COMPREHENSIVE POLYMER SCIENCE

First Supplement

COMPREHENSIVE POLYMER SCIENCE

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Preface

Supplementary volumes to the seven-volume work *Comprehensive Polymer Science*, published in 1989, are designed to provide up-to-date and comprehensive reviews of polymer topics that were either not included in the original main work or for which recent developments justify authoritative critical reviews. Supplementary volumes are planned to be published every two years.

For this *First Supplement*, we have attempted to choose topics that provide a balance between the areas of polymer chemistry, physics and technology. Thus, in addition to several chapters on polymer chemistry, chapters on the following areas of current interest are included:

Functionalized polymers, their synthesis and properties
Computer modeling in polymer science
Degradation and mutual diffusion of polymers
Liquid crystalline polymers
Structure and properties of polymers for photonic applications, for Langmuir–Blodgett films and for polymer composites
Reactive processing

To assist readers of *Comprehensive Polymer Science* to explore specific areas of polymer science in greater depth, a guide to numerous books, handbooks and encyclopedias has also been included as an Appendix. This Appendix is intended for use with the whole series of volumes.

We would like to acknowledge the help of many of our colleagues in selecting topics for the *First Supplement* and to thank Dr Helen McPherson of Pergamon Press and her editorial team for their work in ensuring that the same high standards of production and publishing have been achieved as in the seven volumes of *Comprehensive Polymer Science*.

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Contents

1

Inhibition and Retardation in Radical Polymerization

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1.1 INTRODUCTION

It is a familiar observation that free-radical polymerizations are frequently very sensitive to the presence of small quantities of 'impurities'. Substances which produce very large decreases in the rate of polymerization when added in low concentrations are classed as inhibitors or retarders. These terms have been taken over from classical chain reaction theory, in which an inhibitor is defined as a substance which deactivates initiating centres and a retarder as one which interrupts propagation. In classical systems distinction between the two is often clear-cut since the initiating and propagating species may be quite different in type and reactivity. Although this is so in some polymerizations, more frequently the two types of species are similar, generally organic free radicals. A familiar (extreme) example is the polymerization of methacrylonitrile initiated by azobisisobutyronitrile; here the initiating radicals are 2-cyanoisopropyl ($Me_2\dot{C}CN$) and the chain carriers $-CH_2\dot{C}(Me)CN$. Generally, in practice, the distinction between inhibitors and retarders of polymerization is rather blurred and the same compound may function in either capacity, depending on its concentration and the nature of the system.

Inhibitors and retarders react with initiating or propagating radicals, respectively, to form species of lower reactivity which are either unable to reinitiate chains or reinitiate only slowly. If the products are inactive, the inhibitor or retarder is classed as ideal, and in such a case the kinetic behaviour of the system is relatively simple. On the other hand, slow reinitiation gives rise to more complex kinetics, which may be difficult to interpret unequivocally without additional evidence.

Inhibition and retardation may be either radical addition or radical abstraction processes. Basically these are copolymerization or chain transfer reactions, respectively, differing from 'normal' copolymerizations or chain transfers in that the radical products have low or zero reactivity.

Conversely, a chain transfer becomes a retardation if it yields an effectively inert product; it is then referred to as a degradative chain transfer.

It should be clear from the above that the extent to which a substance (additive) shows inhibiting or retarding properties depends on the nature of the system of which it is a part. The activities of the monomer and derived radicals play critical roles; the latter determines the rate of interaction with a given additive while the former strongly influences the rate of reinitiation. For example, the polymerization of vinyl acetate, unlike that of many vinyl monomers, is retarded by low concentrations of styrene. In this system highly active vinyl acetate radicals add rapidly to the reactive styrene monomer, producing styryl-type radicals which are unable to add to the relatively unreactive vinyl acetate monomer.

