has been proposed[86] for the polymerisation of acrylonitrile in water, which involves the adsorption and termination of macroradicals on the surface of polymer particles.

Certain indirect data also support the hypothesis that polymerisation takes place on the surface of the particles. Thus an interesting feature of heterophase polymerisation is the dependence of process kinetics on the physical state of the polymer formed, in particular on the particle size and hydrodynamic conditions[126-130]. For example, the rate of polymerisation of acrylonitrile, methyl acrylate, and methyl methacrylate falls on passing from a stable fine sol to a coarse polymeric precipitate, which may be attributed to the decreased surface area of the particles and the decreased number of radicals on the surface[127]. A similar effect was observed following the addition of electrolytes as coagulants[127,128]. On the other hand, the introduction of peptising agents or stabilisers into the system[82,127] (for example cetyltrimethylammonium bromide) increases the stability of the colloidal system and the rate of polymerisation. According to Chapiro[39], the kinetics of the polymerisation of acrylic acid in methanol are also determined by the form of the polymeric precipitate (gel or powder).

Roskin and coworkers[129,130] and Machi and coworkers[131] investigated the effect of stirring on the polymerisation of acrylonitrile in water and of ethylene in the gas phase. Electron photomicrographs led to the conclusion that the polymer-monomer particles approach one another on stirring, which increases the rate of collision of the globules and the rate of termination of the chains on their surface, decreasing the rate of polymerisation of acrylonitrile. Moor and Parts[132] found that the rate of polymerisation of acrylonitrile in the centrifuged polymeric precipitate is lower than in the suspension before separation. This may be due to the increased rate of chain termination when the particles are deposited, owing to their mutual approach and greater isolation of macroradicals from monomer molecules.

Dauphin et al.[44] believe that the role of the polymer phase reduces to an increase of the local concentration of the monomer owing to its adsorption on the polymer surface. However, it has been shown[133] that physical adsorption does not play the main role in the self-acceleration process. The above facts concerning the influence of the transition of the system to a heterogeneous state on the rate of polymerisation also constitute convincing evidence against this hypothesis.

2. The Occlusion Theory. The "Trapping" of Radicals

The immobilised surface theory of Bengough and Morrish[45], which is based on the ease of chain transfer reactions, is inapplicable to monomers such as acrylonitrile and tetrafluoroethylene and is not of general validity. Moreover, Eqn. (9) does not hold in the initial stages of the polymerisation of vinyl chloride (up to a conversion of about 8%).

Bamford and Jenkins gave a qualitative explanation of the characteristics of heterophase polymerisation on the basis of the occlusion theory†. Under conditions promoting the precipitation of the polymer, a macroradical, having reached a certain size, coils up to form a dense structure and is segregated from the liquid phase. The active end of the radical is then occluded in the coiled structure and the rate of the termination reaction falls significantly. During polymerisation, the macrochains coalesce into polymeric aggregates. The aggregation promotes further blocking of the radicals. It is postulated that aggregation entails an insignificant change in the rate of propagation compared with the rate of chain termination, which leads to an increase in the rate of polymerisation with time.

It follows from the occlusion theory that the self acceleration is not determined by the surface but by the mass of the polymer. According to this theory, polymerisation takes place within polymer particles, the degree of occlusion of the radicals and the magnitude of the polymer barrier preventing the penetration of the monomer to the radical end depending on the number and weight of the particles.

The occlusion theory is confirmed by many experimental facts. Thus one of its consequences is that the segregation of the monomer leads to anomalously long lifetimes and high concentrations of macroradicals. Indeed the overall concentration of macroradicals, determined by the ESR method, is 10^{-4}—10^{-5} M for various monomers[6,134-136]. For comparison, we may point out that in polymerisation in solution the concentration is less than 10^{-8} M (except at high conversions). The existence of long-lived radicals in the heterophase polymerisation of ethylene has been postulated by a number of workers[29,137].

If the initiating agent is removed in the initial stages of the polymerisation of acrylonitrile and the unreacted monomer is replaced by a fresh monomer, post-polymerisation is observed[6]. This shows that the radicals persist in the solid monomer and initiate the polymerisation of the fresh monomer. The concentration of these "trapped" radicals, determined by the ESR and inhibitor methods, is 10—13% of the total value, amounting to 7.8×10^{-5} M or 3.7×10^{16} spin ml^{-1} (at 20°C) [36] in a typical experiment.

