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Stable Radicals and the Kinetics of the Radical Polymerisation of Vinyl Monomers

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The literature data and the results of studies by the authors of the review on the kinetics and mechanism of the radical polymerisation of vinyl monomers in the presence of stable radicals of different classes are treated systematically and discussed. The principal kinetic features associated with the influence of the structure of the monomer and the stable radical, the type of initiation, and the nature of the initiator on the polymerisation inhibited by stable radicals are noted. Equations are presented for the calculation of the kinetic parameters of the principal elementary reactions responsible for the initiating and inhibiting effect of stable radicals.
The bibliography includes 155 references.

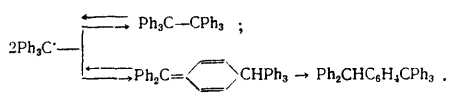
CONTENTS

I. Hydrocarbon radicals 1070
II. Hydrazyl radicals 1070
III. Verdazyl radicals 1071
IV. Aryloxy-radicals 1072
V. Nitroxy-radicals 1072
VI. Radical-anions 1076

The mechanism of the polymerisation of vinyl monomers has been studied in fair detail and numerous reviews and books, for example, Refs.1–4, have been devoted to this problem. The free-radical polymerisation inhibitors have aroused much interest in recent years.

I. HYDROCARBON RADICALS

Gomberg, who synthesised hexaphenylethane,[5] believed it to be the pure triphenylmethyl radical and it was only later established, in 1909, that "Gomberg's radical" is a dimer in thermodynamic equilibrium with the triphenylmethyl radical. For example, in benzene solution at room temperature only about 2% of the dimer is dissociated into free radicals.[6] It is of interest that an extremely stable hydrocarbon with a melting point of 234 °C has been found among triphenylmethyl dimers:



The triphenylmethyl radical inhibits the thermal polymerisation of styrene.[7] As expected, the measured induction period of the polymerisation reaction proved to be much shorter than the value calculated from the consumption of the inhibitor:[3]

$$\tau = \mu \frac{[X]}{W_i} \quad ,$$

where W_i is the rate of initiation, [X] the initial inhibitor concentration and μ the stoichiometric inhibition coefficient equal to the number of reaction chains broken by one inhibitor species.

Hexaphenylethane dissolved in styrene served as the source of radicals in the above investigation.[7] According to the authors' data, the rupture of one reaction chain requires 77 hexaphenylethane molecules, which corresponds to $\mu = 0.013$, in good agreement with the data of Theilacker and Ewald.[6]

In the presence of benzyl and diphenylmethyl radicals, which are more reactive than the triphenylmethyl radicals, the polymerisation of acrylonitrile and methyl methacrylate has no induction period and its rate is comparable to the rate of the initiated reaction.[8,9]

II. HYDRAZYL RADICALS

Numerous studies have been devoted to the influence of the stable 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical[10] on the rate of polymerisation of vinyl monomers. The high stability and relative availability of DPPH made it possible to employ this stable radical in the study of the photolysis and radiolysis of various compounds, cage effects, and the decomposition of initiators.[11–15]

DPPH is an effective inhibitor of the polymerisation of styne and vinyl acetate.[16–19] With increase of the DPPH concentration, the induction period shortens, which is caused, according to the authors, by the additional initiation due to the stable radical. It follows from the analysis of the dependence of τ on the initiator concentration [DPPH] that approximately 10% of the initial amount of the DPPH is consumed in chain initiation. However, one should note that the amount of the hydrazyl radical consumed in the initiation of the reaction is determined by the nature of the monomer. At the end of the inhibition period the steady-state rate of polymerisation falls. The bifunctionality of DPPH (weak initiation and strong inhibition) has also been noted in the polymerisation of styrene.[20]

Despite the above experimental facts and on the basis of the high activity of DPPH in relation to the growing chain alone, Matheson, Bartlett, and co-workers believe that it is possible to use this radical for the determination of the kinetic characteristics of the polymerisation—the rate of chain initiation and the ratio of the rate constants for chain propagation and termination $k_p/k_t^{1/2}$. It is then assumed that one radical terminates only one kinetic chain.

The mechanism proposed earlier[21,22] for the interaction of DPPH with active free radicals R$^\cdot$ consisted in the addition of R$^\cdot$ in the *para*-position in one of the phenyl groups. Further investigations showed that DPPH reacts to form a complex mixture of products: biphenyl, diphenylamine, 1-(4-cyanoisopropylphenyl)-1-phenyl-2-picrylhydrazine, and small amounts of $\alpha\alpha'$-diphenyl-2-picrylhydrazine.[23,24] If the reaction is propagated in the presence of oxygen, then

the interaction of peroxy-radicals with DPPH complicates the mechanism still further.[25-27]

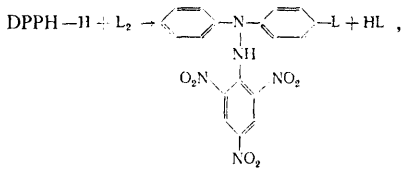
The possibility of the interaction of one DPPH species with several free radicals was first demonstrated experimentally by Hammond et al.[28] in a study of the decomposition of αα'-azobisisobutyronitrile (AIBN). It was assumed that the destruction of the cyanoisopropyl radicals with participation of DPPH is accompanied by the regeneration of the latter:

$$(CH_3)_2\dot{C}CN + DPPH \rightarrow CH_2{=}C(CH_3)CN + H{-}DPPH\,;$$
$$H{-}DPPH - (CH_3)_2\dot{C}CN \rightarrow (CH_3)_2CHCN + DPPH.$$

The complexity of the interaction of DPPH with free radicals was also confirmed by the result of the determination of the initiation efficiency factor f for AIBN.[22] Its values proved to be appreciably lower than those obtained by other workers using independent methods.