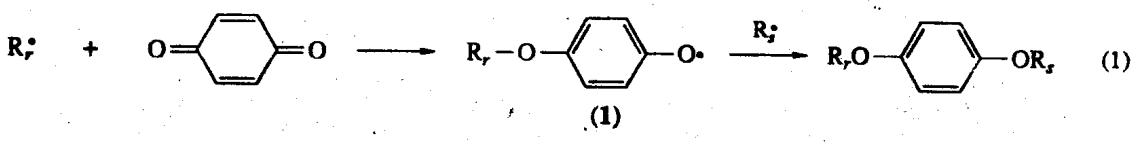
1.2 SOME ASPECTS OF THE CHEMISTRY OF INHIBITION AND RETARDATION

Inhibitors and retarders are of diverse chemical types and include stable free radicals, quinones, aromatic derivatives (especially nitro compounds), but also hydrocarbons, some elements (O_2, I_2, S) and many oxidizing cations such as Fe^{3+}, Cu^{2+}, Ce^{4+}, Hg^{2+}, Tl^{2+} and Ag^{+} which enter into redox reactions. The literature reveals divergent views of the nature of the mechanisms involved. These have been reported in several texts[1-3] and we shall not elaborate them, but merely indicate some types of reaction involved.

Polymerizations of monomers which can undergo degradative chain transfer show 'self-retardation' (in the absence of added retarder). Allyl derivatives often behave in this way; for example, allyl acetate on hydrogen atom abstraction yields the acetoxyallyl radical $CH_2{=}\dot{C}H{-}CHOCOMe$, which is too stable to reinitiate polymerization readily.[4,5] Such inactive radicals normally interact with other radicals in the system. Isopropenyl acetate behaves similarly.[6] The participation of these reactions lowers the molecular weight of the product and introduces departures from classical kinetics.

Systems containing stable free radicals, Fe^{3+} and Cu^{2+} are discussed later (Sections 1.3.1 and 1.3.2 respectively).

Quinones are generally thought to add to propagating chains through an oxygen, giving a rather unreactive oxygen-centred radical (**1**) which may terminate a second chain (equation 1; R_r, R_s represent radicals containing r, s, monomer units, respectively). Tracer studies have shown that with styrene several quinone residues may be incorporated in a single chain, suggesting that the adduct radical (**1**) in equation (1) is able to reinitiate polymerization of styrene.[7] Thus quinone can behave as a comonomer under appropriate conditions. However, with methyl methacrylate the reactions in equation (1) predominate, the polymeric product containing two initiator fragments and one quinone residue per molecule.[8]



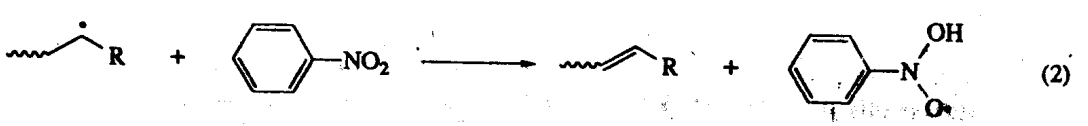
(1)

(1)

Hydroquinone and its derivatives (*e.g.* hydroquinone methyl ether) are often used to stabilize commercial monomers. They are less powerful retarders than quinone; in the presence of oxygen retardation is enhanced by quinone formation from hydroquinone. These phenolic types are effective scavengers of oxygen-centred radicals, *e.g.* those which may arise from peroxide impurities.

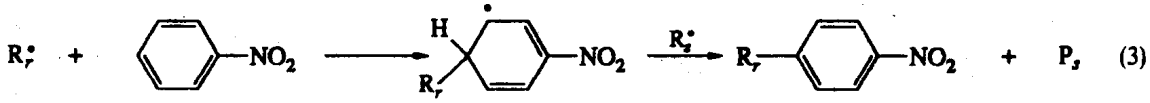
Bagdasar'ian and Sinitsina[9] emphasized that active (polymer) radicals enter into addition reactions with aromatic hydrocarbons (even benzene) in preference to abstracting hydrogen atoms from the rings. The resulting radicals are relatively inactive, so that the aromatic derivatives function as retarders. Values of k_z/k_p were reported for many such additions (k_z, k_p are the rate coefficients for addition and propagation reactions, respectively), and it was shown that a linear relation exists between $\log k_z$ and the logarithm of the methyl affinity of the hydrocarbon.

The same workers[9] suggested that nitrobenzene retards through transfer of a β-hydrogen from the propagating radical (equation 2).