With increase of temperature, the concentration of "trapped" radicals decreases appreciably[36]:

Temperature, °C	20	25	40	60
Number of "trapped" radicals per ml × 10^{-16}	3.7	2.3	0.8	0.1

Analogous results were obtained by Ingram et al.[134]

"Trapped" radicals have been detected by the ESR method in the polymerisation of methyl methacrylate and methacrylonitrile in hexane[135], in the polymerisation of methacrylic acid in bulk {$[R^{\cdot}] \simeq 10^{-5}$ M},[138] in the polymerisation of other monomers[135,141], and in the copolymerisation of methyl methacrylate and methacrylic acid in benzene {$[R^{\cdot}] = 10^{-4}$—10^{-5} M}.[139] Kargin, Ryabov, and coworkers[120] found that the relation between the concentration of "trapped" radicals and conversion in the polymerisation of methacrylic acid in bulk passes through a maximum.

The "trapped" radicals can initiate the polymerisation of various monomers. Copolymers of acrylonitrile with vinyl acetate, vinylidene chloride, methyl methacrylate, and styrene have been obtained in bulk in this way[140]. At low temperatures, when chain transfer to the monomer is

† This theory is discussed in detail in the monograph of Bamford et al.[6]

insignificant, "trapped" radicals were detected in poly(vinyl chloride); following the addition of DMF, they are activated and initiate the polymerisation of styrene and methyl methacrylate[142]. Bamford and Jenkins[48] investigated the kinetics of the polymerisation of various monomers initiated by "trapped" polyacrylonitrile radicals.

The occlusion theory is qualitative, since it is difficult to express the quantitative relation between the rate constants and the degree of occlusion.

An interesting quantitative interpretation of the kinetics of heterophase polymerisation has been made by Mickley et al.[26], who attempted to eliminate the contradiction between the occlusion and surface theories. The authors suggested that in the initial stages the rate of polymerisation is proportional to the amount of polymer formed, since polymer particles are fairly small and do not prevent contact between the radicals "trapped" within the particles and the liquid phase. After subsequent growth and aggregation of the particles, only a thin surface layer of the aggregates remains in contact with the liquid phase and radicals are "trapped" either owing to chain transfer to the surface of the particles or owing to the penetration of the macroradicals diffusing from the liquid phase to the active surface region of the particles. In this stage, the rate of polymerisation is proportional to the volume of this active layer or approximately to the area of the polymer phase, i.e. $[P]^{2/3}$. The following kinetic equation for the stage in which the rate of polymerisation depends on the polymer volume V_P was derived on the basis of the above mechanism:

$$v = k[M][I]^{1/2} + k[I]^{1/2}\frac{k_{trP}D_L[R_a]V_P}{D_L k_{tr}a} \qquad (10)$$

For the stage where the rate of polymerisation depends on the surface area of the polymer phase S_P, we have

$$v = k[M][I]^{1/2} + k[I]^{1/2}\frac{k_{trP}D_L'[R_a^{\cdot}]\delta S_P}{D_L k_{tr}a}, \qquad (11)$$

where $k = k_p k_{in}^{1/2}/k_t^{1/2}$, [I] is the concentration of the initiator, k_{tr} and k_{trP} are the constants for chain transfer to the monomer and polymer respectively, D_L' and D_L are diffusion coefficients in the liquid phase of the macroradicals and monomeric radicals respectively, $[R_a^{\cdot}]$ is the average concentration of radicals in the active volume, V_P and S_P are the total volume and total surface area of the polymer particles per unit volume of the system, δ is the depth of penetration of the radicals into the particle, and a is the ratio of the concentrations of the monomeric radicals on the surface and in the active volume of the particles.

The proportionality of the rate of polymerisation of vinyl chloride to [P] in the first stage and to $[P]^{2/3}$ in the second stage has been confirmed experimentally[26]. However the usefulness of the above equations is doubtful in view of the difficulty of evaluating some of the parameters.

Cotman et al.[49] made a critical examination of the equation of Bengough and Norrish[45] and suggested that instead of the power exponent 2/3 one should use in Eqn. (9) a variable exponent α depending on the polymerisation conditions. The variation of α with the rate of polymerisation indicates a more complex relation between v and [P] than suggested by Bengough and Norrish. The studies by Bort[114-118] on the morphology of the polymer phase formed made a definite contribution to the elucidation of the question of the site where the chain propagation reaction occurs. Bort[148] obtained experimental evidence showing that the polymerisation of vinyl chloride takes place within the polymer particles, since a change in their surface area for a fixed mass of the polymer does not affect the form of the kinetic curves (except at high rates of polymerisation). Consequently the increase in surface area during heterophase polymerisation is not a factor responsible for self acceleration.

