ASPECTS OF SOME INITIATION AND PROPAGATION PROCESSES

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In this lecture I shall consider three topics in free-radical polymerization — selective initiation, the nature of the propagation reaction, and new initiators of polymerization. All three are being studied at present in our laboratories, and one of them has been the subject of interesting investigations by Japanese workers.

SELECTIVE FREE-RADICAL INITIATION

Selective initiation of free-radical polymerization is, as far as I am aware, a novel phenomenon. Conventional initiators such as benzoyl peroxide and azo-bis-isobutyronitrile, which produce active radicals, are not significantly discriminating in their behaviour towards different monomers, provided these can be polymerized by a radical mechanism; indeed the rate of initiation by azo-bis-isobutyronitrile at a given concentration is essentially the same for a number of common monomers[1,2]. Recent work[3] has revealed the existence of a type of initiator which is strongly selective, the rate of initiation apparently depending on the electron-accepting properties of the monomer.

Our interest in selective initiation of free-radical polymerization arose during studies of initiation by chelate derivatives of metals, which will now be described briefly. Three groups of workers have shown that certain metal acetylacetonates can act as sources of initiating radicals[4-6]. Both Kastning *et al.*[5] and ourselves[6] have pointed out the relatively high activity possessed by manganic acetylacetonate $Mn^{III}(acac)_3$ compared to the simple chelates of other metals. At 80°C the rate of polymerization ω of bulk methyl methacrylate is given as a function of chelate concentration by the equation

$$\omega = 1\cdot05 \times 10^{-2} \, [Mn(acac)_3]^{\frac{1}{2}} \, \text{mole l.}^{-1}\text{sec}^{-1}. \tag{1}$$

The square root relation suggests a free-radical mechanism. If chain transfer and retardation are absent and termination occurs predominantly by disproportionation we may apply the familiar equation

$$-\bar{P}_n \frac{d[M]}{dt} = \frac{k_p^2 \, [M]^2}{k_t} \tag{2}$$

in which $\bar{P}_n$ is the number-average degree of polymerization, M represents monomer, and k_p, k_t are the velocity coefficients of propagation and termination, respectively. The relation (2) holds in the present case with $k_p k_t^{-\frac{1}{2}} = 0\cdot17 \, \text{mole}^{-\frac{1}{2}} \, \text{l.}^{\frac{1}{2}}\text{sec}^{-\frac{1}{2}}$, a value close to that normally obtained in the free-radical polymerization of methyl methacrylate at 80°C. These observations

therefore lend support to the proposed free-radical character of the reaction. The rate of initiation I corresponding to Eq. (1) is given by Eq. (3):

$$I = 5 \cdot 1 \times 10^{-5} \, [\text{Mn(acac)}_3] \text{ mole l.}^{-1} \text{sec}^{-1} \tag{3}$$

and the activation energy and frequency factor for initiation by Eq. (4)

$$E_i = 26 \cdot 2 \text{ kcal mole}^{-1}$$
$$A_i = 8 \cdot 2 \times 10^{11} \text{ sec}^{-1} \tag{4}$$

Rather similar results are obtained with styrene, the rates of polymerization and initiation in bulk monomer at 80°C being shown in Eq. (5).

$$\omega = 2 \cdot 14 \times 10^{-3} \, [\text{Mn(acac)}_3]^{\frac{1}{2}} \text{mole l.}^{-1} \text{ sec}^{-1}$$
$$I = 6 \cdot 25 \times 10^{-5} \, [\text{Mn(acac)}_3] \text{ mole l.}^{-1} \text{ sec}^{-1} \tag{5}$$

Comparison of equations (3) and (5) indicates that manganic acetylacetonate initiates the polymerizations of methyl methacrylate and styrene at approximately the same rate.

We have suggested[6], in agreement with Arnett and Mendelsohn[4] that the intial step in these reactions involves the scission of the ligand as a free-radical and the reduction $\text{Mn}^{\text{III}} \rightarrow \text{Mn}^{\text{II}}$, as in Eq. (6).

$$\tag{6}$$
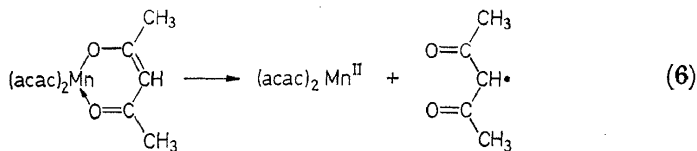
The change in the oxidation state of the manganese atom has been verified by measurements of magnetic susceptibility[7]. The process is probably somewhat more complicated than that represented by Eq. (6); monomer may be involved in the initiation process since the order in monomer of the overall polymerization reaction may exceed unity. Thus, with methyl methacrylate in benzene solution and styrene in toluene solution the order is close to 1·5. This aspect is currently being investigated and will not be discussed further here.

