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Kinetics and Mechanism of the Inhibited Polymerisation of Vinyl Monomers

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New data on the kinetics and mechanism of reactions involving the inhibition of the radical polymerisation of vinyl monomers obtained during the last 10-15 years are described systematically and discussed. Equations describing the kinetics of the inhibited polymerisation, accompanied by side and secondary reactions such as additional initiation, chain regeneration, secondary inhibition, and inhibitor regeneration reactions are examined and analysed. The principal kinetic features associated with the structure of the monomer and the inhibitor, the type of initiation, and the influence of the medium are noted. Data are presented on the inhibiting activities of the compounds considered and the advantages of the latter relative to known stabilisers are demonstrated.
The bibliography includes 127 references.

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I. INTRODUCTION

One of the main criteria of a radical-chain polymerisation mechanism is the presence of inhibitors—substances whose addition in insignificant amounts to the reaction system can lower the rate of the process until its complete arrest.[1] The fundamental importance of inhibitors consists in the fact that they can be used as a kind of probe for the investigation of the polymerisation mechanism and as counters of active centres.

The practical value of inhibitors is determined by their application for the prevention of the undesirable formation of high-molecular-weight products under the conditions of the synthesis, purification, and storage of monomers.

The commonest inhibitors of the radical polymerisation of vinyl monomers are oxygen, quinones, phenols, aromatic amines, nitro-compounds, transition metal salts, and certain systems manifesting an increase in the reactivity of chemical compounds when they are mixed (synergism). In each specific case, the inhibiting activity of compounds of the above classes is different and depends significantly on particular physicochemical factors.

The retardation of polymerisation is associated with the interaction of active radicals with a relatively ineffective (weak) inhibitor, which results either in a decrease in the concentration of the active centres or in the formation of species incapable of propagating the kinetic and molecular chains.

In the presence of highly effective (powerful) inhibitors, the reaction is accompanied by an induction period during which there is no polymerisation. At the end of the induction period, steady-state kinetics are usually established and the rate of the process can be identical with the rate of the inhibited polymerisation or can be lower than the latter. The character of the dependence of the induction period τ on the intial inhibitor concentration $[X]_0$ is determined by the structures of the inhibitor and the monomer, the method and mechanism of initiation (thermal, material, etc), the nature of the initiator (azo-compound, peroxide, etc) and certain other physicochemical conditions in polymerisation.[2-6] A linear dependence of the induction period in polymerisation on the inhibitor concentration is usually encountered. In many cases, the induction periods increase faster or more slowly with increasing inhibitor concentration, which is usually due to the regeneration of the inhibitor or the additional initiation (or regeneration) of the chain.[6] During these reactions, the relation between the kinetic parameters and the concentrations of the reaction system components is various.

For different mechanisms of the interaction of the inhibitor with the active radicals, the stoichiometric inhibition coefficient μ may lie within a fairly wide range.

II. EQUATIONS FOR THE INHIBITION REACTION RATE CONSTANT

1. The Bagdasar'yan–Bamford Equation

The time variation of the rate of inhibited polymerisation makes it possible to find the inhibition reaction rate constant.[3,6] The mechanism of the radical-chain polymerisation in the presence of a highly effective inhibitor may be formulated in the following simplest form:

$$\begin{aligned} I &\xrightarrow{K_{cons}} 2R_0, \\ R_0 + M &\xrightarrow{K_i} R, \\ R + M &\xrightarrow{K_p} R, \\ R + R &\xrightarrow{K_t} \text{polymer}, \\ R + X &\xrightarrow{K_X} \text{polymer}, \end{aligned}$$

where I, M, and X are the initiator, monomer, and inhibitor molecules, R_0 and R are the primary and polymeric radicals, and K_{cons}, K_i, K_p, K_t, K_x are the rate constants for the corresponding elementary reactions.

Using the steady-state relations for any instant during the induction period,

$$W_i = K_t[R]^2 + K_X[R][X], \quad (1)$$

(W_i is the rate of initiation), and for the rate of consumption of the inhibitor,

$$-\frac{d[X]}{dt} = K_X[R][X], \quad (2)$$

it is possible to obtain the Bagdasar'yan–Bamford equation:

$$F_1 \equiv -\frac{1}{\varphi} + \ln\frac{1+\varphi}{1-\varphi} = \frac{K_X W_{max}}{K_p[M]}t + A, \quad (3)$$

in which the reduced rate φ is equal to the ratio of the rate of reaction at any instant to the steady state rate of polymerisation W/W_{max} and A is the constant of integration.

Eqn.(3) describes the polymerisation kinetics in the presence of an "ideal" inhibitor.[2,7] The Bagdasar'yan–Bamford equation is applicable only to inhibited polymerisation in which side reactions take place without the participation of the inhibitor itself and their contribution to the overall process kinetics does not vary with time. It is also valid in the presence of a chain regeneration reaction. In all these cases, the dependence of the duration of the induction period in the polymerisation reaction on the initial inhibitor concentration is usually linear.

The fundamental importance of Eqn.(3) is determined by two factors. Firstly, the plot of the function against time is linear and the inhibition constant can be found from its slope.[6] Secondly, the relation

$$W_i = \frac{\mu[X]_0}{\tau}, \quad (4)$$

which is the theoretical basis of the universal inhibition methods for the rigorous determination of the rate of initiation, can be obtained from it.

2. The Equation Describing the Kinetics of Inhibited Polymerisation Taking into Account Chain Initiation by the Inhibitor Molecules

The time variation of the rate of polymerisation can be influenced by the reaction involving the additional initiation by inhibitor molecules, which is characteristic of certain substances of both radical and non-radical nature. In such cases, special relations must be used to find the inhibition constants.[8,9]

In the interaction of the inhibitor with the monomer, leading to the formation of active centres, the steady-state relation (1) changes:

$$W_i + K_i[X][M] = K_X[R][X] + K_t[R^2], \quad (5)$$

(K_i is the rate constant for the additional initiation reaction) and the consumption of the inhibitor obeys the equation

$$-\frac{d[X]}{dt} = K_i[X][M] + K_X[R][X]. \quad (6)$$

At the end of the induction period, the reaction takes place at a steady-state rate W_∞ and

$$W_i = K_t[R]_\infty^2. \quad (7)$$

Ultimately, the kinetics of the inhibited polymerisation are described in this instance by the equation

$$F_2 \equiv -2\theta\ln(\varphi+\theta) - (1-\theta)\ln(1-\varphi) + (1+\theta)\ln(1+\varphi) + \frac{1/\theta-\theta}{2}\ln\left|\frac{\varphi-\theta}{\varphi+\theta}\right| = \frac{K_X W_\infty}{K_p[M]}(1-\theta^2)t + B, \quad (8)$$

from which it is possible to find the inhibition constant K_X/K_p, provided that the parameter $\theta = K_i[M]/K_X[R]_\infty$ is known. The quantity θ can be found in its turn from the reduced rate φ at the point of inflection (φ_b) in the S-shaped relation between the rate of inhibited polymerisation and time. If φ obeys Eqn.(8), then it follows from the condition for the point of inflection that

$$\theta^3 + \frac{2\varphi_b}{1+\varphi_b^2}\theta^2 - \frac{2\varphi_b^4-\varphi_b^2}{1+\varphi_b^2}\theta + \frac{\varphi_b^5+2\varphi_b^3-\varphi_b}{1+\varphi_b^2} = 0. \quad (9)$$

If the kinetics of the inhibited polymerisation are described by the Bagdasar'yan–Bamford equation, then $\theta_b = 0.643$. In the presence of additional initiation, φ_b varies from 0.643 to 1.0. Fig.1 illustrates the dependence of θ on φ_b calculated by Eqn.(9).

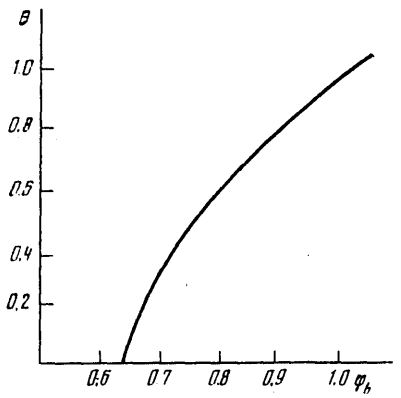


Figure 1. Dependence of the parameter θ on φ_b according to Eqn.(9).[9]

Eqn.(8) can be transformed into

$$F_2 \equiv K_i[M]\left(\frac{1}{\theta}-\theta\right)t + B,$$

which makes it possible to find the additional initiation rate constant K_i.