DPPH reacts with inorganic and organic acids via an ionic mechanism:[29]

$$DPPH + L^- \rightleftarrows [DPPH{-}L]^-\,,$$
$$[DPPH{-}L]^- + H^+ \rightarrow DPPH{-}H + {}^1/_2L_2\,,$$



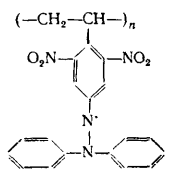
where L^- is the anion. It follows from the data presented that the inhibition of polymerisation processes by DPPH cannot be regarded as proof of the radical character of the reaction.

By measuring the DPPH concentration spectrophotometrically, Bengough[30] observed that the induction period in the polymerisation of vinyl acetate is not the same as the time required for the complete disappearance of the stable radical from the reaction system. This is apparently associated with the fact that the stoichiometric inhibition coefficient is not unity.

Analogous results were obtained also in the study of the thermal polymerisation of styrene inhibited by DPPH.[31] The rate of formation of active radicals, found from the time variation of the absorption intensity (λ = 525 nm), proved to be seven times greater than the value calculated from the equation relating the induction period to the initial concentration of the stable radical. This difference between the rates of initiation is caused not only by the stoichiometry of the inhibition but also by the characteristics of the mechanism of the thermal initiation[32,33] and the possibility of the decomposition of DPPH by UV radiation.[24]

The limits of the applicability of DPPH in the study of the kinetics of the decomposition of certain compounds and in the determination of their initiating activity have been analysed[34] and it has been shown that acceptable results are obtained only for the ratio [DPPH]/[I] ≤ 0.5.

Multiradical inhibitors based on DPPH, of the type[35,36]



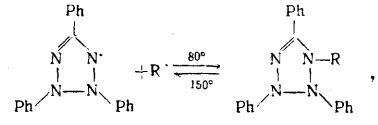
are of definite interest.

It follows from the literature data[16-38] that, when DPPH is used as the source of radicals, it is essential to know and take into account the chemical side reactions. Some investigators explained the decrease of the steady-state rate of polymerisation in the presence of DPPH (secondary inhibition) as the influence of the products of the primary inhibition responsible for the induction period.[37] The retardation of the reaction is usually attributed to the presence of nitro-groups. In order to test this hypothesis, 2-(2,6-dinitrophenyl)-1,1-diphenylhydrazyl was used to study the decomposition of AIBN under the conditions of heterophase polymerisation.[39] In the polymerisation of styrene[40] in the presence of this radical, there was indeed no additional initiation and the decrease of the steady-state rate was much smaller than in the case of the classical DPPH.

Braun and Peschk[41,42] prepared a series of hydrazyl radicals without nitro-groups and investigated their recombination with cyanoisopropyl and polystyryl radicals. The inhibiting activity of the hydrazyl radicals depended not only on their structure but also on the presence of oxygen in the system. The only exception was 2-(2',4',6'-trimethoxycarbonylphenyl)-1,1-diphenylhydrazyl radical, which could be used for quantitative measurements of the rate of initiation, since oxygen did not affect its inhibiting activity and the induction period was directly proportional to the radical concentration. In particular, the rate of initiation of the polymerisation of styrene (with AIBN as the initiator) determined with its aid agrees satisfactorily with the literature data.[3]

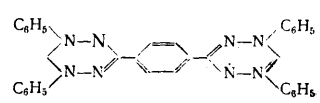
III. VERDAZYL RADICALS

In the first study[43] devoted to this class of stable radicals, it was already shown that the 1,3,5-triphenylverdazyl radical suppresses the polymerisation of styrene. In subsequent detailed investigations[44,45] of the polymerisation of styrene, methyl methacrylate, and certain other vinyl monomers, the high efficiency of the inhibiting effect of the verdazyl radical and the possibility of using it to determine the rate of chain initiation were established. It was found that the products of the recombination of verdazyl radicals with active radicals are capable of homolytic dissociation with formation of a stable radical (the activation energy for the homolysis is approximately 140 kJ mol^{-1}):[46]



where R$^\cdot$ is the initiator or polymer radical.

In the polymerisation of certain acrylic monomers (for example, oligourethane acrylate), the regeneration of the verdazyl radical was not observed and the inhibition efficiency appreciably diminished with increase of temperature.[47] In contrast to the 2,4,6-triphenyl-3,4-dehydro-s-tetrazine-1-verdazyl monoradical, the participation of the phenylenebisverdazyl radical



in the reactions entailed a sharp decrease of the rate of polymerisation.

The triphenylverdazyl radical is capable of reacting with acrylonitrile[40] via the double bond with an activation energy of about 45 kJ mol^{-1}, which indicates a relatively high

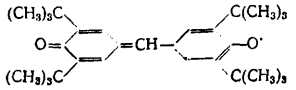
initiating activity of the verdazyl radical compared with many other stable radicals.

As in the case of DPPH, the accuracy of the determination of the rate of decomposition of the initiators with the aid of the triphenyl verdazyl radical depends on the ratio of the inhibitor and initiator concentrations. When a verdazyl radical is employed, this ratio should not exceed 2.[34]

The above characteristic features of the behaviour of verdazyl radicals limit their application to the reliable estimation of various kinetic parameters. The capacity of verdazyl radicals for relatively rapid oxidation by peroxy-compounds [48–50] at comparatively low temperatures (10–20 °C) precludes the determination of the characteristics of the initiation of polymerisation in their presence.

IV. ARYLOXY-RADICALS

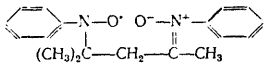
Among the radicals of this class, only the so-called galvinoxy-radical[51]



has been used in polymerisation. The decomposition of azocumene,[52] certain peroxy-compounds,[53–55] and AIBN [56] as well as the mechanism of the thermal polymerisation of deuteriated pentafluorostyrene[57] have been investigated with its aid. The galvinoxy-radical interacts with cyanoisopropyl radicals mainly by recombination. However, owing to the low photochemical and thermal stability of this radical and its ability to react with oxygen,[24] it cannot be used in accurate kinetic measurements.