(2)

Alternative routes proposed include those in equation (3), where P_s is a polymer molecule with s units,[10–12] and equation (4a).[13–15]



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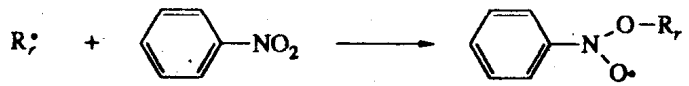
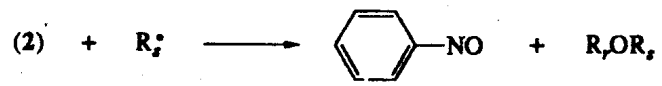


(4a)

(2)

Some reactions of the radical (2) which have been suggested are shown in equations (4b) to (4e).[14,16–18]



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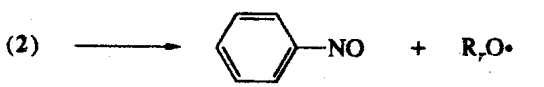

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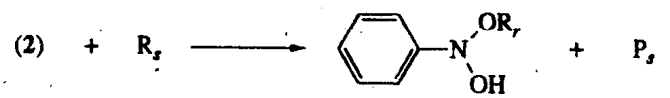

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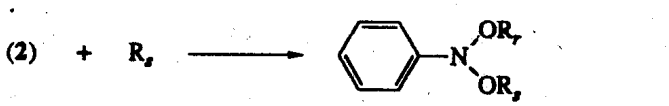


(4e)

Aromatic nitrocompounds are generally less effective than quinones. They illustrate the influence of the monomer on retarding activity. The materials effectively inhibit the polymerization of vinyl acetate, behave as retarders with styrene and have little effect on methyl methacrylate or methyl acrylate polymerizations.

1.3 THE KINETICS OF IDEAL INHIBITION AND RETARDATION

1.3.1 Ideal Inhibition

The participating reactions in pure inhibition are represented in Scheme 1, in which I represents the initiator and Z the inhibitor. $R_0^\bullet$ and $R_r^\bullet$ are initial and propagating radicals, respectively, and M represents monomer; f is the efficiency of initiation.

Reaction (c) with rate coefficient k_{zi} represents the inhibition process. Assuming stationary conditions for the radical concentrations, we find

$$[R_0] = \frac{2fk_d[I]}{k_i[M] + k_{zi}[Z]} \tag{5a}$$

so that the rate of initiation $\mathscr{I}$ is

$$\mathscr{I} = k_i[M][R_0] = \frac{2fk_dk_i[I][M]}{k_i[M] + k_{zi}[Z]} \tag{5b}$$

Evidently the rate of initiation, and hence the overall rate of polymerization, is decreased in the presence of the inhibitor; if $\mathscr{I}_0$ is the rate of initiation in the absence of inhibitor, we have from

$$\mathrm{I} \xrightarrow{2fk_d} 2\mathrm{R}_0^{\bullet} \qquad \text{(a)}$$

$$\mathrm{R}_0^{\bullet} + \mathrm{M} \xrightarrow{k_i} \mathrm{R}_1^{\bullet} \qquad \text{(b)}$$

$$\mathrm{R}_0^{\bullet} + \mathrm{Z} \xrightarrow{k_{zi}} \text{inactive products} \qquad \text{(c)}$$

$$\mathrm{R}_1^{\bullet} + \mathrm{M} \xrightarrow{k_p} \mathrm{R}_2^{\bullet} \qquad \text{(d)}$$

$$\mathrm{R}_r^{\bullet} + \mathrm{M} \xrightarrow{k_p} \mathrm{R}_{r+1}^{\bullet} \qquad \text{(e)}$$

$$\mathrm{R}_r^{\bullet} + \mathrm{R}_s^{\bullet} \xrightarrow{k_t} \text{polymer} \qquad \text{(f)}$$

Scheme 1

equation (5)

$$\mathscr{J} = \mathscr{J}_0 \frac{k_i[\mathrm{M}]}{k_i[\mathrm{M}] + k_{zi}[\mathrm{Z}]} \qquad (6)$$