At high average rates of polymerisation, α approaches 2/3, which reflects the limiting relation between the rate v and the amount of polymer precipitated. In this case, the rate of polymerisation exceeds so much the rate of diffusion of macroradicals in the solid phase that there is not sufficient time during the chain propagation step for them to penetrate into the polymeric aggregate and therefore they remain on the surface. Moreover, the permeability of the aggregate decreases owing to the greater density of its structure at high rates of polymerisation and the increase of the polymer barrier to the diffusion of macrochains.

3. The Two-phase Model

Analysis of the morphological structure of the solid phase formed and of the kinetic data lead to the conclusion that in the general case the topochemistry of the polymerisation process is determined by the nature of the interaction of the polymer with the medium. It is possible to distinguish three regions where polymerisation takes place—the liquid phase, the surface, and the bulk of the polymer phase.

If the solvent power of the medium is sufficiently high for a solution of the polymer to exist, the polymer may accumulate largely owing to the formation of macromolecules in the solution. The usual kinetics of homogeneous polymerisation are characteristic of this process. When the swellability of the polymer is very low, the reaction takes place mainly on the surface and in the bulk of the particles formed. Kinetically, the radicals on the surface and in the bulk of the particles are non-equivalent, the activity of the latter being lower in the mutual termination and possibly propagation reactions.

On the basis of these concepts, Talamini[144] proposed a simple mechanism to describe the polymerisation of vinyl chloride in bulk. Since vinyl chloride is a poor solvent for its polymer (the Flory—Huggins constant for this system is 0.88 at 50°C [145]), the separation of the initially homogeneous system into two phases (a dilute liquid monomer-polymer phase and a concentrated solid polymer-monomer phase) takes place at very low conversions (about 0.1%). Subsequently the polymerisation process occurs simultaneously in both phases but at different rates, since the properties of the phases are different (viscosity, monomer concentration, etc.). With increase of conversion, the amount of the dilute phase diminishes and that of the concentrated phase rises. Assuming that the ratio of the rates of polymerisation in the two phases is constant, and that the kinetic constants do not vary with conversion, the following equation was obtained[144,146]:

$$\frac{\Delta[M]}{[M]} = \frac{1}{g}\exp(gk[I]^{1/2}t - 1) \qquad (12)$$

where $k = k_p k_{in}^{1/2}/k_t^{1/2}$ is a constant, $g = -\{1 + [M]_c/[P]_c - v_c[M]_c/v_d[P]_c\}$ is an acceleration factor characterising the autocatalytic effect (the subscripts c and d refer to the concentrated and dilute phases respectively, and v is the

rate of polymerisation. When the exponential function is expanded as a series, we obtain

$$\frac{\Delta[M]}{[M]} = \frac{1}{g}\left\{gk[I]^{1/2}t + \frac{g^2k^2}{2!}([I]^{1/2}t)^2 + \frac{g^3k^3}{3!}([I]^{1/2}t)^3 + \ldots\right\} \quad (13)$$

Eqn. (13) accounts for the higher (more than 0.5) order of the reaction with respect to the initiator. The agreement between the experimental data and the theoretical curve calculated by Eqn. (12) is fairly satisfactory for vinyl chloride up to 50—60% conversion (polymerisation temperature 50°C, initiators—benzoyl and lauroyl peroxides and azobisisobutyronitrile)[146]. Russo et al.[147] used this hypothesis as a basis for a kinetic mechanism of radiation-induced polymerisation of vinyl chloride.

Among the available models, that described above gives perhaps the most accurate description of the quantitative aspect of the kinetics of heterophase polymerisation of vinyl chloride. It postulates the proportionality of the rate of reaction to the weight of the polymer formed and is also confirmed by Bort's data[114] concerning the existence of a solution of poly(vinyl chloride) in the monomer. However, it is still not clear to what extent it is applicable to the polymerisation of acrylonitrile, where the solubility of the polymer in the monomer is much lower than in the poly(vinyl chloride)—vinyl chloride system.

Of the kinetic mechanisms giving a clear and correct description of the physical and chemical processes occurring in heterophase polymerisation, we shall also mention Dainton's mechanism[82,83] proposed for the polymerisation of acrylonitrile in water. It includes reactions in the liquid and solid phases and takes into account interfacial processes—the aggregation of macromolecules and primary polymer particles (microglobules), the "trapping" of the radicals from the liquid phase, chain termination reactions at the interfaces between the phases and within the phases, and adsorption of monomer molecules by polymer particles.

A. Reactions in the liquid phase. 1. Initiation $I \rightarrow 2R_1^{\cdot}$. 2. Chain propagation $R^{\cdot} + M_{aq} \rightarrow R^{\cdot}$. 3. Chain termination $R^{\cdot} + R^{\cdot} \rightarrow P$.