3. Kinetic Equation Taking into Account the Effects of the Secondary Inhibition (Retardation) of Polymerisation

The effect of a highly efficient inhibitor on polymerisation can produce not only an induction period but can also lower the rate of reaction with increasing inhibitor concentration.[6,10] The decrease in the concentration of growing chains is usually associated with their interaction with the primary inhibition products Y:

$$R + X \xrightarrow{K_X} Y;$$
$$R + Y \xrightarrow{K_Y} \text{polymer}.$$

In a steady-state process, we have during the induction period

$$W_i = K_X[R][X] + K_Y[R][Y] + K_t[R]^2.$$

The consumption of the inhibitor is described by Eqn.(2) in this case also. When account is taken of the material balance relation $[Y] = [X]_0-[X]$ and the steady-state equations for the non-inhibited polymerisation

$$W_i = K_t[R]^2 \tag{10}$$

and at the end of the induction period

$$W_i = K_t[R]_\infty^2 + \alpha K_Y[R]_\infty[X]_0 \tag{11}$$

(α is the stoichiometric secondary inhibition coefficient), we obtain

$$F_3 \equiv -\frac{1}{\varphi} - \ln(1-\varphi) + (1-\varphi_\infty^2)\ln\varphi + \varphi_\infty^2 \ln\left(\varphi + \frac{1}{\varphi_\infty^2}\right) = \frac{K_X W_\infty}{K_p[M]} t + C. \tag{12}$$

In the last equation, φ is the ratio of the rate of polymerisation at any instant W_t to the steady-state rate of the inhibited reaction W_∞ and φ_∞ is the ratio of W_∞ to the steady-state rate of the non-inhibited process W.

Thus the primary inhibition constant K_X/K_p is determined from the slope of the linear time variation of F_3. Evidently, if the inhibition products Y do not have a retarding influence on the subsequent polymerisation ($W\infty = W$ and $F_\infty = 1$), then Eqn. (12) becomes identical with Eqn.(3).

The secondary inhibition (retardation) rate constant K_Y is calculated from the relation obtained from a calculation for the polymerisation scheme in the presence of a relatively ineffective inhibitor[3,6] and the analysis of the non-steady state equation (11):

$$K_Y = \frac{(1-\varphi^2)K_t W}{\alpha\varphi K_p[M][X]_0}$$

4. Refinement of the Conditions Governing the Applicability of the Kice Equation to the Solution of the Converse Kinetic Problem in Inhibited Polymerisation

Studies have been published comparatively recently[11-13] in which, on the one hand, a new approach was described to the analysis of the Kice equation[14] and, on the other, the conditions governing its application were defined more rigorously.

Kice's fundamental assumptions concerned two factors: the inhibitor does not participate in the chain initiation stage and the quadratic chain termination rate constant is independent of the presence of the inhibitor.

Smirnov and Karapetyan[11] suggested that only one evident simplifying condition be used—the quasi-steady-state nature of the active and inactive radicals. As before, in this instance the reduced rate φ is determined by the ratio of the concentrations of the growing chains in the presence and absence of the inhibitor, namely $[R]_X$ and [R] respectively:

$$\varphi = \frac{W_X}{[M]_X} \Big/ \frac{W}{[M]} = [R]_X/[R].$$

The usual mechanism of radical polymerisation in the presence of a molecular inhibitor was supplemented by reactions involving initiation by the inhibitor

$$R_0 + X \xrightarrow{K_{iX}} R_X,$$

chain regeneration

$$R_X + M \xrightarrow{K_r} R$$

and chain cross-termination

$$R + R_X \xrightarrow{K_{tX}} \text{inactive product}.$$

(K_{iX}, K_r, and K_{tX} are the rate constants for the corresponding reactions).

If $\varphi^2/(1-\varphi^2) \gg K_rK_t/K_pK_{tX}$, which is always valid for typical inhibitors ($K_r/K_p \gg 1$, $\varphi \gg 0.1$), then the kinetics of the inhibited polymerisation are described by the equation

$$A\left(\varkappa + \frac{2\epsilon}{\varphi}\right) = C + B, \tag{13}$$

where

$$\kappa = K_X[X]/\{K_{cons}f[I](K_t)_{X=0}\}^{0.5},$$
$$C = K_rK_tK_X[M][X]/K_{tX}\kappa,$$
$$\epsilon = K_{iX}[X]/(K_{iX}[X] + K_{iM}[M]).$$

(K_{iM} is the rate constant for the reaction $R_0 + M \rightarrow R$).

$$A = \frac{\theta}{2}\left(\frac{B}{\varphi} - 1\right),$$
$$B = \varphi\left(1 + \theta\frac{1-\gamma\varphi^2}{\varphi^2}\right)^{0.5},$$
$$\gamma = (K_t)_X/(K_t)_{X=0},$$
$$\theta = 4(K_t)_{X=0}K_{tXX}/K_{iX}^2.$$

(K_{tXX} is the rate constant for the reaction $R_X + R_X \rightarrow$).

When $\varepsilon = 0$ and $\gamma = 1$, Eqn.(13) becomes identical with the Kice equation:

$$A\varkappa = C + B.$$

in which A and B depend only on φ and θ. Under the usual inhibition conditions, the reduced rate φ is a function of κ, C, and θ. The deviations from the kinetics described by Eqn.(13) are observed for low values of φ and unduly high rates of chain regeneration.

The relation $\theta \ll 1$ holds for the inhibited polymerisation. Here $B < 1$ for any φ and the chain regeneration parameter C can assume any values, including $C \gg B$. When the latter inequality holds, the reduced rate and the expressions for the rates of inhibited polymerisation are determined by the mechanism of the inhibition reaction.

When the active radical R interacts with the inhibition product, we have

$$\varphi = (C/\varkappa)^{0.5}$$
$$W_X = K_p (K_{cons} f K_r / K_X K_{tX})^{0.5} [M]^{1.5} [I]^{0.5} [X]^{-0.5}.$$

If chain termination takes place via the interaction of inhibitor radicals with one another, then

$$\varphi = 2C/\varkappa\theta^{0.5},$$
$$W_X = \{K_p K_r (K_{cons} f / K_{tXX})^{0.5} / K_X\} [M]^2 [I]^{0.5} [X]^{-1}.$$

Both expressions for the rate of the inhibited polymerisation show that the very fact of inhibition does not in any way imply an increase in the kinetic order with respect to the initiator.

In the presence of stable radicals and transition metal ions not involved in the initiation of the reaction and not promoting the chain regeneration, the inhibition mechanism changes. The inhibition steps are expressed in the form

$$R + X \xrightarrow{K_X} \text{inactive products},$$
$$R + M^{2+}L_2^- \xrightarrow{K_X} M^{3+}L_2^-R^-,$$
$$R + M^{3+}L_3^- \xrightarrow{K_X} M^{2+}L_2^- + RL\,(L = \text{ligand}).$$

In such cases the inhibition reaction rate constant can be found from the equation

$$K_X = \frac{2(1-\varphi^2)(K_{cons} f [I] K_t)^{0.5}}{\varphi [X]}$$

This equation is identical with the relation presented previously and obtained for the rate constant for the interaction of the inhibitor with the polymeric radical K_Y under weak inhibition conditions where there are no induction periods and only a decrease in the rate of polymerisation is observed. However, stable radicals and transition metal salts are usually effective inhibitors of radical polymerisation. In their presence, the rate of polymerisation and hence also φ vary with time and are virtually zero during the induction period, which reduces significantly the possibility of employing the last equation for finding the rate constant for relatively ineffective inhibition.

III. INHIBITORS AND MECHANISMS OF THE INHIBITION REACTIONS UNDER THE CONDITIONS OF RADICAL POLYMERISATION

Fairly extensive experience has now accumulated concerning, on the one hand, the search for effective stabilisers of vinyl monomers and, on the other hand, the determination of the kinetic features and mechanisms of the inhibiting action of different classes of substances. In general, one should note that the problem of the chemistry of the inhibition of radical polymerisation had not received due attention for a long time. At the same time, these questions are always of current interest, especially in connection with the selectivity of the action of inhibitors. Depending on the reactivity of the monomer (or its polymeric radical), temperature, the presence of various kinds of admixtures in the medium, the structure of the inhibitor itself, etc., the mechanism of the interaction of the inhibitor with the active radical can in many instances be ambiguous.