When $k_{zi}[\mathrm{Z}] \gg k_i[\mathrm{M}]$, $\mathscr{J}$ and the rate of polymerization become effectively zero. During this inhibition period the inhibitor is being consumed by reaction with the radicals generated by decomposition of the initiator (reaction a; Scheme 1) and the consequent decrease in [Z] is accompanied by a corresponding increase in $\mathscr{J}$, according to equation (6). Therefore polymerization gradually becomes perceptible, and steadily increases in rate; eventually when all the inhibitor has been consumed the rate of polymerization assumes its normal value, corresponding to the uninhibited reaction. A typical 'inhibited polymerization' thus shows three stages: an inhibition period with effectively zero rate of polymerization; a transition period with gradually increasing rate; and finally uninhibited polymerization at the normal rate. If the inhibitor is a powerful one (*i.e.* if k_{zi} is large) a low concentration suffices to give effectively complete inhibition and the end of the inhibition period will be relatively sharp; otherwise a reduced initial rate will be observed which slowly increases with time. In this simple discussion it has been assumed that the concentrations of I and M do not change significantly. A good early example of the phenomena we have been describing is provided by the work of Bevington, Ghanem and Melville[19] on the polymerization of styrene with quinone as inhibitor (Figure 1).

The length of the inhibition period t_{in} is usually measured by back extrapolation of the final, almost linear, portion of the conversion–time curve to the time axis. This period represents the time required for all the inhibitor to react with initial radicals (reaction c; Scheme 1) and since these are produced at a uniform rate $\mathscr{J}_0$ given by

$$\mathscr{J}_0 = 2fk_d[\mathrm{I}] \qquad (7)$$

we have

$$\mathscr{J}_0 t_{in} = [\mathrm{Z}]_0; \quad \mathscr{J}_0 = [\mathrm{Z}]_0/t_{in} \qquad (8)$$

where $[\mathrm{Z}]_0$ is the initial value of [Z], if each radical reacts with one inhibitor molecule. More generally, when m radicals react with each Z molecule

$$\mathscr{J}_0 = m[\mathrm{Z}]_0/t_{in} \qquad (9)$$

According to equations (8) and (9) a plot of t_{in} *versus* $[\mathrm{Z}]_0$ (such as may be derived from the results in Figure 1, for example) should be linear with slope $1/\mathscr{J}_0$ or $m/\mathscr{J}_0$. The measurements therefore provide a method for the direct determination of the rate of initiation $\mathscr{J}_0$ in the absence of inhibitor. Further, if $\mathscr{J}_0$ is known, the efficiency of initiation may also be estimated from equation (7). If necessary, a correction for the decrease in [I] during the induction period may be applied.

Although, in principle, the use of inhibitors provides a direct and convenient method of measuring rates of initiation, it is subject in practice to some uncertainties. A very powerful inhibitor may

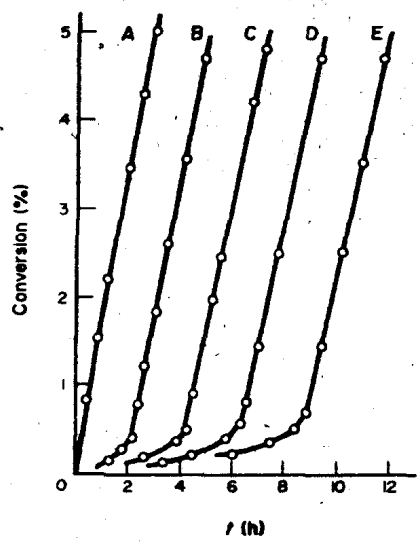
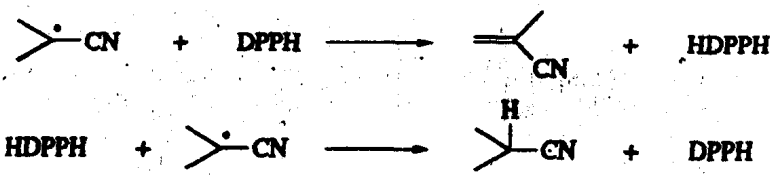


Figure 1 Conversion–time curves for polymerization of styrene at 60 °C initiated by azobisisobutyronitrile (0.5 g dm^{-3}) in the presence of quinone as inhibitor.[19] Concentrations of quinone (g dm^{-3}): A, zero; B, 0.050; C, 0.075; D, 0.123; E, 0.157 (reproduced by permission of the Royal Society of Chemistry from ref. 19)

interfere with (secondary) geminate or cage recombination;[20–23] this latter normally occurs between radicals formed in pairs from an initiator molecule and is responsible for the efficiency of initiation (f) being less than unity. Common vinyl monomers cannot compete significantly with this process, but if an inhibitor does so its use will lead to spuriously high values of f_0.