B. Processes in the polymer phase. 1. Conversion of the critical particles p into primary polymer particles P:

$$p + p \rightarrow P$$

and

$$p + P \rightarrow P\ .$$

2. Slow aggregation of the primary particles:

$$\begin{matrix} P + P \rightarrow P \\ P + P^{\cdot} \rightarrow P^{\cdot} \end{matrix}$$

3. Particle growth:

$$P^{\cdot} + M_a \rightarrow P^{\cdot}\ .$$

C. Interfacial processes. 1. Weak adsorption of the monomer by polymer particles $M_{aq} \rightarrow M_a$. 2. Activation of the particles—trapping of radicals by polymer particles:

$$R^{\cdot} + P \rightarrow P^{\cdot}\ .$$

3. Chain termination by radicals from different phases:

$$R^{\cdot} + P^{\cdot} \rightarrow P\ .$$

Kiuchi et al.[148] were able to relate the concentration of the adsorbed monomer (acrylonitrile) $[M]_a$ to its concentration in the aqueous phase $[M]_{aq}$:

$$[M]_a = \frac{\beta}{V_e^{0.5}}[M]_{aq}^2\ , \quad (14)$$

where β is a coefficient varying with the dimensions and the physical state of the polymer particles and V_e is the effective volume of the reactant.

4. The Emulsion Polymerisation Model

Some investigators[10,11] stress the similarity of the systems under consideration, particularly of polymerisation in an aqueous medium, to typical emulsion polymerisation systems. This analogy is based on the morphological and kinetic characteristics of both processes—self acceleration, high average rates and high molecular weights of the polymers, globular nature of the particles, etc. In both cases, the number of polymer particles remains constant in the course of polymerisation. In heterophase polymerisation, the number of particles per cm^3 of the medium is 10^{12}—10^{14}, which is the lower limit in emulsion polymerisation. The monomer consumed in the growing polymer particles is constantly replenished, as in emulsion polymerisation, by diffusion of the monomer molecules from the liquid phase.

Thomas and Webb[150], who employed emulsion polymerisation as a model, calculated k_p from the rate of polymerisation of acrylonitrile in water. The resulting value $k_p = 2 \times 10^4$ litre $mole^{-1}$ s^{-1} agrees satisfactorily with Dainton's data[82,83].

Kiuchi et al.[149] concluded that the principal centres of heterophase polymerisation of acrylonitrile are polymer particles, as in emulsion polymerisation. However, it was found that the relation between the rate of polymerisation and the number of particles is much less pronounced than in typical emulsion polymerisation. The authors explain this difference by the fact that in the first case the heterogeneity of the system due to the insolubility of polyacrylonitrile in the monomer allows each polymer particle to contain more than one radical and therefore it cannot be regarded as an independent centre of propagation of the reaction.

Recently a kinetic mechanism, based on the Smith—Ewart theory was proposed[151] (polymerisation of methyl methacrylate in water). It was suggested that chain propagation takes place on the surface of the particles, the number of which remains constant after the coalescence of the macromolecules. Then

$$v = k_p\frac{\bar{n}N}{N_A}[M]_a, \quad (15)$$

where N is the number of particles, $\bar{n}$ the average number of radicals per particle (proportional to the surface area of the particle or its volume raised to the power 2/3), N_A the Avogadro number, and $[M]_a$ the concentration of methyl methacrylate in the polymer particle assuming it to be proportional to its concentration in the aqueous phase, i.e. $[M]_a = k_1[M]_{aq}$.

After rearrangement, we obtain

$$v = k_p k_1 V_p^{2/3}\frac{N^{1/3}[M]_{aq}}{N_a}\ , \quad (16)$$

where V_p is the overall volume of the polymer phase. It follows from Eqn. (16) that the rate of polymerisation is proportional to the number of particles raised to the power 1/3 and to the concentration of the monomer raised to the power 5/3. Experimental data agree satisfactorily with these conclusions.

5. Theory of Monomolecular Chain Termination. Other Theories.

According to the theory of Thomas and Pellon[12], the occlusion of certain macroradicals can reach such an extent that they become incapable of chain propagation and bimolecular chain termination reactions. This effect resembles the monomolecular chain termination reactions. Thus one may assume that radicals are destroyed via bi- and mono-molecular reactions:

$$-\frac{d[R^{\cdot}]}{dt} = k_t[R^{\cdot}]^2 + k_t'[R^{\cdot}]$$

Having postulated a steady state, the authors obtained an equation for the polymerisation of acrylonitrile in bulk:

$$v = (A^2 + B[I])^{1/2} - A \qquad (17)$$

where

$$A = \frac{k_t' k_t[M]}{2k_t}; \quad B = \frac{k_{in}(k_p[M])^2}{k_t}.$$

Eqn. (17) agrees with experimental data up to 50% conversion of the monomer. Bamford and Jenkins[6] criticised the theory of monomolecular chain termination on the grounds that, for the theory to be valid, the concentration of blocked radicals must be much higher than that of the "trapped" radicals found experimentally.