The first more or less systematic data concerning these questions have been published in monographs.[2-5] Subsequently, in the course of one and a half decades, only isolated studies appeared in the scientific literature. The most interesting of the latest reviews in which a wide range of inhibitors and the mcehanisms of their action are considered are those of Lazareva and Sidorov[15] and Barabashina et al.[16] The principal value of these reviews consists in the fact that they deal not only with the methods for the stabilisation of pure monomers but attention has been given to information about the most probable mechanisms of the inhibition of polymerisation occurring in individual stages of the synthesis of the monomers and for different ways of isolating, purifying, fractionating, and processing such monomers.

A chapter in the monograph of Gladyshev and Popov is devoted to questions of the regulation of the gel-effect in radical polymerisation with the aid of relatively ineffective inhibitors.[17]

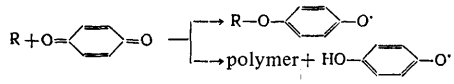
Apart from the previously known classes of stabilisers enumerated above, many inhibitors and inhibiting systems have been described in the patent literature. For example divinylacetylene,[18] hexamethylenetetramine,[19] salts of dibutyldithiocarbamic acid,[20] the composition containing phosphoric acids and (or) phosphoryl oxide, cresol, benzaldehyde,[21] aromatic amines with different structures,[22-27] *p*-methoxyphenol[28] and other phenols,[29] combinations of inhibitors of the amine and phenolic types,[30] compounds containing the nitroso-group linked to a carbon atom of the aromatic ring,[31] etc., have been proposed for the inhibition of the polymerisation of acrylates and methacrylates.

There have been comparatively few studies devoted to the relation between the structure of polycondensed aromatic hydrocarbons and their ability to inhibit the polymerisation of vinyl monomers. These questions were raised for the first time and in several studies.[32-35] It has been shown[36] that condensed aromatic hydrocarbons do not influence the chemically initiated polymerisation of methyl methacrylate but do inhibit the photosensitised reaction, reducing its rate without inducing an induction period. The inhibiting activity increases in the sequence naphthalene < phenanthrene < anthracene < chrysene. The inhibiting effect of the above substances is associated with their transition to the triplet state under the influence of light.

In their study of the polymerisation of vinyl acetate initiated by azobisisobutyronitrile in the presence of aniline and its derivatives,[37] Simonyi and Tudos[37] suggested that, when the substituent is changed, the stoichiometry of the inhibition reaction does not change but a decrease in the inhibition rate constant has been observed. Thus the constants K_X for aniline, *N*-methylaniline, and *NN'*-dimethylaniline are respectively 17, 6, and 0.7. After the introduction of a substituent into the benzene ring in the *para*- and *meta*-positions, the activity of the inhibitor is described by the Hammett equation. *ortho*- and poly-substituted anilines exhibit a reduced reactivity.

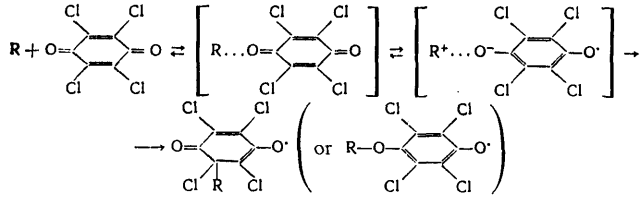
Many quinonoid compounds and their derivatives effectively inhibit radical polymerisation. The inhibiting activity of quinones is determined not only by their chemical structure and oxidation-reduction potential but also by the electron-donating capacity of the

macroradical and the polarity of the medium (usually the monomer itself).[38] Depending on these factors and the physicochemical conditions in the reaction, there is a possibility of recombination and disproportionation:[3]



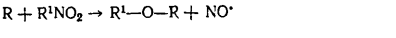
or the formation of an inactive radical via an intermediate charge-transfer complex (CTC).[39,40]

Further studies showed[41] that the rate-limiting stage in the interaction of the active radical with quinones is the conversion of the CTC into the inhibitor radical. The reaction involving methacrylates and acrylates is slow but can be accelerated by the addition of certain electron-donating compounds, for example, phenothiazine. The mechanism of the inhibition by quinones has been represented as follows in the case of the polymerisation of methyl methacrylate in the presence of chloranil:

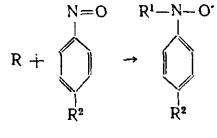


Regardless of the mechanism of the interaction of the quinone with the growing radical, the stoichiometric inhibition coefficient is in all cases close to two.

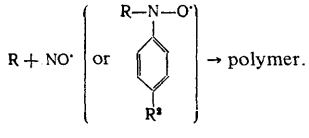
Polymerisation in the presence of nitro- and nitroso-derivatives is usually accompanied by an induction period and retardation of the reaction.[16] Compared with quinones, nitro-compounds reduce the rate of the process to a lesser extent, since their interaction with macroradicals is more difficult. Their inhibiting capacity is determined by the nature of the monomer, the type of polymerisation (in bulk or in solution), increasing with increase in the number of nitro-groups. From the mechanism of the inhibition of polymerisation by substances in this class,[16,42-45] it also follows that $\mu \simeq 2$:



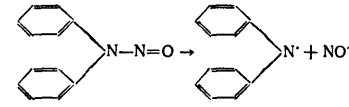
or



and further



Nitro-compounds can interact with growing chains but also with primary initiator radicals.[46] In certain cases, the nitroso-compound can decompose with formation of nitric oxide and a product having the properties of a stable radical:[47]



The stoichiometric inhibition coefficients of dimethyl-*p*-nitrosoaniline and *p*-nitrosodiphenylamine in the polymerisation of styrene, acrylonitrile, and methyl acrylate depend on the monomer concentration.[48] For example, the decrease in the mole fraction of the monomer from 1 to 0.3 in the acrylonitrile–DMF–*p*-nitrosodiphenylamine system entails an increse in μ from 0.86 to 1.8, while in the methyl acrylate–DMF–*p*-nitrosodiphenylamine system μ increases from 1.54 to 1.94 as the mole fraction of the monomer is reduced from 1 to 0.5. Tudos and co-workers[48] explained the changes in the stoichiometric coefficient on the basis of the hot radical theory.[48]

The results of studies on the inhibiting capacity of nitroso-compounds under radical polymerisation conditions proved to be closely related to the problem of the removal of the stabiliser from the monomer before its conversion into the polymer. This is usually achieved by fractionation with preliminary extraction of the inhibitor. The optimum solution of this problem is achieved by the monomer stabilisation method in which the inhibitor is effective during the storage of the monomer but does not affect its polymerisation.

One of the versions of the solution of this problem consists in the use of inhibitors interacting with the components of the reaction medium (for example, with the initiator) and then losing their activity. The radical-anion complexes of tetracyanoquinodimethane may serve as an example of inhibitors of this kind.[49,50]

Another version involves the use of inhibitors which are sparingly soluble in the monomers. During the storage of the latter, when the rate of the initiation of the polymerisation is low, there is sufficient dissolved inhibitor for effective stabilisation. However, this concentration of the inhibitor does not have a significant influence on the polymerisation under the properties of the high-molecular-weight products formed. The results obtained in the study of polymerisation in the presence of added cupferronates (ammonium salts of *N*-nitroso-*N*-phenylhydroxylamine and its derivatives) in fact correspond to this particular version.[51] Sodium, potassium, ammonium, and copper cupferronates inhibit effectively the polymerisation of acrylates and methacrylates in solution in DMF. The duration of the induction period increases linearly with increasing concentration of the additives. In contrast to the polymerisation of styrene, for which the stoichiometric inhibition coefficient is two[16] (analogously to the mechanism adopted for inhibition by nitro- and nitroso-compounds), in the polymerisation of acrylates and methacrylates, μ = 1.5. In these cases, an interaction has been observed between the cupferronates and the monomers with formation of free radicals and a decrease in μ.

In the polymerisation of methyl acrylate, butyl acrylate, and methyl methacrylate, the dependence of the induction period on the concentrations of the cupferronates is non-linear and the steady-state rate of the inhibited reaction is less than that of the non-inhibited reaction.

One of the features of the above salts of practical importance is that they inhibit polymerisation not only in air but also under oxygen-free conditions.

The differences in the influence of various cupferronates on polymerisation are caused by their different solubilities. Copper and sodium cupferronates exhibit the highest and lowest solubilities respectively in acrylic monomers. The results of Gol'dfein et al.[51] make it possible to plot calibration relations for the polymerisation inhibition periods observed in saturated solutions of cupferronates in monomers as a function of the concentration of the salts.