When the work was extended to the fluorinated derivative $\text{Mn}(\text{CF}_3\text{CO:CH}\cdot\text{CO}\cdot\text{CH}_3)_3$ (Mn(facac)$_3$) some interesting differences in behaviour were found. At 80°C this chelate is a much more active initiator than Mn(acac)$_3$ towards bulk methyl methacrylate, as will be apparent from a comparison of Eqs. (1), (3) and (7).

$$\omega = 2 \cdot 63 \times 10^{-2} \, [\text{Mn(facac)}_3]^{\frac{1}{2}} \text{ mole l.}^{-1} \text{ sec}^{-1}$$
$$I = 3 \cdot 8 \times 10^{-4} \, [\text{Mn(facac)}_3] \text{ mole l.}^{-1} \text{ sec}^{-1} \tag{7}$$

According to Eq. (7), $Mn(facac)_3$ initiates this polymerization at $80°C$ approximately twice as rapidly as azo-bis-isobutyronitrile at the same molar concentration. The free-radical nature of the reaction is proved by the following observations: (i) the square root relation (7) between the overall rate of polymerization and the chelate concentration, which holds over a very wide range of concentration; (ii) the value of $k_p k_t^{-\frac{1}{2}}$, deduced as already described, is close to the normal figure (although about 10 per cent lower, perhaps indicating the occurrence of some transfer or retardation); (iii) the tacticity of the polymer deduced from n.m.r. spectra is identical with that of a polymer prepared at the same temperature with a conventional free-radical intiator.

Both the activation energy and frequency-factor for the initiation reaction given in Eq. (8) are smaller than the corresponding quantities for $Mn(acac)_3$ (Eq. 4); the low frequency-factor is noteworthy and will be referred to later.

$$E_i = 15·8 \text{ kcal mole}^{-1}$$
$$A_i = 2·0 \times 10^6 \text{ sec}^{-1}$$

(8)

In the presence of $Mn(facac)_3$ styrene polymerizes only slowly, the rate being lower than that of the thermal uncatalysed reaction at $80°C$ ($Table\ 1$).

Table 1. Polymerization of styrene at $80°C$ in the presence of $Mn(facac)_3$.

[Mn(facac)$_3$] (mole l.$^{-1}$)	10^5 Rate of polymerization (mole l.$^{-1}$sec^{-1})
0	1·16 (thermal)
5×10^{-5}	0·43
$2·5 \times 10^{-4}$	0·16

These results suggest that the fluorinated chelate is a strong retarder of the polymerization of styrene, quite regardless of its possible function as an initiator. It is easy to confirm this by experiments with a conventional initiator. $Figure\ 1$ refers to initial rates of polymerization for a series of values of $[Mn(facac)_3]$ with a constant concentration of benzoyl peroxide; it is clear that the initial rate is strongly depressed by $Mn(facac)_3$.

Thus we have a situation in which both initiation and retardation by the chelate must be considered. The required kinetic expressions are readily deduced on the assumption of a stationary radical concentration, and lead to the expression (9) for the reduced rate of polymerization ω/ω_0 (i.e. the rate expressed as a fraction of the value obtained in the absence of chelate).

$$\frac{\omega}{\omega_0} = \frac{1}{\sigma} \left\{ \left(1 + \sigma^2 + \frac{4ak_t}{b^2[\text{C}]} \right)^{\frac{1}{2}} - 1 \right\}$$

(9)