In the second place, the value of m is often debatable. This may be illustrated by reference to the familiar stable free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH), one of the most widely used inhibitors. The high extinction coefficient of DPPH at visible wavelengths of light greatly facilitates spectrophotometric estimation of low concentrations. According to Bengough,[24] in the polymerization of methyl methacrylate inhibited by DPPH the final disappearance of colour corresponds closely with the end of the induction period, in conformity with the mechanism discussed above. However, some other monomers behave in less simple fashion. Thus with styrene, Matheson *et al.*[25] found that the final rates of polymerization were lower than those measured in the absence of DPPH. With vinyl acetate little polymerization occurs for some time after the colour has disappeared. These results suggest that the products of reaction between DPPH and initiator radicals may not be inert, as required for an ideal inhibitor, but may themselves be inhibitors or retarders. Hammond, Sen and Boozer[26] expressed doubts about the value of DPPH as a reagent for counting radicals. They presented evidence indicating the occurrence of a 'double transfer' with radicals from azobisisobutyronitrile (equation 10). As a consequence of this chain process a single DPPH radical might react with several initiator radicals. A similar mechanism for reaction with polymer radicals was proposed by Burnett and Cowley.[27]



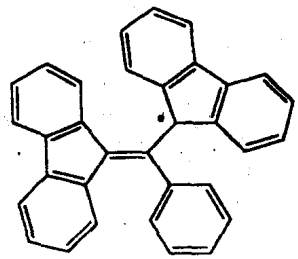
(10)

Bevington[28] has shown that the products of reaction between radicals from azobisisobutyronitrile and DPPH do not contain major proportions of isobutyronitrile or the corresponding hydrazine, as required by the reactions in equation (10). Consequently, Bevington disputes the conclusions of Hammond *et al.*, although he agrees with these authors that DPPH is probably not a good reagent for counting radicals in exact work.

The Koelsch radical (1,3-bis(diphenylene)-2-phenylallyl; 3) has been used apparently successfully to determine rates of initiation.[29,30]

Triphenylmethyl is also an inhibitor, but is able to initiate polymerization in some systems.

The foregoing suggests that systems showing pure inhibition without retardation will be relatively uncommon, since an inhibitor for which $k_{zi}[Z]_0 \gg k_i[M]$ is also likely to conform to $k_z[Z]_0 \gg k_p[M]$,



(3)

where k_z refers to reaction between Z and propagating chains. This will not invalidate determination of $\mathscr{I}_0$ by the technique outlined. For a pure inhibitor the sufficient condition for this measurement is that all initiating radicals should be trapped by the inhibitor during the inhibition period; for an inhibitor and retarder it is sufficient that bimolecular termination should be completely suppressed (*i.e.* all $R_0^{\cdot}$ and R· radicals trapped) during the inhibition period.

The kinetic equations for polymerization in the presence of a substance which is both an inhibitor and a retarder may be obtained by replacing $\mathscr{I}_0$ in the appropriate relations in Section 1.3.2 (equations 17, 18 and 20–22) by $\mathscr{I}$ from equation (6).

1.3.1.1 Note on the use of the stationary state assumption

It is appropriate to note here that stationary state equations should not be applied indiscriminately to systems in which radical concentrations are likely to change rapidly at some stage, *e.g.* near the end of an inhibition period. Thus in the system considered above the rates of change of $[R_0^{\cdot}]$ and $[R\cdot]\left(=\sum_1^{\infty} R_r^{\cdot}\right)$ are given by

$$\frac{d[R_0^{\cdot}]}{dt} = 2f k_d[I] - k_i[M][R_0^{\cdot}] - k_{zi}[Z][R_0^{\cdot}] \tag{11}$$

$$\frac{d[R\cdot]}{dt} = k_i[M][R_0^{\cdot}] - k_t[R\cdot]^2 \tag{12}$$

The stationary state assumption $d[R_0^{\cdot}]/dt = d[R\cdot]/dt = 0$ implies that

$$\frac{d[R\cdot]}{dt} \ll 2f k_d[I]$$

$$\ll (k_i[M] + k_{zi}[Z])[R_0^{\cdot}] \tag{13}$$

and

$$\frac{d[R\cdot]}{dt} \ll k_i[M][R_0^{\cdot}]$$

$$\ll k_t[R\cdot]^2 \tag{14}$$

In doubtful cases when the stationary state method has been used to derive numerical parameters, the validity of the above inequalities should be examined with the aid of their proposed values.