The interaction of cupferronates with acrylates and methacrylates leads to their deactivation and is one of the causes of the non-linearity of the concentration variation of the induction period. After a time, the cupferonates gradually decompose. In terms of stability, they can be arranged in the following sequence: copper > sodium > potassium > ammonium cupferronates. Furthermore, the degree of their deactivation depends on the chemical structure of the monomer: it is highest in methyl methacrylate and lowest in methyl acrylate.

At certain stages in the synthesis of the monomers, the reaction mixtures contain fairly large amounts of water. The presence of water in the monomers influences also the solubility of the cupferronates and hence their inhibiting activity. The presence of water in the monomer has a greater effect on the induction period in polymerisation the higher the solubilities of the cupferronate and water in the monomer.

Metal salts have different effects on the kinetics and mechanism of the radical polymerisation of vinyl monomers.[2-4] Thus a concentration-dependent inversion of the catalytic properties is characteristic of iron and copper chlorides.[52,53] The inhibiting effect of aliphatic acid salts depends on the nature of the metal in the salt and also on the medium in which the reaction takes place (in bulk or in solution) and on the size of the anion.[54] The inhibiting influence of zinc, cobalt, and lead stearates on the polyerisation of styrene and methyl methacrylate, initiated by the inhibition in such cases consists in the interaction of the active radical with the intermediate complex formed between the stearate and the peroxide. Transition metal chlorides and aliphatic acid salts have not found extensive practical applications.

The influence of the medium on the kinetic parameters of the inhibition of the polymerisation of vinyl monomers in the presence of iron and copper chlorides has been analysed.[57] For example, in the inhibition of the polymerisation of acrylonitrile in aqueous sodium thiocyanate solution, the inhibition constant increases by 2–3 orders of magnitude compared with the polymerisation in solution in DMF.[58]

Metal salts of dialkyldithiocarbamic acid have come to be recommended as effective inhibitors of the polymerisation of acrylic monomers. These compounds readily accept peroxy- and alkyl radicals. The mechanism of the inhibiting effect is complicated in the presence of hydroperoxides, because the interaction of the salt with the active radical or hydroperoxide results in the formation of a paramagnetic compound with an enhanced inhibiting capacity.[59] The efficiency of the inhibition then depends on the ratio of the concentrations of the components of the reaction system and on the nature of the metal salts,[60] increasing in the sequence

$$Zn(S_2CNR_2) < Ni(S_2CNR_2)_2 \ll Cu(S_2CNR_2).$$

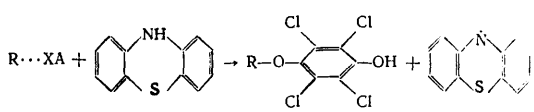
The mechanism of the inhibition of polymerisation by dialkyldithiocarbamates cannot be regarded as established at the present time. Some workers[61] believe that the site in the salt molecules most vulnerable to attack by active radicals is at the sulphur atoms. Others[62,63] postulate interaction with the metal ion and that this is responsible for the transfer of electrons from the ligand to the radical, which is feasible in view of the presence of a covalent bond between the metal and sulphur atoms.[64]

Copper diethyldithiocarbamate (CDTC) exhibits effective inhibiting activity in the polymerisation of acrylic acid in aqueous solution and in solutions in acetic acid and isopropyl acetate.[65] In all cases, the dependence of the induction period on the salt concentration is linear and the stoichiometric inhibition coefficients are greater than unity and depend on the type of solvent. The highest inhibiting capacity of CDTC has been observed in aqueous solution and the lowest in acetic acid. The values of μ obtained in the polymerisation of acrylic acid in air and under oxygen-free conditions are virtually identical, which indicates the same stoichiometry of the interaction of CDTC with alkyl and peroxy-radicals. The mechanism of the inhibition in these cases is apparently analogous to the mechanism of the inhibition of oxidation reactions by phosphorodithioates[66] accompanied by electron transfer to the active radical. The increase in μ (in excess of 2) can be associated with the interaction of the radicals with two sulphur atoms.

The rate of polymerisation of acrylic acid in organic media is fairly considerably reduced compared with the rate in aqueous solution. This is due to the formation of complexes by acetic acid and isopropyl acetate with the polymeric radicals[67,68] and the reduction of the reactivity of the latter. The interaction of these solvents with the growing chains is also responsible for the decrease in μ in the polymerisation of acrylic acid in solutions in acetic acid and isopropyl acetate compared with the reaction in water. The primary (K_X/K_p) and secondary (K_Y/K_p) inhibition constants have been found for the systems indicated by Eqns.(14) and (15) respectively.

A mixture of chloranil (CA) and phenothiazine (PT) proved to be an effective inhibiting system.[69] In contrast to the polymerisation of styrene, where chloranil is a powerful inhibitor,[70] in methyl acrylate only a slight inhibition is observed and CA has no influence on the polymerisation of methyl methacrylate. On the other hand, when PT or the oligomeric product of its oxidative condensation (OPT) was added, a synergistic effect with a distinct induction period was observed.[71,72] It has been shown[69] that the rate-limiting stage of the inhibition process involves the interaction of the growing chain with a CA molecule and not with the PT...CA complex. The sharp increase in K_X, approximately by two orders of magnitude in the presence of PT or OPT, can be satisfactorily accounted for by the mechanism above.[41]

The interaction of PT with CTC leads to the formation of the PT· radical:

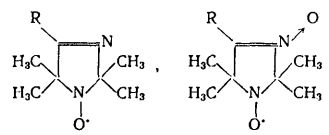


The PT· radical can interact with R, M, and XA to form a new radical capable of terminating yet another chain. However, the stoichiometric inhibition coefficient proved to be less than two which is due to the regeneration of the chain in the interaction of PT· with a methyl methacrylate molecule. In the polymerisation of methyl acrylate, the inhibiting effect of the CA–PT system is appreciably smaller. In this case not only the active radicals but also the CTC enter into the reaction with CA. Thus the structure of the monomers and the donor–acceptor properties of the monomers and the growing radicals play a decisive role in the inhibition mechanism.

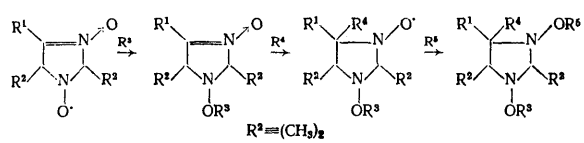
The study of the kinetics of the inhibition of the polymerisation of vinyl monomers in the presence of binary systems has been suggested.[73,74] It has been shown that mixtures of CA with triethylamine and also of anthracene with phenothiazine and oligophenothiazine effectively inhibit the radical polymerisation of methyl methacrylate. The existence of critical inhibitor and initiator concentrations is associated, according to the authors, with the inhibiting effect of *NN*-diethylaminovinyltrichloro-*p*-benzoquinone, formed as a result of the conversion of the CTC into a radical pair. The observed synergistic effect can be explained by the radical-chain reactions involving the consumption of the inhibitors.

Stable radicals incapable of recombining are effective inhibitors of the polymerisation of vinyl monomers. Data concerning the use of hydrazyl, verdazyl, iminoxy-, and arylnitroxy-radicals in addition to certain radical-anions as spin-trapping agents as well as polymerisation in the presence of these substances, indicating the complexity of the inhibition mechanism, have been quoted in a recently published review.[50]

Nitroxy-radicals of the type of imidazoline and imidazolidine proved to be extremely interesting from both theoretical and experimental standpoints.[75,76] They belong to the class of five-membered nitrogen-containing heterocyclic free radicals:



Compared with the types of stable radicals listed above, the nitroxy-radicals based on imidazoline and imidazolidine have a number of advantages. The additional nitrogen atom of the *N*-oxide group combined with the functional group in the 4-position in the heterocycle makes it possible to achieve complex formation and cyclometallation without the involvement of the radical centre. The presence of the imine or imine *N*-oxide (nitrone) group in the imidazoline molecule leads to a much greater stability of the nitroxy-radical in an acid medium, which is an important factor in the practical employment of such radicals as inhibitors of polymerisation, occurring, for example, under the conditions of the synthesis of methacrylates. Imidazoline *N*-oxides, as agents interrupting oxidation chains and as trapping agents for short-lived radicals of various types, should manifest the highest inhibiting activity under these conditions:



According to the scheme formulated above, the stoichiometric inhibition coefficient should be greater than unity.