V. NITROXY-RADICALS

Until the beginning of the 1960s, only one classical nitroxy-radical, namely Banfield's radical or the nitroxynitroxide radical



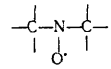
was used as the polymerisation inhibitor and free radical acceptor. Bevington and Ghenem[58] inhibited the polymerisation of styrene and methyl methacrylate with this radical. In air Banfield's radical is relatively unstable, its stability being appreciably higher in an inert atmosphere. The induction period of the polymerisation reaction in the presence of this radical is shorter than the value calculated from the formula $\tau = [X]_0/W_i$, which can be explained by its partial decomposition.

Tudos et al.[59] suggested that τ diminishes owing to the involvement of the radical in initiation reactions. Only on this hypothesis do the rates of initiation of polymerisation obtained[59,60] agree satisfactorily with literature data.

The influence of Banfield's radical, like, incidentally, that of other inhibitors, on the rate of polymerisation depends on the nature of the monomer and, in copolymerisation, also on the ratio of the concentrations of the monomers employed. Thus in solution in acrylonitrile the radical reacts with the monomer itself and the reaction is autocatalytic.[39] For this reason, Banfield's radical is unsuitable for the determination of the quantitative characteristics of the polymerisation of acrylonitrile. In the copolymerisation of acrylonitrile and styrene with participation of this radical, the stoichiometric inhibition coefficient exceeds unity,[61] which indicates the regeneration of the inhibitor in competition with the additional initiation reaction. At 50 °C and at a relatively low monomer concentration, the contribution of Banfield's radical to chain initiation in the copolymerisation of acrylonitrile with methyl methacrylate in dimethylformamide (DMF) is slight. With increase of temperature and the content of acrylonitrile, the effect becomes appreciable.[62] In the copolymerisation of styrene with maleic anhydride in solutions of acetonitrile, acetone, and tetrahydrofuran (THF) in the presence of Banfield's radical, the induction period in the process increases with decrease in the concentration of the monomers.

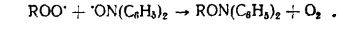
At the end of the induction period the rate of copolymerisation becomes lower than the rate of reaction in the absence of the inhibitor and depends appreciably on the concentration of the latter.[63] These results show that the use of Banfield's radical for accurate measurements of the rate of initiation without taking into account side reactions cannot be regarded as justified.

The successful development of the chemistry of stable radicals during the last twenty years[24,38] has led to the discovery of a new class of extremely stable non-aromatic nitroxy-radicals (iminoxy-radicals) with a localised free-radical centre:[64,65]

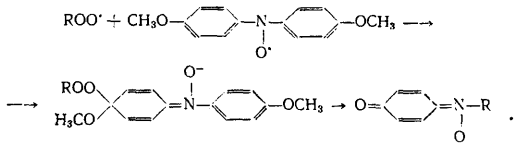


In the first studies[66–72] devoted to the use of nitroxy-radicals of this class as radical counters and antioxidants, interesting features of their behaviour were already observed. It was shown that, in contrast to the classical aromatic nitroxy-radicals, the non-aromatic nitroxy-radicals recombine rapidly with alkyl radicals but do not interact with peroxy-radicals.

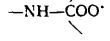
Classical aromatic nitroxy-radicals interact with the radicals ROO'; for example, at 60 °C the rate constant for the reaction of the di-(4-methoxyphenyl)-nitroxy-radical with peroxy-radicals is 6×10^5 dm^3 mol^{-1} s^{-1}.[63] It had been suggested earlier[73,74] that aromatic nitroxy-radicals interact with peroxy-radicals in accordance with the mechanism



In our view, the attack by the peroxy-radical in the *para*-position in one of the benzene rings of the diarylnitroxy-radical with formation of a quinonoid structure is more probable:[75,76]



We believe that the proposed mechanism agrees better with experimental data including the accumulation of compounds of the quinonitroxide type in the reaction products.[77] It is noteworthy that non-aromatic nitroxy-radicals can also react with peroxy-radicals if the latter have a favourable chemical structure. Thus the oxidation of primary and secondary aliphatic amines[78] results in the formation of peroxy-radicals of the iminoperoxy-type:



Such radicals interact with non-classical nitroxy-radicals to form the corresponding hydroxylamine with subsequent regeneration of the stable radical:

$$-NH-\underset{\diagdown}{\overset{\diagup}{C}}OO^{\cdot} + \rangle N-O^{\cdot} \rightarrow \rangle NOH + -N=\underset{\diagdown}{\overset{\diagup}{C}} + O_2 ;$$

$$-NH-\underset{\diagdown}{\overset{\diagup}{C}}OO^{\cdot} + \rangle NOH \rightarrow -NH-\underset{\diagdown}{\overset{\diagup}{C}}OOH + \rangle NO^{\cdot}.$$

Analogous results have been obtained in the inhibition of the oxidation of dimethylaminoethyl methacrylate.[79] In the oxidation of the alkyl methacrylates, the active intermediate chain centres are polyperoxy-radicals without reducing properties. Chain termination takes place as a result of the interaction of the nitroxy-radicals with alkyl radicals, the inhibitor not being regenerated. When a tertiary amino-group is introduced into the methacrylate, the chain termination mechanism changes—the above reactions become most important and the nitroxy-radical is regenerated.

The mechanism of the interaction of the nitroxy-radicals with alkyl radicals has been investigated.[80,81] The main product of the reaction of the 2,2,6,6-tetramethyl-4-oxopiperidin-1-yloxy-radical with the cyanoisopropyl radical was an ether derived from a heterocyclic hydroxylamine.

The view that recombination is the only pathway involved in the interaction of nitroxy-radicals with active radicals is widely held. In particular, the unique capacity of nitroxy-radicals for regeneration in reactions where they inhibit the oxidation of olefins, polyolefins, and hydrocarbons has been explained on the basis of this idea.[82-87] It follows from these investigations that the regeneration takes place as a result of the reaction

$$\rangle NOR + ROO^{\cdot} \rightarrow \rangle NO^{\cdot} + \text{products}.$$

However, the results of Shlyapnikov et al.[88] do not agree with these ideas. Experiment has shown that the 2,2,6,6-tetramethyl-4-oxopiperidin-1-yloxy-radical is regenerated approximately 10^3 times faster than would be the case if this happened solely via the reaction presented above. According to the authors, this is associated with chain termination not only via recombination but also due to disproportionation, which leads to the formation of the hydroxylamine.