Durup and Magat[152] suggested that, when the degree of blocking of the macroradicals is a maximum, chain termination is due solely to the primary radicals. However, this hypothesis fails because post-polymerisation takes place at a decreasing rate despite the removal of the source of primary radicals.

Schindler and Breitenbach's analysis[153] of kinetic data for the polymerisation of vinyl chloride is based on the relation which the authors found between the decrease of the chain termination constant owing to the occlusion of free radicals and conversion:

$$k_t = \frac{k_{ti}}{(1 + k^*C)^{1/2}}, \qquad (18)$$

where C is the conversion, k_{ti} the constant for the initial rate of termination, and $k^* = 50$ is a dimensionless constant.

It was established that, up to 20% conversion at 50°C, the following equation holds:

$$C = \frac{k^* v_i^2}{4} t^2 + v_i t \qquad (19)$$

where v_i is the initial rate of polymerisation. This expression is analogous to Eqn. (13) to within the second term.

However, Cotman et al.[49] showed that the constant k^* depends on the rate of polymerisation and tends to increase with the increase of the initial rates of polymerisation. A deficiency of the kinetic equations (17)—(19) is their empirical nature and hence limited applicability.

Magat[154] examined the quantitative aspect of the polymerisation of vinyl chloride. He believed that a steady state is not attained by the system for a long time owing to the low rate of chain termination. Thus self acceleration is caused by the increase in the concentration of macroradicals during the reaction. Despite the fact that the results for vinyl chloride agree satisfactorily with the experimental data, the equation obtained for a non-steady state is inapplicable to the polymerisation of acrylonitrile and vinylidene chloride[154].

If the polymer is capable of crystallising, the kinetic mechanism is complicated still further, since it is then necessary to take into account the differences between the rate constants for the elementary reactions involving the crystalline and amorphous phases[17,155]. The kinetics of heterophase polymerisation can be influenced also by the different reactions of the radicals, as shown for polyethylene[106,156].

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One may suppose that further advances in the field of heterophase polymerisation will be achieved by studying both chemical and physical processes accompanying the formation of the polymer phase, in particular by studying different chemical reaction in such systems, the morphological structure and swelling of the polymer particles, the adsorption and diffusion of monomer molecules in the particles, the ratio of the concentrations of the monomer in the liquid and solid phases, etc.

ADDENDUM

Quite recently a number of studies were published on the kinetics and mechanism of heterophase polymerisation and copolymerisation[157-164]. Among these, an investigation[157] where the kinetics of the polymerisation of vinyl chloride in bulk were interpreted qualitatively and quantitatively on the basis of the two-phase theory, is of interest. It is noted that the polymer phase consists of particles swollen in the monomer, the composition of which remain constant up to about 70% conversion. However, in contrast to the theory developed by Talamini[144], the above theory does not include the hypothesis of a steady distribution of radicals between the two phases corresponding to thermodynamic equilibrium, since owing to sorption processes the concentration of radicals in the polymer particles increases continuously with conversion, which is the reason for the autocatalytic nature of the polymerisation. Quantitative calculations showed that at low conversions the chain propagation and termination reactions already take place preferentially within the particles and the number of radicals in the liquid phase is independent of the rate of their termination. The proposed mechanism accounts for the decreased rate of polymerisation (discussed above) on formation and aggregation of particles as due to the increased rate of termination of radicals within the particles in consequence of the increase of their concentration in the effective volume of the condensed phase; the increase in the initial rate of polymerisation of vinyl chloride in bulk and the decrease of self acceleration following the introduction of chain transfer agents[33,34] are explained by the increase of the rate of liberation (desorption) of radicals into the liquid phase.

The kinetic data[158] obtained for the polymerisation of vinyl chloride in bulk (weak post-polymerisation at 25°C, low radical concentration, and a reaction order close to 0.5 with respect to intensity of irradiation) can also be interpreted satisfactorily on the basis of the two-phase model.

Thus, despite their somewhat limited applicability to different monomers, some of the theories discussed (the occlusion and two-phase theories) permit a satisfactory explanation of many characteristics of heterophase polymerisation.

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Institute of Chemical
Physics, USSR
Academy of Sciences,
Moscow