It has been shown[77,78] that the 2,2,5,5-tetramethyl-3-oxo-4-phenylimidazolin-1-yloxy-radical (TMPIZ) effectively inhibits the polymerisation of styrene and methyl methacrylate. It was of interest that the form of the dependence of the duration of the induction period on the initial concentration of the stable (linear) radical and the stoichiometric inhibition coefficients (μ = 1.5 for styrene and μ = 1.25 for methyl methacrylate) are independent of the nature of the initiator (an azo-compound or a peroxide), as has been observed, for example, for iminoxy-radicals and especially for arylnitroxy-radicals.[50]

TMPIZ has a weak inhibiting effect on the polymerisation of methyl methacrylate in the presence of both concentrated and dilute sulphuric acid. At the same time, the form of the dependence of the steady-state rate on the TMPIZ concentration is determined by the concentration of sulphuric acid in water. The inhibition constants K_X/K_p are therefore found by taking into account the kinetics of the polymerisation at the end of the induction period—using Eqns.(3) and (12) respectively in the presence of concentrated and dilute acid.

The inhibiting activity of TMPIZ, a nitroxy-radical derived from imidazoline, in an acid medium made it possible to use it for the determination of the rate of initiation of the polymerisation by sulphuric acid and also of the rate constants for the chain propagation and termination reactions corresponding to different contents of the acid in water and in the reaction system.[78]

In the inhibition of the thermal polymerisation of methyl methacrylate in the presence of sulphuric acid, the dependence of the induction period on the TMPIZ concentration is markedly more non-linear than might have been expected in the presence of an additional initiation reaction. It is most likely that this is associated with the characteristics of the mechanism of the thermal initiation. Some workers[79,80] suggest that the thermal polymerisation is initiated by triplet radicals and that all the radicals interact with the inhibitor. Others draw attention to the possibility of the interaction of the inhibitor with the monomer[81-83] and of reactions between the inhibitor and an intermediate formed at a rate exceeding the rate of initiation.[84] The kinetics of the inhibited polymerisation have been analysed in greatest detail taking into account these reactions in relation to styrene,[85] where the inhibitors were divided by the author into two groups—interacting and not interacting with the intermediate, which is a biradical in thermal initiation.

IV. POLYMER STABILISERS—EFFECTIVE INHIBITORS OF RADICAL POLYMERISATION

1. Polymerisation in Bulk and Certain Features of the Inhibition of Thermo-oxidative Polymerisation

Despite the fundamental difference between their structures, aromatic amines and phenols are often combined in a single group of inhibitors.[86] In the presence of oxygen, these compounds inhibit effectively radical polymerisation, but in its absence they manifest only the properties of weak inhibitors.[17] Furthermore, both amines and phenols tend to form hydrogen bonds with peroxy-radicals, which tends to increase the rate of the inhibition reaction.

In many cases the abstraction of a hydrogen atom from the reagent by an active radical is the decisive elementary step in the initiation stage, for example:

$$RO_2 + R^1—NH—R^2 \rightarrow ROOH + R^1—\dot{N}—R^2,$$

$$R \text{ (or } RO_2) + R^1—\dot{N}—R^2 \rightarrow \text{polymer},$$

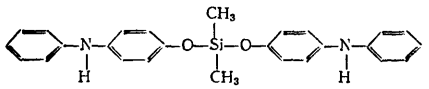
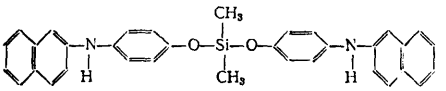
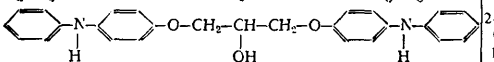
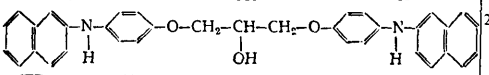
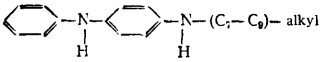
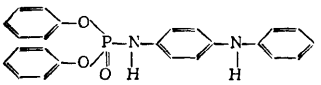
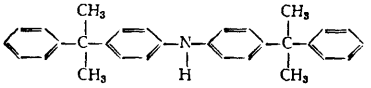
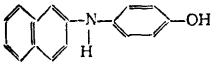
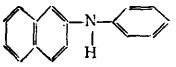
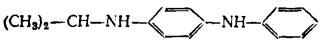
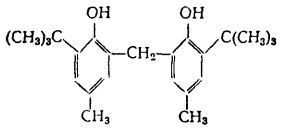
$$R^1—\dot{N}—R^2 + R^1—\dot{N}—R^2 \rightarrow \text{inactive product}.$$

The high rate of interaction of RO_2 with the amine molecule is then caused by the formation of polar activated complexes $ROO^-...H^+$

...N<and not by the low energy of the N–H bond. The inhibiting activity of aromatic amines depends on the polarity of the substituents in the benzene ring: electropositive substituents increase and electronegative substituents diminish the inhibiting effect.

During the last decade, new highly effective inhibitors of the polymerisation of vinyl monomers in the presence of oxygen have been found in the class of aromatic amines,[87-94] which had been synthesised previously as additives to polymeric materials for their stabilisation. These compounds, some of which are listed in Table 1, are readily soluble in many organic solvents, acrylic and methacrylic monomers, and concentrated sulphuric acid.

Table 1. New effective inhibitors of the polymerisation of vinyl monomers.[87-94]

Structural formula	Chemical name	Technical name
	dimethyldi-(*p*-phenylamino-phenoxy)silane	S-1
	dimethyl(β-naphthylamino-*p*-phenoxy)silane	S-41
	2-hydroxy-1,3-di-(*p*-phenylamino-phenoxy)propane	S-47
	2-hydroxy-1,3-di-(β-naphthylamino-*p*-phenoxy)propane	S-49
	*N*-(C_7-C_9)-alkyl-*N'*-phenyl-*p*-phenylene diamine	S-789
	(*p*-phenylamino-phenyl) amide of diphenylphosphoric acid	S-875
	4,4'-bis(αα'-dimethyl benzyl)-diphenylamine	S-933
	*p*-hydroxyphenyl-β-naphthylamine (hydroxyneozone)	HN
	phenyl-β-naphthyl-amine	neozone D
	phenyl-*p*-isopropyl-amino phenyl-amine	diaphen FP
	2,2'-methylenebis-(6-t-butyl-4-methyl)phenol	22-46

In the presence of the above amines, the oxidative polymerisation of styrene and acrylic and methacrylic acids and their esters, initiated by azobisisobutyronitrile (ABIN), is preceded by induction periods whose duration increases linearly with increase in the concentration of the additive. As can be seen from Fig.2, if the induction period is adopted as the criterion of the inhibiting activity, all the substances presented are found to be superior to hydroquinone—the most widely used stabiliser at the present time. The width of the transitional region between the non-steady-state and steady-state kinetics depends little on the inhibitor structure. Under oxygen-free conditions, the test substances have almost no inhibiting influence on the polymerisation of acrylates and methacrylates in bulk for the initial degrees of conversion.

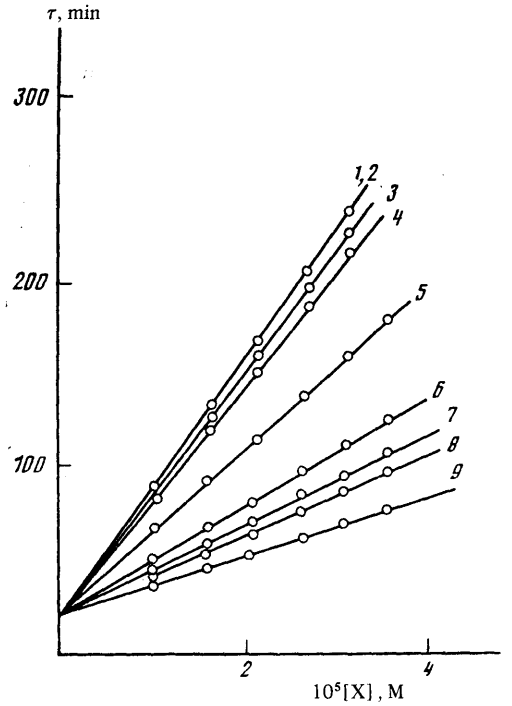


Figure 2. Dependence of the induction period in the polymerisation of methyl methacrylate (τ) on the concentration of inhibitors (60 °C); [ABIN] = 10^{-3} M: (1) S-1; (2) S-47; (3) S-49; (4) S-41; (5) S-789; (6) S-875; (7) HN; (8) HQ; (9) PT.[94]