The efficiency of nitroxy-radicals as free radical acceptors has stimulated their application in the study of the mechanisms of polymerisation initiation. This application has developed in a number of investigations.[89-96] The authors established that, in the general case, when the nitroxy-radical is added to the monomer–initiator system, the polymerisation is suppressed but the radical is able to react only with some of the initiator radicals, while in the case where peroxides are used it does not interact with the primary radicals at all. For this reason, the products of the reactions of the primary radicals with the monomer are formed in this case in almost quantitative yields. They interact with the nitroxy-radicals and form stable adducts, whose structure has been reliably established. Under certain conditions, the nitroxy-radical can catalyse the decomposition of peroxides.[97]† Thus nitroxy-radicals can be used as effective analytical reagents and information about the fine details of the initiation mechanism can be obtained with their aid.

In the first studies of the influence of classical aromatic nitroxy- and iminoxy-radicals on the rate of radical polymerisation,[98,99] the rate constants for the interaction of the stable radicals with the styrene macroradicals were determined by EPR. The calculations were performed on the assumption that chain termination takes place in 1 : 1 proportions. Furthermore, a study was made of the reactions of stable biradicals with the alkyl radicals formed on decomposition of AIBN in ethylbenzene and dioxan.[100] It was observed that the probability of the recombination of the radical centre depends on the residual unpaired electron in the biradical.[101] The first reaction (with one of the localised free-radical centres) proceeds more readily than the second, which the authors explain within the framework of the adiabatic nature of the recombination reaction.

The interaction of certain mono- and di-radicals with styrene and α-methylstyrene at 100–120 °C has been investigated by EPR.[102] The authors suggest that the stable radicals are consumed in reactions involving addition to the monomer molecules (additional initiation) and in the course of recombination with the active radicals produced. The following mechanism has been proposed for the monoradicals (X):

$$CH_2=\underset{C_6H_5}{\underset{|}{CH}} + X^{\cdot} \xrightarrow{k_M} X-CH_2-\underset{C_6H_5}{\underset{|}{CH}} ;$$

$$R^{\cdot} + X^{\cdot} \xrightarrow{k_X} \text{products}.$$

However, the authors did not take into account the fairly high capacity of styrene for thermal polymerisation, whose rate is high at the temperatures indicated. For this reason, some of the stable radicals should be consumed in reactions with the species initiating the thermal polymerisation. This factor has been taken into account in two investigations[103,104] of the influence of pressure on the reactions occurring in the styrene–iminoxy-radical system at 80 °C. Assuming that the thermal initiation takes place in accordance with Mayo's mechanism,[105] the authors obtained an equation for the rate of consumption of the nitroxy-radical in the monomer:

$$-d[X]/dt = 2k_{DA}[M]^2 + 2k_M[M][X] ,$$

where k_{DA} is the rate constant for the reaction of the iminoxy-radical with the Diels–Alder adduct and [M] is the monomer concentration. The validity of this equation requires additional evidence in view of the uncertainty of the mechanism of the initiation of the thermal polymerisation of styrene[33] and the latest data concerning the influence of iminoxy-radicals on the rate of this reaction.[106,107]

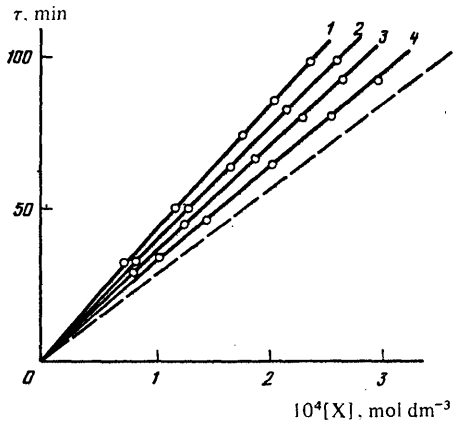
In a study of the propagation of the chloroprene ω-polymer in the presence of iminoxy-radicals,[108] yet another piece of evidence for the free-radical nature of the ω-polymerisation of this monomer was obtained.

The advances in the chemistry of nitroxy-radicals have made it possible to synthesise polymeric free radicals in which the nitroxy-radical forms part of the composition of the polymer chain unit.[109] Such macromolecular stable radicals inhibit effectively the polymerisation of styrene and methyl methacrylate initiated by AIBN [110-112] and also the polymerisation accompanying the synthesis of unsaturated ethers.[113]

The influence of di(4-ethoxyphenyl)nitroxy-radical on the polymerisation of styrene has been investigated.[114] The decrease of the inhibiting activity of the arylnitroxy-radical in the presence of benzoyl peroxide, despite the linear dependence of τ on the concentration of the additive, was observed for the first time in the above study. In contrast to the polymerisation initiated by AIBN, a slower increase in the rate of reaction during the induction period and a decrease of the steady-state rate with increase of the arylnitroxy-radical concentration were then observed. It will be shown below that these effects are associated with the interaction of the benzoate radical with the aryl nitroxy-radical.

† This observation was subsequently used by one of the present authors for the selective inhibition of certain undesirable oxidation reactions—see, for example, Maslov et al.[154]

The 2,2,6,6-tetramethyl-4-hydroxypiperidin-1-yloxy-radical[115] was one of the first nitroxy-radicals used as the counter of active centres in the polymerisation of tetrafluoroethylene.[116] The possibility of determining the rate of chain initiation with the aid of this iminoxy-radical was justified in the above investigation by the fact that the induction period is directly proportional to the inhibitor concentration and the polymerisation is not retarded at the end of the inhibition period. A 1 : 1 stoichiometry of chain termination was adopted, as in many other studies.[117–125]



Dependence of the induction period in the polymerisation of styrene on the concentration of the iminoxy-radical: 1) 2,2,6,6-tetramethyl-4-oxopiperidine-1-yloxy-ester of α-cyano-ββ′-diphenylacrylic acid; 2) 2,2,6,6-tetramethyl-4-salicylideneaminopiperidin-1-yloxy-radical; 3) 2,2,6,6-tetramethyl-4-stearyliminopiperidin-1-yloxy-radical; 4) 2,2,6,6-tetramethyl-4-benzoylpiperidin-1-yloxy-radical; initiator—azobisisobutyronitrile (3×10^{-2} mol dm^{-3}); 45 °C; the dashed line corresponds to $\mu = 1$.