1.3.2 Ideal Retardation

The component reactions in a polymerization showing ideal retardation are set out in Scheme 2. Here Z represents the retarder which enters into reaction with propagating chains ($R_r^{\cdot}$) to form a dead polymer molecule containing r units, as shown in reaction (e). $\mathscr{I}_0$ is the rate of initiation, assumed unaffected by the presence of the retarder.

Some simple and interesting conclusions follow from this mechanism. First, we see immediately from Scheme 2 that

$$\frac{d[R\cdot]}{dt} = \mathscr{I}_0 - k_z[Z][R\cdot] - k_t[R\cdot]^2 \tag{15}$$

$$\mathrm{I} \xrightarrow{2f_d} 2\mathrm{R}_0^{\bullet} \qquad \text{(a)}$$

$$\mathrm{R}_0^{\bullet} + \mathrm{M} \xrightarrow{k_i} \mathrm{R}_1^{\bullet} \qquad \mathscr{I}_0 \qquad \text{(b)}$$

$$\mathrm{R}_1^{\bullet} + \mathrm{M} \xrightarrow{k_p} \mathrm{R}_2^{\bullet} \qquad \text{(c)}$$

$$\mathrm{R}_r^{\bullet} + \mathrm{M} \xrightarrow{k_p} \mathrm{R}_{r+1}^{\bullet} \qquad \text{(d)}$$

$$\mathrm{R}_r^{\bullet} + \mathrm{Z} \xrightarrow{k_z} \mathrm{P}_r + \text{inert products} \qquad \text{(e)}$$

$$\mathrm{R}_r^{\bullet} + \mathrm{R}_s^{\bullet} \xrightarrow{k_t} \text{polymer} \qquad \text{(f)}$$

Scheme 2

and

$$-\frac{\mathrm{d}[\mathrm{Z}]}{\mathrm{d}t} = k_z[\mathrm{Z}][\mathrm{R}\cdot] \tag{16}$$

where $[\mathrm{R}\cdot] = \sum_r [\mathrm{R}_r^{\bullet}]$ is the total concentration of propagating chains.

A retarder present in sufficiently high concentration terminates a large proportion of the growing chains and the rate of bimolecular termination $k_t[\mathrm{R}\cdot]^2$ becomes infinitesimally small. In such conditions $\mathrm{d}[\mathrm{R}\cdot]/\mathrm{d}t$ is effectively zero and we may write equation (15) in the following form

$$\frac{\mathrm{d}[\mathrm{R}\cdot]}{\mathrm{d}t} = 0 = \mathscr{I}_0 - k_z[\mathrm{Z}][\mathrm{R}\cdot] \tag{17}$$

so that

$$[\mathrm{R}\cdot] = \mathscr{I}_0/k_z[\mathrm{Z}] \tag{18}$$

In general, if the mean degree of polymerization $\bar{P}_n$ (or the mean kinetic chain length $\bar{\nu}$) is $\gg 1$, the rate of polymerization is conventionally taken as

$$\omega = -\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = k_p[\mathrm{M}][\mathrm{R}\cdot] \tag{19}$$

Retarded polymerization may, however, give rise to short chains and in these circumstances consumption of monomer by reaction (b) in Scheme 2 is not necessarily negligible. This necessitates a correction to equation (19), which becomes

$$\begin{aligned}\omega &= k_p[\mathrm{M}][\mathrm{R}\cdot] + k_i[\mathrm{M}][\mathrm{R}_0^{\bullet}] \\ &= k_p[\mathrm{M}][\mathrm{R}\cdot] + \mathscr{I}_0\end{aligned} \tag{20}$$

In strongly retarded polymerizations expressions (19) and (20), together with equation (18), give for the retarded rate ω_r

$$\omega_r = \frac{k_p[\mathrm{M}]}{k_z[\mathrm{Z}]}\mathscr{I}_0 \tag{21}$$

from equation (19), and

$$\omega_r = \left(\frac{k_p[\mathrm{M}]}{k_z[\mathrm{Z}]} + 1\right)\mathscr{I}_0 \tag{22}$$

from equation (20).