Another extremely important and objective characteristic of the efficiency of the inhibitor is the stoichiometric coefficient μ. For bifunctional inhibitors such as the S-1, S-41, S-47, and S-49 products, one may expect that in each case μ = 4. However, it was found that in all instances the values of μ found by Eqn.(1) are greater than four. This difference from the theoretical value of μ is associated with the regeneration of the amines as a consequence of the interaction of the inactive inhibitor radical with the growing chain not only via recombination but also via disproportionation. The ratio of these two types of chain termination depends on the structures of both the monomer and the inhibitor. Thus, as a consequence of steric hindrance, the contribution of the recombination reaction in the polymerisation of butyl acrylate is smaller than in the polymerisation of methyl acrylate. This leads to higher values of μ in the inhibition of the polyermisation of butyl acrylate by the above compounds (approximately by a factor of two). Furthermore, the

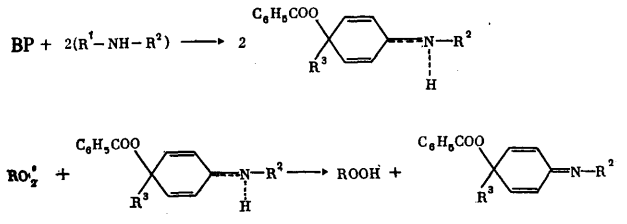
stoichiometric coefficients in the case of both acrylate and methacrylate are greater for S-1 and S-47 than for S-41 and S-49 respectively. The differences between the structures of the amines in each of these pairs are due to the replacement of the benzene ring, linked to the NH group, by the naphthalene ring. In the latter case, the delocalisation of the unpaired electron in the aminyl radical is more significant. This increases the probability of the addition of active radicals not to the nitrogen atom (a process which is sterically hindered) but to one of the carbon atoms of the naphthalene rings, which increases in its turn the contribution of recombination to the overall chain termination.

When the polymerisation process is acted upon by other aromatic amines, also of the polyfunctional type (S-789, S-875, S-933, etc), μ is almost independent of the structure of the inhibiting additive but is determined to a significant extent by the structure of the monomer and the nature of the initiator.[92] In such cases, the active radicals interact with only one NH group, located between two benzene rings. At the same time $\mu \geqslant 2$ also indicates the regeneration of the inhibitor.

The aromatic amines investigated can be arranged in series in terms of their inhibiting activity. For the inhibited oxidative block polymerisation of methyl methacrylate, this series assumes the following form in relation to hydroquinone and phenothiazine:

S-1 > S-41 > S-47 > S-49 > S-789 > S-875 > S-933 > HN > HQ > PT.

In the initiation of the polymerisation of vinyl monomers by benzoyl peroxide (BP), the inhibiting activity of the compounds enumerated above diminishes appreciably. This is caused by the interaction of the peroxide initiator with an amine molecule, which is indicated by the sharp change in the colour of the BP solutions in the monomers when amines are introduced into them. By analogy with the mechanism of the interaction of BP with an arylnitroxy-radical,[95] it is assumed[92] that the following reactions occur under the conditions investigated:



Under the real conditions of the synthesis, purification, and storage of acrylic and methacrylic monomers, spontaneous polymerisation frequently occurs and leads to the formation of undesirable high-molecular-wight products. Such polymerisation usually proceeds at elevated temperatures (80–150 °C) in air (naturally in the absence of special initiators) and is thus thermo-oxidative in character. The ballast polymers formed block the industrial apparatus and put it out of order. Furthermore, all this entails considerable losses of the monomers. The search for thermal polymerisation inhibitors in the study of the mechanism of inhibition under these conditions therefore assumes special importance.

The main characteristic feature of the inhibition of the thermal polymerisation of acrylates and methacrylates, in contrast to the initiated polymerisation, is the presence of a break in the dependence of the induction period (at high temperatures) on the inhibitor concentration (Fig.3). From this it follows that there is a critical inhibitor concentration $[X]_{cr}$ above which a sharp increase in the duration of the induction period is observed. The quantity $[X]_{cr}$ then depends significantly not only on temperature but also on the structure of the monomer and the inhibitor.

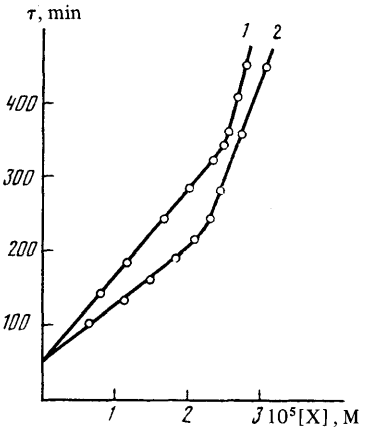


Figure 3. Dependence of the induction period in the thermal polymerisation of methyl methacrylate in air on the concentrations of S-1 (curve *1*) and S-47 (curve *2*) at 100 °C.[94]

For many branched chain reactions, especially for the oxidation of organic compounds, the presence of critical phenomena has been established, including the critical inhibitor concentration.[96,97]

Analogous effects may be observed also in the inhibition of the thermo-oxidative polymerisation of vinyl monomers. The decomposition of polymeric peroxides, leading to the initiation of new reaction centres, occurs also during the induction period and can be regarded as degenerate chain branching. It is noteworthy that degenerate chain branching[98] was not taken into account in any of the previous studies concerned with the inhibition of thermo-oxidative polymerisation.[99–103] These ideas were first put forward in studies[91,92] of the inhibiting capacity of the aromatic amines indicated above.

Kinetic analysis of the radical-chain mechanism of oxidative polymerisation in the presence of inhibitors leads to an equation for the variation of the concentration of polyperoxides (P):

$$\frac{d[P]}{dt} = \nu W_i + \varphi[P], \qquad (14)$$

where $\nu = K_p[M]/\mu K_X[X]$ is the length of the kinetic chain in the presence of the inhibitor, $\varphi = K_3(\nu\alpha - 1)$ the self-acceleration factor, and α the efficiency of the inhibition by polyperoxides.

The condition $\varphi = 0$ is attained at the critical inhibitor concentration $[X]_{cr}$ determined by the rates of chain propagation and decomposition of the polymeric peroxides and also by the occurrence of secondary reactions (for example, the regeneration of the inhibitor):

$$[X]_{cr} = \alpha K_p[M]/\mu K_X. \qquad (15)$$

For $[X] \leqslant [X]_{cr}$, the inhibitor is consumed fairly rapidly inducing only very short induction periods. For $[X] > [X]_{cr}$, the inhibitor concentration diminishes slowly, which leads to a sharp increase in the induction period. The abruptness with which the dependence of τ on [X] passes through $[X]_{cr}$ is determined by the ratio of the rates of initiation and decomposition of polyperoxides (K_i/K_d).

Equations have been obtained[103] for the induction period and for the rate of oxidative polymerisation in the presence of an antioxidant and the lower and upper limits to the inhibitor concentration, the critical rate of initiation, and the critical monomer concentration were established. At inhibitor concentrations below the lower limit, the antioxidant hardly influences the kinetics of the oxidative polymerisation and can be regarded as an inert admixture. Under these conditions, the concept of the induction period is valid only for a reaction taking place in a closed system, while its duration is determined solely by the concentration of oxygen and the rate of its consumption. At inhibitor concentrations greater than the upper limit, the antioxidant acts as an oxidant in relation to the monomer and the polymerisation inhibitor and the concept of the induction period is valid for both closed and open systems. A system passes from the non-inhibited oxidative polymerisation regime to the inhibited reaction regime precisely in the region between the lower and upper limits of the antioxidant concentration.

Extremely interesting phenomena have been observed in the study of the oxidative polymerisation of styrene inhibited by 2,6-di-t-butylphenols.[104,105] The polymerisation kinetics have in these instances a stepwise character, being accompanied by primary (τ_1) and secondary (τ_i) induction periods. The observed kinetics are associated with the period of formation of a secondary inhibitor X^2, whose concentration oscillates as a function of time, i.e. with an auto-oscillatory regime. Since the studies were performed in a closed system, the oscillations in the concentration of the secondary inhibitor are caused, according to the authors, by the involvement of the intermediates in the reaction and are non-decaying in the observed time interval. During the secondary induction periods, the rate of polymerisation decreases sharply with increase in the antioxidant concentration. According to the expression for the induction period in polymerisation in the presence of oxygen,[106,107]

$$\tau = \frac{\mu K_X [O_2]_0 [X]_0}{(K_p [M] + K_X [X]_0) W_i}$$

the latter should be absent at the end of the primary induction period. The role of oxygen in the formation of X^2 should then be indirect and should be shown by the products of the oxidative reaction of phenols. In a general form, the proposed mechanism of the auto-oscillatory regime in the inhibition of the radical polymerisation of styrene includes three main reactions leading to the formation of the secondary products Y and the intermediate Q and to the regeneration of the inhibitor X^2:

$$RO_2^{\cdot} + X^1 \rightarrow Y,$$
$$R + Y \rightarrow Q \rightarrow \text{inactive product},$$
$$Q + X^1 \rightarrow X^2.$$

An attempt has been made[108] to model mathematically the auto-oscillatory polymerisation in the presence of phenols. The main postulate was the idea that polymerisation is then an unbranched radical-chain process (this is in fact achieved at the end of the primary induction period).