The reaction of the 2,2,6,6-tetramethyl-4-oxopiperidin-1-yloxy-radical[126] with primary and polymeric radicals in the inhibition of the polymerisation of styrene and methyl methacrylate has been studied.[127] The inhibition mechanism proposed by the authors includes a stage involving the recombination of the active and stable radicals with formation of the corresponding ethers. This conclusion is confirmed by the fact that the ether does not influence the rate of polymerisation, while the reduced radical (hydroxylamine) induces a marked decrease in the rate of the process. In fact, there is no retardation of the polymerisation at the end of the induction period.

At the same time there exist data in conflict with the idea of a simple stoichiometry of chain termination. Comparative estimation of the inhibiting activities of the iminoxy- and arylnitroxy-radicals in the initiated polymerisation of styrene showed[128] that the stoichiometries of the reactions with polystyrene radicals are the same for different classes of nitroxy-radicals. However, this fact was not explained.

The study of the inhibiting properties of the 2,2,6,6-tetramethyl-4-oxopiperidin-1-yloxy- and 2,2,6,6-tetramethyl-4-hydroxypiperidin-1-yloxy-radicals in the polymerisation of oligourethaneacrylate[47] showed that the former radical induces under identical conditions a longer induction period than the latter. This means that the 2,4-bis(2,2,6,6-tetramethyl-4-ureidopiperidin-1-yloxy)tolylene biradical inhibits the polymerisation of oligourethaneacrylate more effectively than would be the case for simple stoichiometry of the termination reaction.

In the inhibition of the copolymerisation of styrene with acrylonitrile by the 2,2,6,6-tetramethylpiperidine-1-yloxy-radical, it was found[61] that the stoichiometric inhibition coefficient depends on the nature of the initiator and is much greater than unity when AIBN is used. According to Shlyapnikov et al.,[129] the occurrence of side reactions hinders the application of the inhibitor method to the determination of the relatively low rates of the chain initiation reactions in processes involving the degradation of polymers in an inert atmosphere.

In order to refine the mechanism and find the quantitative characteristics of the inhibition by iminoxy-radicals, it is most convenient to study their influence on the polymerisation of thoroughly investigated monomers (styrene and acrylate and methacrylate esters) in the presence of initiators with known rates of decomposition (AIBN and benzoyl peroxide). In the polymerisation initiated by AIBN, the rate of consumption of stable radicals during the inhibition period is lower in all the monomers than the rate of initiation, i.e. $\mu > 1$ [130–133] (see Figure). Such increase of μ can be explained, for example, by the regeneration of the inhibitor. However, in certain cases when the period τ has come to an end, the rate of polymerisation becomes lower than the rate of the non-inhibited process. With increase of the concentration of the additive, the induction period shortens, which is apparently caused by the addition of the stable radical to the monomer at the double bond (i.e. by the additional initiation).

Thus the effective inhibition of polymerisation by iminoxy-radicals is accompanied by complex reactions. In order to elucidate certain details of the inhibition process, the influence of ethers R_0–X (R_0 is a primary radical) and hydroxylamines X–H on the polymerisation has been investigated[155] and it has been established that ethers do not affect the polymerisation kinetics, while the rate of the process diminishes somewhat in the presence of hydroxylamines. Consequently the regeneration can be explained by the fact that some of the iminoxy-radicals disproportionate in a reaction with active radicals, forming nitroso-compounds.[134] The latter suppress the polymerisation, each terminating two kinetic chains per inhibitor molecule. Apparently the involvement of iminoxy-radicals in this stage is in fact responsible for the increase of the stoichiometric coefficient, while the decrease of the steady-state rate of polymerisation is associated with chain termination by hydroxylamines.

The radical-chain mechanism of the polymerisation of vinyl monomers, initiated by AIBN, in the presence of added iminoxy-radicals can be represented in the following way on the basis of the foregoing:

$$\text{AIBN} \rightarrow 2R_0^{\cdot} + N_2\uparrow ; \qquad \text{(I)}$$

$$R_0^{\cdot} + M \xrightarrow{k_i} R^{\cdot} ; \qquad \text{(II)}$$

$$R^{\cdot} + M \xrightarrow{k_p} R^{\cdot} ; \qquad \text{(III)}$$

$$X + M \xrightarrow{k_i} R^{\cdot} ; \qquad \text{(IV)}$$

$$R^{\cdot} + X \xrightarrow{k_t} RX ; \qquad \text{(V)}$$

$$X + R^{\cdot} \xrightarrow{k_t} XH + \text{inactive products;} \qquad \text{(VI)}$$

$$X + M \xrightarrow{k_s} R^1\text{—N=O} + HM ; \qquad \text{(VII)}$$

$$R^1\text{—N=O} + R^{\cdot} \rightarrow R^1\text{—N(O}^{\cdot}\text{)—R} ; \qquad \text{(VIII)}$$

$$R^1\text{—}\underset{\underset{O^\cdot}{|}}{N}\text{—}R + R^\cdot \rightarrow R^1 - \underset{\underset{OR}{|}}{N}\text{—}R\ ; \qquad (IX)$$

$$XH + R^\cdot \rightarrow X + RH\ ; \qquad (X)$$

$$R^\cdot + R^\cdot \rightarrow \text{polymer.} \qquad (XI)$$

The additional initiation with the aid of the stable radical proceeds slowly ($k_i \cong 10^{-6}$ dm^3 mol^{-1} s^{-1} at 60 °C), the secondary inhibition is slight, and in the course of the induction period the contribution by the quadratic termination to the overall chain termination is small. For these reasons, disregarding reactions (IV), (X), and (XI), the kinetic equation describing the consumption of the iminoxy-radicals assumes the following form:

$$-d[X]/dt = W_i(k_1 + k_2 + k_3)/(k_1 + k_2 + 2k_3). \qquad (1)$$

The inhibitor should be consumed in accordance with a linear law at a rate lower than that of initiation, which has been confirmed satisfactorily by experimental data. The stoichiometric inhibition coefficients are calculated in these cases from the formula

$$\mu = 1 + \frac{2k_3}{k_1 + k_2 + k_3}\ . \qquad (2)$$

The time variation of the rate of inhibited polymerisation obeys the Bagdasar'yan–Bamford equation:

$$-\frac{1}{\varphi} + \ln\frac{1+\varphi}{1-\varphi} = (k_X + k_3)[R]_\infty t + \text{const}\ , \qquad (3)$$

where $\phi = W_t/W_\infty$ is the ratio of the rates of polymerisation at any instant W_t and the steady-state W_∞, $[R]_\infty$ is the steady-state concentration of the polymeric radicals, and $k_X = k_4 + k_5$. Eqns.(1) and (2) are valid at relatively low temperatures (40–60 °C). The consumption of iminoxy-radicals increases with increasing temperature owing to the suppression of the thermal initiation and their addition to the monomer, the experimental quantity μ_{exp} therefore diminishes. The contribution of these reactions can be taken into account by calculating the rate of consumption of the inhibitor in the monomer at an elevated temperature $\omega_0 = \{-d[X]/dt\}_0$. Then, denoting the rate of consumption of iminoxy-radicals in the inhibition reaction by $\omega = d[X]/dt$, we obtain

$$W_i = \mu_{exp}(\omega_0 + \omega), \qquad (4)$$

where μ_{exp} is the experimental (apparent) stoichiometric inhibition coefficient. An expression for the true value of μ can be readily obtained from Eqn.(3):

$$\mu = \frac{W_i\mu_{exp}}{W_i - \omega_0\mu_{exp}} \qquad (5)$$

The set of equations (2), (3), and (5) makes it possible to estimate the inhibition rate constant k_X and the rate constant for the regeneration of the inhibitor k_3 as well as the activation energies E for these reactions (see Table). It is essential to note that the relative errors of the tabulated rate constants and activation energies are approximately 10 and 15% respectively. The differences are most probably associated with the different structures of the stable radicals investigated. However, hitherto it has not been possible to establish a reliable correlation between the chemical structure of the iminoxy-radicals and the parameters noted above, characterising their inhibiting effect. Comparison of the quantities k_X, k_3, E_X, and E_3 suggests that the substituent exerts the main influence on the pre-exponential factor (i.e. on the steric factor) and not on the activation energy.

The tabulated k_X differ from the literature data. The constants for the interaction of nitroxy-radicals with primary and polymeric radicals found by different workers vary from 10^4 to 10^8 dm^3 mol^{-1} s^{-1}.[98,114,128,135] This scatter is not surprising, since in many cases no account was taken of the details of the inhibition mechanism associated with the complex stoichiometry of the chain termination, the inhibitor generation, the additional initiation, the influence of the type of initiation and of the nature of the initiator, the characteristic features of oxidative polymerisation, etc.

Kinetic parameters of the inhibition of the polymerisation of styrene and methyl methacrylate by iminoxy-radicals (60 °C, initiator—AIBN).* [130–133,155]

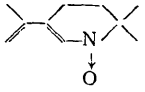
Radical	$10^{-5}k_X$, dm^{3}mol^{-1}s^{-1}	$10^{-5}k_3$, dm^3 mol^{-1} s^{-1}	E_X, kJ mol^{-1}	E_3, kJ mol^{-1}
(A)	5.0; 6.4	1.9; 1.6	16; 12	26; 23
(B)	7.0; 6.8	1.5; 1.2	13; 14	26; 29
(C)	2.0; 4.9	0.7; 1.6	12; 10	21; 25
(D)	2.5; 6.8	0.8; 1.2	13; 13	23; 27
(E)	3.5; —	0.7; —	11; —	25; —
(F)	3.0; 6.0	0.2; —	16; 17	36; —

Notation: (A) = 2,2,6,6-tetramethyl-4-oxopiperidin-1-yloxy-ester of α-cyano-ββ′-diphenylacrylic acid; (B) = 2,2,6,6-tetramethyl-4-salicylideneaminopiperidin-1-yloxy-radical; (C) 2,2,6,6-tetramethyl-4-palmitylimino-piperidin-1-yloxy-radical; (D) = 2,2,6,6-tetramethyl-4-stearyliminopiperidin-1-yloxy-radical; (E) = 2,2,6,6-tetramethyl-4-hydroxypiperidin-1-yloxy-radical; (F) = 2,2,6,6-tetramethyl-4-benzoylpiperidin-1-yloxy-radical.

*The first and second numbers represent respectively the data for styrene and methyl methacrylate.

The kinetics and mechanism of the polymerisation inhibited by nitroxy-radicals change significantly on passing from initiation by azo-compounds to initiation by peroxy-radicals. The mechanism of the interaction of iminoxy-radicals with peroxy-radicals is determined by the chemical structure of the latter and the nature of the solvent. Thus the rates of decomposition of benzoyl peroxide (BP) in DMF and of t-butyl and dicumenyl peroxides in benzene are independent of the presence of iminoxy-radicals in the mixture.[136,137] On the other hand, the decomposition of acetylphenyl peroxide in carbon tetrachloride[138] and of dicyclohexyl peroxydicarbonate in benzene and chlorobenzene[139] is accelerated with formation of free-radicals and non-radical products.