Here a, b are the rate constants for initiation (first order) and retardation (second order) by the chelate C, respectively, and

$$\sigma = \frac{2(Ik_t)^{\frac{1}{2}}}{b[\text{C}]}$$

(10)

where I is the rate of initiation by the conventional initiator (benzoyl per-oxide). In the present experiments $I = 1\cdot9 \times 10^{-7}$ mole l.$^{-1}$ sec^{-1}; the rate of thermal initiation is less than 1 per cent of this value, and is negligible for present purposes. There are two unknown quantities in Eqs. (9) and (10), viz. a and b. The curve in *Figure 1* is calculated from Eqs. (9) and (10) with the use of the values

$$a = 5\cdot3 \times 10^{-5} \text{ sec}^{-1}$$
$$k_t^{\frac{1}{2}}/b = 0\cdot129 \text{ mole}^{\frac{1}{2}} \text{ l.}^{-\frac{1}{2}} \text{ sec}^{\frac{1}{2}}$$

(11)

and is seen to be a good fit to the experimental results. Assuming[8] $k_t = 9 \times 10^7$ mole^{-1}l. sec^{-1}, we find from Eq. (11) that $b = 7 \times 10^4$ mole^{-1}l. sec^{-1}. The value of b is high (corresponding to strong retardation) but this is not surprising, since it is known that polystyryl radicals are very susceptible to oxidation by derivatives of transition metals in their higher oxidation states, particularly in non-polar solution[1]. Thus, polystyryl radicals react rapidly with ferric chloride in N,N-dimethylformamide solution, the velocity coefficient at 60°C being[1] $5\cdot4 \times 10^4$ mole^{-1}l.sec^{-1}. The retardation reaction in the present system is likely to be similar in character, involving the reduction of Mn^{III} to Mn^{II}, with ligand transfer, so that as a result the polystyrene molecules formed probably carry terminal $CF_3COCHCOCH_3$ groups. Undoubtedly this type of reaction is facilitated by the additional positive charge on the metal atom arising from electron-attraction by the CF_3 group. Reaction between oxidizing transition metal derivatives and polymethyl methacrylate radicals is much slower[9], and retardation in the $Mn(facac)_3$–methyl methacrylate system is correspondingly less pronounced. (Styryl radicals react with $FeCl_3$ approximately 30 times as fast as methyl methacrylate radicals[9].)

Of much greater interest, however, is the value of a, At high values of $[C]$, Eq. (9) approximates to the relation:

$$\frac{\omega}{\omega_0} = \frac{a}{b}\left(\frac{k_t^{\frac{1}{2}}}{I}\right) + \frac{(Ik_t^{\frac{1}{2}})}{b[C]}\left(1 - \frac{a^2 k_t}{b^2 I}\right)$$

(12)

according to which a straight line results when ω/ω_0 is plotted against $[C]^{-1}$. This is seen to be the case in *Figure 1*, for values of $[C] > 3 \times 10^{-4}$ mole l.$^{-1}$, approximately. The intercept on the ω/ω_0 axis gives a measure of a, and it is immediately clear that the intercept is very close to zero, and indeed could be equal to zero, within experimental error. If a had the value $3\cdot8 \times 10^{-4}$ sec^{-1} as with methyl methacrylate (Eq. 7) the intercept would be $0\cdot11$; the observed value is certainly less than 10 per cent of this. The magnitude of a given in Eq. (11) is a maximum, and the curve in *Figure 1* could be fitted with $a = 0$. These considerations show that initiation of the polymerization of styrene by $Mn(facac)_3$, if it occurs at all, is very slow, com-pared to the initiation of methyl methacrylate polymerization.

We are therefore led to the conclusion that free-radical initiation by $Mn(facac)_3$ is *selective*, the rate depending on the character of the monomer, even with readily polymerizable monomers. On the other hand, we have already seen that there are good reasons for believing that $Mn(acac)_3$ does not initiate selectively.
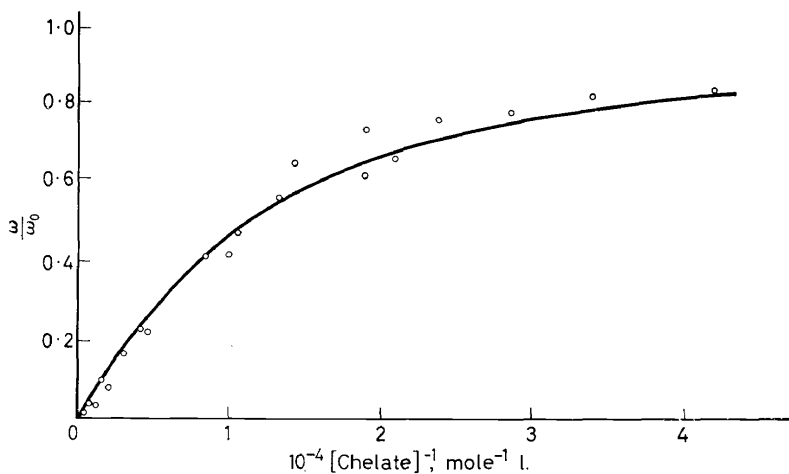
Figure 1. Retardation of styrene polymerization at $80\,^{\circ}C$ by $Mn(facac)_3$.
[Benzoyl peroxide] $= 2\cdot0 \times 10^{-3}$mole $l.^{-1}$. The curve is calculated from Eq. (9), with the parameters given in Eq. (11).