2. Inhibition of the Polymerisation of Acrylates and Methacrylates in the Presence of Sulphuric Acid

Sulphuric acid is one of the main components in the synthesis of acrylic and methacrylic monomers. The problem of the inhibition of polymerisation in the presence of sulphuric acid is of particular current interest since the acid is capable of intensifying the formation of polymers and can deactivate many of the known stabilisers.

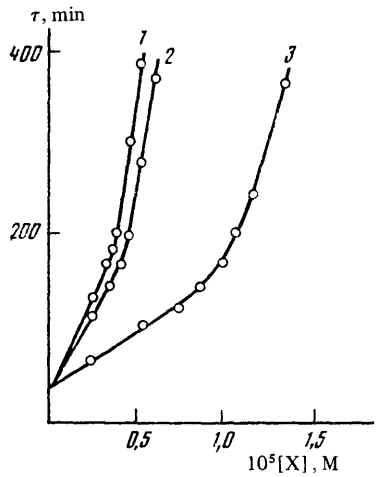


Figure 4. Dependence of the induction period in the polymerisation of methyl acrylate in air in the presence of 5 vol.% of H_2SO_4 on the concentrations of inhibitors at 75 °C: (1) S-1; (2) S-41; (3) HN.[51]

In order to understand the mechanism of inhibition in the presence of sulphuric acid, it is essential to know the specific features of the influence of the acid itself on the elementary polymerisation stages. In the study of the influence of sulphuric acid on the photopolymerisation of methyl methacrylate under oxygen-free conditions,[109–111] the formation of a complex between the acid and the monomer was observed. The increase in the rate and in the degree of polymerisation was explained by the increase in the reactivity of the monomer (or the macroradical) and also by the increase in the macroscopic viscosity and the change in the conformation and in the effective rigidity of the growing chains. The influence of sulphuric acid on the kinetics and mechanism of the polymerisation of acrylic monomers has been investigated[112] at elevated temperatures in the presence of oxygen. The introduction of sulphuric acid decreases sharply the induction period induced by the inhibiting effect of oxygen, and increases the rate of polymerisation. The dependence of the rate and of the induction period on the sulphuric acid concentration has a fairly complex character involving an extremum. The data obtained indicate the formation of complexes between the monomer and acid having different quantitative compositions. The formation of the complex accelerates the decomposition of the peroxide as a result of its protonation by the acid with subsequent homolysis of the -O—O- bond, analogously to the mechanism of the induced decomposition of hydroperoxides in the presence of certain acids.[113]

The compounds listed in Table 1 inhibit effectively the polymerisation of acrylic monomers also in the presence of sulphuric acid.[51,114] With increase in its content in solution, the induction period is sharply reduced, which is associated both with the increase in the rate of initiation and with the interaction of the inhibitor with the acid, lowering its efficiency. In contrast to polymerisation in bulk, where critical phenomena were manifested at fairly high temperatures, in polymerisation in the presence of sulphuric acid they are observed also at relatively low temperatures (Figs.4 and 5).

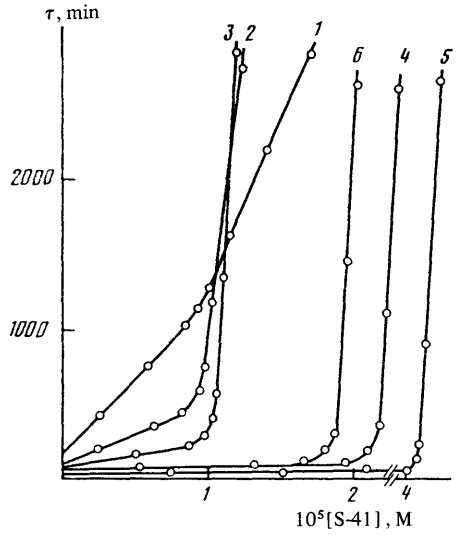


Figure 5. Dependence of the induction period in the polymerisation of methyl methacrylate in air on the S-41 concentration at 60 °C and different initial sulphuric acid concentrations (Vol.%): (1) 2; (2) 5; (3) 10; (4) 20; (5) 30; (6) 41.[51]

Table 2. The critical concentrations of inhibitors in the polymerisation of acrylates and methacrylates in the presence of sulphuric acid.[51]

Inhibitor	$10^5[X]_{cr}$, M, 100 °C	
	methyl acrylate (5 vol.% H_2SO_4)	methyl methacrylate (30 vol.% H_2SO_4)
S-1	0.7	0.8
S-41	0.9	1.3
S-47	—	1.3
S-49	—	1.1
HN	3.0	2.0
HQ	90.0	8.0

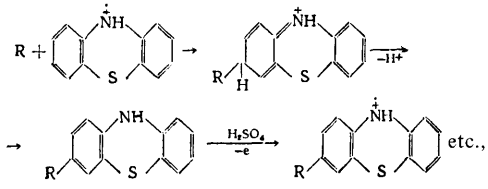
Eqns.(14) and (15) are likewise applicable to the inhibited polymerisation of acrylates and methacrylates in the presence of sulphuric acid. Since the latter accelerates the decomposition of polyperoxides, the observed effects are manifested more strikingly under these conditions. This justifies the view that the critical concentration of the inhibitor can be regarded in such cases as the main parameter characterising the efficiency of the inhibitor. Table 2 presents the values of $[X]_{cr}$ for certain new polymerisation inhibitors and compares them with hydroquinone.

The critical inhibitor concentration, the abruptness with which the dependence of τ on [X] passes through it, and the stoichiometric inhibition coefficient depend on the concentration of the acid in the system. The decrease in μ with increasing concentration of the acid is possible when, as a result of the interaction with it, the substances S-1, S-41, etc. are converted into compounds which either do not inhibit polymerisation or are characterised by a much lower value of μ. A dynamic equilibrium is established between both forms of the substance and an increase in the content of sulphuric acid shifts it towards the less effective inhibitor, which in fact reduces the stoichiometric coefficient.

The EPR spectra of the systems investigated do indeed indicate the interaction of the unpaired electron with the nitrogen and hydrogen atoms, as a result of which the amine (X) is converted into a radical-cation:[51]

$$2X + 3H_2SO_4 \leftarrow 2X^{\dot{+}} + 2HSO_4^- + H_2O + H_2SO_3.$$

Such a reaction had been proposed earlier in a study[115] where an intensification of the inhibiting effect of phenothiazine was observed in the presence of sulphuric acid. The increase in μ was explained by the following inhibition mechanism:



The dependence of the efficiency of the inhibiting effect of the phenothiazine–sulphuric acid system on the acid concentration at a constant phenothiazine concentration passes through an extremum. According to the authors, this is associated with the dual function of sulphuric acid, in the presence of a high concentration of which in the system the initiating effect begins to predominate over the inhibiting effect.

The magnitude of the EPR signal and hence the amount of the radical-cation also vary with the composition of the reaction medium. In sulphuric acid and also in the presence of its excess, the EPR signal is smaller than, for example, in a methyl methacrylate–sulphuric acid solution.

As shown previously,[86] phenols and aromatic amines are used as a rule as antioxidants. On the other hand, in the presence of sulphuric acid the conversion of aromatic amines into stable radical-cations imparts to them the ability to inhibit polymerisation also in the absence of oxygen. At the end of the induction period, polymerisation under oxygen-free conditions proceeds at a steady-state rate, diminishing with increase in the initial inhibitor concentration. This is associated with the retardation of the reaction by the products of the interaction of the active radicals with the amine radical-cations. The kinetic data obtained are consistent with Eqn.(15), which is indicated by the linearity of the relation between $(1-\varphi^2)/\varphi$ and the inhibitor concentration (Fig.6).