Thus (for pure retardation) the rate is first order in the rate of initiation and inversely proportional (or linear in) $1/[\mathrm{Z}]$. These are, of course, instantaneous relations. As the retarder is consumed

(equation 16) the radical concentration and the rate of polymerization increase until finally both reach stationary values corresponding to the unretarded reaction (equations 23 and 24).

$$[R\cdot] = \left(\frac{\mathscr{I}_0}{k_t}\right)^{1/2} \tag{23}$$

$$\omega = k_p[M]\left(\frac{\mathscr{I}_0}{k_t}\right)^{1/2} \tag{24}$$

As the polymerization proceeds the order in $\mathscr{I}_0$ therefore decreases from 1.0 to 0.5.

Secondly, from equations (16) and (18) we see that under conditions of strong retardation

$$-\frac{d[Z]}{dt} = \mathscr{I}_0 \tag{25}$$

that is, the rate of consumption of retarder is equal to the rate of initiation. This conclusion from the simple Scheme 2 is indeed obvious, since under the conditions specified the great majority of the chains started by the initiator terminate by reaction with the retarder. Note that the occurrence of chain transfer in the system does not invalidate equation (25). If the concentration of Z can be conveniently monitored this result provides a method for determining rates of initiation. Measurements of the retarded rates of polymerization and application of equation (21) then provide values of k_z/k_p.

For powerful retarders, only very low concentrations can be present if rates of polymerization are to be measurable. In such cases [Z] cannot be regarded as constant during a single experiment, and use of equations (21) and (25) as described above is not appropriate.

Thirdly, it follows from equations (16) and (21) that

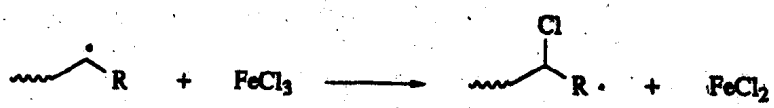
$$-\frac{d[Z]}{dt}\Big/\left(-\frac{d[M]}{dt}\right) = \frac{k_z[Z][R\cdot]}{k_p[M][R\cdot]} = \frac{k_z[Z]}{k_p[M]}$$

or

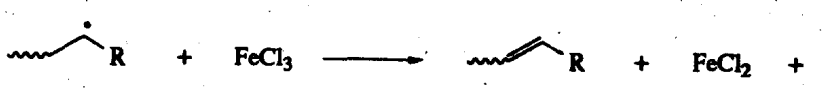
$$\frac{d\ln[Z]}{d\ln[M]} = \frac{k_z}{k_p} \tag{26}$$

Hence, if a polymerization conforms to Scheme 2, measurements of the rates of consumption of retarder and monomer enable k_z/k_p to be evaluated. This method does not involve assumption of a stationary state.

Bamford, Jenkins and Johnston[31,32] studied the free-radical polymerizations of acrylonitrile (AN), methacrylonitrile (MAN), methyl acrylate (MA) and styrene in *N*,*N*-dimethylformamide (DMF) in the presence of iron(III) chloride and concluded that the behaviour of these systems was that expected for ideal retardation. Retardation results from the redox reaction between propagating radicals and the salt, so that the latter is reduced to the iron(II) state, which does not react further. (Redox processes of this type for some radicals in aqueous systems were studied by Collinson, Dainton and McNaughton.[33]) There are clearly two possibilities, shown in equations (27a) and (27b). Data obtained by Entwistle[34] for the monomers mentioned indicated the presence of chlorine in the polymer and so support the reaction in equation (27a); however, the earlier workers[31] preferred the second alternative.



(27a)



(27b)

Some results for the acrylonitrile–DMF–$FeCl_3$–azobisisobutyronitrile systems are presented in Figures 2(a) and 2(b).[31] The linear plot in Figure 2(a) is consistent with equation (21), $Z = FeCl_3$ with [M] and $\mathscr{I}_0$ effectively constant, while Figure 2(b) shows that with [M] and [Z] constant the rate of polymerization is directly proportional to $\mathscr{I}_0$, as required by equation (21). Apparently $FeCl_3$ and $FeCl_3 \cdot 6H_2O$ behave similarly. Equation (21), when applied to the slope of the line in Figure 2(a) leads to $k_p/k_z = 0.30$. This value was combined with a published value of k_p to give[31]

$$k_z = 6.5 \times 10^3 \text{ mol}^{-1}\text{ dm}^3\text{ s}^{-1} \tag{28}$$