At concentrations of the iminoxy-radicals exceeding the BP concentration by approximately a factor of two, the induced decomposition of the peroxide in the monomer takes place with formation of a heterocyclic nitroxide (nitrone)



and benzoic acid.[140]

Under polymerisation conditions where [BP] ≫ [X], the formation of side products is apparently suppressed and the induced decomposition accompanied by the formation of a donor–acceptor complex Q_1 becomes the main process:[141]

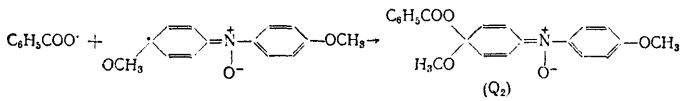
$$BP + X \rightleftarrows Q_1 \rightleftarrows 2C_6H_5COO^\cdot + X\ .$$

The effective rate constants for the decomposition of the BP bound in the complex are approximately 10^2 dm^3 mol^{-1} s^{-1} in styrene and 5×10^3 dm^3 mol^{-1} s^{-1} in methyl methacrylate (60 °C). The effective activation energy for the decomposition reaction is about 80 kJ mol^{-1}, which is appreciably lower

than for the free initiator molecule (125 kJ mol^{-1}). Thus iminoxy-radicals are unsuitable for the determination of the rate of chain initiation by peroxide initiators.

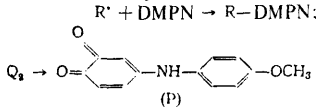
The significant differences between the reactivities of iminoxy-radicals and aromatic nitroxy-radicals[24,142] lead to their different effects on the kinetics of polymerisation initiated by peroxides. Whereas the role of iminoxy-radicals reduces to the acceleration of the decomposition of BP (naturally apart from the inhibition itself), nitroxy-radicals [for example, di(4-methoxyphenyl)nitroxy-radicals (DMPN)] interact with BP to form non-radical products.[143] The reaction in the monomers proceeds via a more complex multistage mechanism:

$$BP + DMPN \rightarrow 2C_6H_5COO^{\cdot} + DMPN:$$

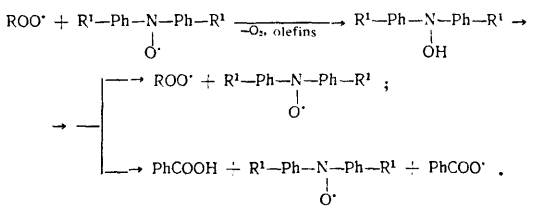


$$C_6H_5COO^{\cdot} + M \rightarrow R^{\cdot}$$

$$R^{\cdot} + DMPN \rightarrow R{-}DMPN:$$



The aminoquinone (P) formed is a probable polymerisation inhibitor. It follows from the above mechanism that, whereas in an inert atmosphere two stable radicals are consumed per BP molecule, in the presence of air the stoichiometry changes owing to the regeneration of the arylnitroxy-radical:[73,128,144]



The change in stoichiometry does not lead to new kinetic effects. At the end of the induction period induced by the presence of the aminoquinone, the polymerisation proceeds at a constant rate W_∞, which is lower than the rate of the non-inhibited reaction W.

The following equation corresponds to the radical-chain polymerisation mechanism in the presence of the aminoquinone and with allowance for secondary inhibition:[130]

$$-\frac{1}{\varphi_t} - \ln(1-\varphi_t) + (1-\varphi_\infty^2)\ln\varphi_t + \varphi_\infty^2 \ln\left(\varphi_t - \frac{1}{\varphi_\infty^2}\right) = \frac{k_X}{k_p}\frac{W_\infty}{M}t + A,$$

where $\phi_t = W_t/W_\infty$, $\phi_\infty = W_\infty/W$, and A is a constant. The inhibition constants k_X for different monomers are in the range 10^4–10^5 dm^3 mol^{-1} s^{-1} (60 °C) and the activation energy for the inhibition reaction is 23 kJ mol^{-1}.

VI. RADICAL-ANIONS

In contrast to neutral stable radicals, charged radicals usually initiate ionic polymerisation.[145,146] The initiating activity of radical-anions depends on the difference between the electron affinities of the monomer and the initiator. The radical-anions formed from compounds with a very high electron affinity can therefore prove to be incapable of initiating anionic polymerisation. Having an excess charge, the radical-anions usually possess electron-donating properties and are involved in various charge-transfer reactions.

The influence of radical-anions on the polymerisation of vinyl monomers via a radical mechanism has been investigated in relation to the effect of tetracyanoquinodimethane salts, which dissociate in solution with formation of the tetracyanoquinodimethane radical-anion $TCQM^{\cdot-}$. When the polymerisation is initiated by benzoyl peroxide, the introduction into the solution of the lithium salt of tetracyanoquinodimethane (Li TCQM) leads to a sharp acceleration of the polymerisation and a decrease in the molecular weight of the polymer. An increase in the rate was observed only in those cases where the concentration of the salt did not exceed that of the peroxide by a factor greater than two and the highest rate of the process was attained for equal contents of Li TCQM and BP.[147–150]

Studies of the kinetics of the polymerisation and the interaction of BP and $TCQM^{\cdot-}$ showed that a one-electron transfer reaction takes place between the radical-anion and the peroxide molecule with subsequent reactions between the resulting neutral TCQM and the benzoate anion R^- and also between the benzoate radical $R^{\cdot}$ and yet another $TCQM^{\cdot-}$ radical-anion:

$$TCQM^{\cdot-} + BP \rightarrow R^{\cdot} + R^- + TCQM:$$

$$TCQM^{\cdot-} + R^{\cdot} \rightarrow Q^-;$$

$$TCQM + R^- \rightarrow Q^-.$$

These reactions take place at a high rate even before the onset of polymerisation. The initiating radicals are formed in the oxidation-reduction interaction of the intermediates with the BP molecules which fail to react ($\overline{BP}$):

$$\overline{BP} + Q^- \xrightarrow{k_R} R^{\cdot} + R^- + R_Q^{\cdot}$$

The polymerisation is initiated by the BP–Li TCQM system by a factor of several tens faster than as a result of the thermal decomposition of BP.

If the initial Li TCQM concentration is greater than twice the peroxide concentration, then free $TCQM^{\cdot-}$ radical-anions remain in the reaction system and inhibit the polymerisation.