The dependence of the steady-state rate of polymerisation on the inhibitor concentration in the presence of atmospheric oxygen has a completely different character. The rate initially increases, but,

having reached a maximum at $[X]_{cr}$, it begins to fall. An increase in the concentration of sulphuric acid in the solution intensifies these effects. The increase in the rate of the process is due to the accumulation of inhibition products—hydroperoxides, the rate of decomposition of which increases in its turn with increasing concentration of the acid. This in fact promotes a more striking manifestation of the extremum in the relation between W and [X] at high acid concentrations. The decrease in the steady-state rate is caused by the consumption of the polymerisation-initiating peroxides and hydroperoxides during the induction period, whose duration increases sharply in the region of $[X]_{cr}$.

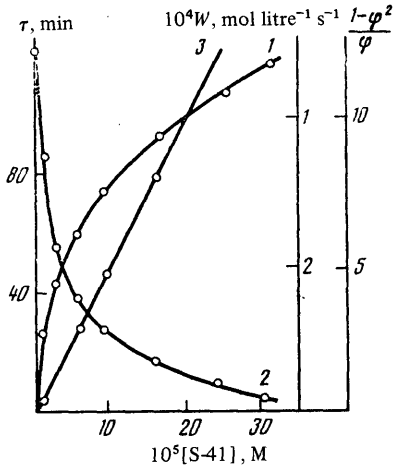


Figure 6. Dependence of the induction period (curve *1*), the steady-state rate of polymerisation of methyl methacrylate (curve *2*), and the ratio $(1-\varphi^2)/\varphi$ (curve *3*) on the concentration of S-41 under oxygen-free conditions and in the presence of 20 vol.% of H_2SO_4; 60 °C; [ABIN] = 2×10^{-4} M.[51]

If initiating products are formed in the inhibition reactions, then this is reflected in the form of the dependence of the induction period on the inhibitor concentration. Indeed, at fairly high concentrations of sulphuric acid, the above dependence deviates from linearity for $[X] < [X]_{cr}$. With increase in the inhibitor concentration, the induction period increases to an increasingly smaller extent and rises sharply only when $[X]_{cr}$ is attained.

V. CHARACTERISTIC FEATURES OF THE INHIBITION OF BULK AND HETEROPHASE POLYMERISATION

The study of inhibition in viscous media makes it possible to simplify greatly the kinetic schemes and to determine in many instances the reactivities of weakly reactive compounds in radical reactions.[17] The principal effect distorting the kinetic picture in polymerisation at relatively high conversions is the gel-effect. In order to control this effect (in order to displace the instant of its appearance to the region of higher conversions or to suppress it completely), one can introduce a relatively ineffective inhibitor into the reaction medium.

In polymerisation in highly viscous media (at high conversions and in systems containing a polymer), quadratic chain termination becomes diffusion-controlled and the constant K_t decreases sharply. In such cases, termination even by a weak inhibitor may become rate-determining and it follows from the expression obtained for the reduced rate

$$\varphi = \frac{W_X}{W} = \frac{(K_t W_i)^{0.5}}{K_X [X]}$$

that the inhibiting effect increases with decrease in K_t and W_i (or with increase in the degree of reaction). Having taken into account the temperature dependence of K_t and K_X, we have

$$\varphi = A \exp[(E_X - 0.5E_0)/RT], \text{ where } A = \frac{A_t W_i^{0.5}}{A_X [X]}$$

Usually $E_X > E_t$ and φ should diminish with increasing temperature, which reduces the gel-effect. Here one should bear in mind that the decrease in φ may be somewhat compensated by the decrease in the inhibition efficiency associated with the increase in K_t as a result of the decrease in the viscosity of the medium as the temperature rises. However, this is observed only when fairly inert products are formed as a result of inhibition.

The decrease in the gel-effect and hence in all the consequences of a high degree of polymerisation can be achieved by introducing oxygen into the reaction system at a specified conversion. At the same time, the most effective inhibition of homopolymerisation at high conversions or under the conditions of a heterophase reaction is observed when oxygen and a weak inhibitor act simultaneously. Calculations for the corresponding radical-chain mechanisms lead in such cases to relations from which it follows that

$$\varphi = W_{O_2}/W = 10^{-3} - 10^{-2},$$
$$\varphi = W_{O_2,X}/W_X = 10^{-6} - 10^{-5}.$$

It is seen from a comparison of these data that oxygen increases the activity of the weak inhibitor. In the presence of oxygen, the intensification of the inhibiting effect of phenols, amines, and nitro-derivatives is associated not only with the formation of their oxidised forms (such as quinones, quinone imines, etc.) but also with the increase in the reactivity of these compounds in reactions with peroxy-radicals compared with the reactions with alkyl radicals.[116]

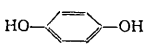
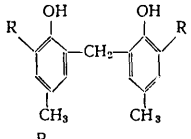
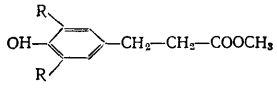
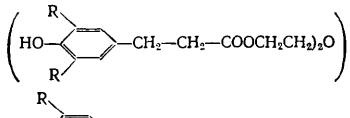
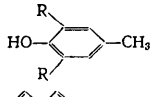
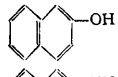
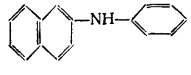
The use of weak inhibitors together with a monomer relatively inactive in relation to copolymerisation is of definite practical concentration interest. If the concentration and reactivity of one monomer are significantly lower than those of the other, then the efficiency of the weak inhibitor increases the degree of conversion more markedly than in the absence of the relatively inactive monomer.

The method of weak inhibition has been used to demonstrate the high activity of certain monomers in copolymerisation reactions.[117]

The characteristic features of the heterophase polymerisation are associated with the low mobility of the macroradicals in the solid phase and with the sharp retardation of the rate of their mutual termination. Under these conditions, the processes involving chain termination by the weak inhibitor may also be significant in the initial stages of the reaction. Therefore in certain cases heterophase polymerisation is a more convenient model for the study of weak inhibition reactions than extensive polymerisation. The efficiency of weak inhibitors in the class of aromatic amines, nitro-derivatives, and phenols increases sharply in the polymerisation of acrylonitrile in bulk compared with the reaction in solution in DMF.[118]

The same effect has been observed in the polymerisation of vinyl chloride and methacrylic acid in bulk and also of methyl methacrylate in the methanol–water precipitating mixture when acted upon by diphenylamine, *m*-dinitrobenzene, and other inhibitors.[119-121] The study of the heterophase polymerisation of various monomers in precipitating media made it possible to obtain data on the reactivites of a large number of inhibitors.[17]

Table 3. The apparent rate constants for the reactions of alkyl (K_X) and peroxy-radicals (K_{XO}) with inhibitors determined during tests (60 °C).[124,126,127]

Inhibitor	Structural formula	10^2K_X; $10^{-4}K_{XO}$, litre mol^{-1} s^{-1}
Hydroquinone		1.8; 21.4
α-Naphthol		1.6; 18.6
22-46		2.1; 39.8
Phenosane 1		0.7; 2.1
Phenosane 28		0.46; 1.7
Ionol		0.7; 2.2
β-Naphthol		0.8; 2.4
Neozone D		0.75; 6.7

Note: R = $C(CH_3)_3$.

The efficiency of weak inhibitors increases in polymerisation emulsion and depends both on their solubility in the chain propagation reaction zone, the topochemistry of the elementary steps, the rate of generation of free radicals, and the number of polymer-monomer species.[122,123]

A series of methods for testing weak radical polymerisation inhibitors, which are strong inhibitors of the oxidative polymerisation and degradation of polymers have been proposed in recent years.[124-127] One of the methods is based on the use of the model reaction involving the heterophase radical polymerisation of acrylonitrile. It is easy to show that the estimation of the apparent inhibition constant K_X in the reaction

$$R + X \rightarrow RH + \dot{X}$$

requires that the following criterion should be satisfied:

$$\frac{W_X}{W} = \frac{(K_i W_i)^{0.5}}{K_X [X]} = \varphi \ll 1.$$

Comparison of data on the inhibition of the polymerisation of acrylonitrile and the inhibition of the oxidative polymerisation and oxidation of hydrocarbons reveal a correlation between the inhibition constants in polymerisation (K_X) and oxidation (K_{XO}) reactions for a series of substituted phenols (Table 3). The correlation makes it possible to predict the reactivities of antioxidants by testing them (in relation to alkyl radicals) with the aid of the model heterophase polymerisation reaction.

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