The study of the reactions of various organic peroxides with the $TCQM^{\cdot-}$ radical-anion has shown that, in conformity with the mechanism proposed, the radical-anion interacts only with those peroxides which possess a sufficiently high electron-accepting capacity (benzoyl and lauryl peroxide). Otherwise $TCQM^{\cdot-}$ only exhibits the polymerisation (cumenyl peroxide). In the presence of lauryl peroxide, whose electron-accepting capacity is lower than that of BP, the rate of initiation of the polymerisation diminishes.

The initiation of polymerisation by the peroxide–$TCQM^{\cdot-}$ radical-anion system is characterised by a low activation energy (~40 kJ mol^{-1}), which makes it possible to carry out the reaction at a high rate and a relatively low temperature.

The possibility that radical-anions can assume the role of radical polymerisation inhibitors was first demonstrated in relation to the radical-anion salt of 7,7,8,8-tetracyanoquinodimethane with dimethylviologen.[151] It was found that $TCQM^{\cdot-}$ inhibits effectively the polymerisation of styrene, acrylate and methacrylate esters, and acrylonitrile, giving rise to distinct induction periods.[152] It was established that $TCQM^{\cdot-}$ interacts not only with active radicals, inhibiting polymerisation, but also with monomer molecules, which leads to the generation of new active centres, which are immediately terminated by the radical-anion. Such additional initiation induces a relative shortening of the induction period with increase in the inhibitor concentration. The rate constant for the additional initiation k_i depends significantly on the nature of the monomer and diminishes in the sequence styrene > methyl methacrylate > methyl acrylate.

The radical-anion complexes dissociate in solution in different ways depending on the nature of the cation, the concentration, the composition of the medium, and temperature. In the general case the $TCQM^{\cdot-}$ radical-anion exists in solution in the form of both free radical-anions and ion pairs, which have different reactivities. It has been shown that the additional inhibition is induced only by the $TCQM^{\cdot-}$ radical-anions present in solution in the form of ion pairs with a cation, while free-radical-anions are more active in the inhibition reaction.[153] A change in the composition of the reaction medium influences the degree of dissociation of the $TCQM^{\cdot-}$ complexes and hence the contribution of the additional initiation to the overall reaction kinetics. As a result, the duration of the inhibition of the polymerisation by the $TCQM^{\cdot-}$ radical-anions is determined not only by the ratio of the inhibitor concentration and the rate of initiation but also by factors influencing the degree of dissociation of the radical-anion salts.

The dependence of the duration of the induction period in the polymerisation of styrene on the TCQM concentration is fairly complex and is determined by the equation[152]

$$\tau = [2k_{decomp}f\alpha(1-\gamma)]^{-1}\ln\left\{1-\alpha(1-\gamma)\frac{[X]_0}{[I_0]}\right\},$$

where $\alpha = k_i[M]/k_{decomp}f$, k_i is the rate constant for the additional initiation of the polymerisation by the ion pairs involving the $TCQM^{\cdot-}$ radical-anion, k_{decomp} the rate constant for the initiator decomposition reaction, f the efficiency of the initiation, and $[I]_0$ and $[X]_0$ are the initial concentrations of the initiator (AIBN in the study indicated) and the TCQM radical-anion salts.

As a result of the additional initiation reaction, the time variation of the rate of the inhibited polymerisation no longer obeys the Bagdasar'yan–Bamford equation[3] and is described by the more complex expression[151]

$$-2\ln(\varphi_t-\theta)-\left(\frac{1}{\theta}-1\right)\ln(1-\varphi_t)+\left(\frac{1}{\theta}+1\right)\ln(1-\varphi_t)+$$
$$+0.5\left(\frac{1}{\theta^2}-1\right)\ln\left|\frac{\varphi_t-\theta}{\varphi_t+\theta}\right|=\frac{k_X}{k_p}\frac{W_\infty}{M}\left(\frac{1}{\theta}-\theta\right)t+\text{const},$$

where $\theta = k_i[M]/k_X[R]_\infty$, $\phi_t = W_t/W_\infty$, W_t is the rate of polymerisation at time t, and W_∞ and $[R]_\infty$ are the steady-state rate and concentration of polymeric radicals.

The plot of the reduced rate of polymerisation ϕ_t against time is represented by S-shaped curves with a point of inflection. The parameter θ is determined from the reduced rate of polymerisation at this point (ϕ_{pi}) from the equation

$$\theta^3-\frac{2\varphi_{pi}}{1+\varphi_{pi}^2}\theta^2-\frac{3\varphi_{pi}^4-\varphi_{pi}^2}{1+\varphi_{pi}^2}\theta-\frac{\varphi_{pi}^5-2\varphi_{pi}^3-\varphi_{pi}}{1+\varphi_{pi}^2}=0.$$

The inhibition constants k_X/k_P are 10^3–10^4 and vary within wide limits depending on the nature of the cation, the solvent, and the monomer, as well as temperature. Furthermore, they decrease with increase of the inhibitor concentration, while the additional initiation constants k_i increase.

The interaction of the $TCQM^{\cdot-}$ radical-anions with macroradicals proceeds via different mechanisms. Together with addition, there is a possibility of electron transfer from the radical-anion to a macroradical having more pronounced electron-accepting properties. Inhibition via the electron transfer mechanism is most likely in the polymerisation of monomers whose polymeric radicals have a higher electron affinity, i.e. the rate of reaction increases in the monomer sequence styrene < methyl methacrylate < methyl acrylate. As a result of electron transfer, the radical-anion is converted into neutral TCQM, which is itself capable of terminating the reaction chains or, by reacting with the electron-donating solvent (for example, DMF), it is reconverted into the radical-anion.[152]

Thus the reactions involving the regeneration of the inhibitor are characteristic of the inhibition of the polymerisation of the methacrylic and especially acrylic monomers by the $TCQM^{\cdot-}$ radical-anion, which is manifested by an increase in the induction period and a change in the sign of the curvature of the plot of τ aginst [X].

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