It seems likely that the initiation of free-radical polymerization by $Mn(facac)_3$ occurs most readily with monomers of relatively high electron-accepting capacity which can polymerize anionically. We believe that, as a result of electron-withdrawal by CF_3, the primary step with $Mn(facac)_3$ is the heterolytic fission of an Mn—O bond (Eq. 13a) giving an anion to which monomers of this type may add (Eq. 13b). The resulting monomer anion is then oxidized by the Mn^{III} atom in the molecule (Eq. 13c), to form a free-radical, which then initiates polymerization.

$$(13)$$
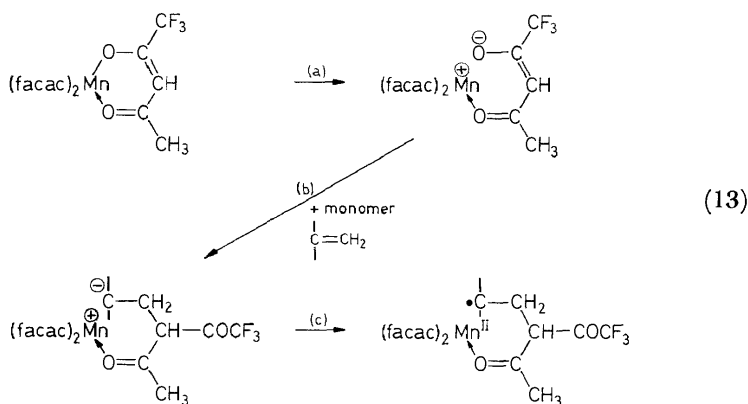
The steps a and b shown above (Eq. 13) as separate, may, in fact, be combined in a single process, with a polar transition state in which the monomer is negatively charged. This mechanism, involving a separation of charge

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in the transition state, is clearly consistent with the observed low frequency-factor for the initiation of polymerization of methyl methacrylate by $Mn(facac)_3$ (Eq. 8).

To obtain further evidence of the validity of these ideas, we have compared the behaviour of $Mn(acac)_3$ and $Mn(facac)_3$ towards acrylonitrile and vinyl acetate, with results shown in *Table 2*. The table also includes observations with styrene and methyl methacrylate for comparison. $Mn(facac)_3$

Table 2. Initiation by $Mn(acac)_3$ and $Mn(facac)_3$.

Temperature (°C)	Monomer	Chelate; 10^4 concentration (mole l.$^{-1}$)	10^6 Rate of polymerization (mole l.$^{-1}$ sec^{-1})
80	Styrene	$\begin{cases} Mn(acac)_3; 2\cdot5 \\ Mn(facac)_3; 2\cdot5 \end{cases}$	34 1·6
60	Vinyl acetate	$\begin{cases} Mn(acac)_3 \ 4\cdot0 \\ Mn(facac)_3; 4\cdot0 \end{cases}$	190 38
80	Methyl methacrylate	$\begin{cases} Mn(acac)_3; 4\cdot0 \\ Mn(facac)_3; 4\cdot0 \end{cases}$	210 530
60	Acrylonitrile	$\begin{cases} Mn(acac)_3; 5\cdot8 \\ Mn(facac)_3; 5\cdot8 \end{cases}$	15 1090

is seen to be a relatively ineffective initiator for the polymerization of vinyl acetate (which is a weak electron acceptor), but it is extremely effective with acrylonitrile, which readily accepts electrons. Styrene and vinyl acetate behave in a similar manner, as do methyl methacrylate and acrylonitrile. These findings are entirely consistent with the electronic properties of the monomers[9a]. It is to be noted, however, that the importance of retardation in the polymerization of vinyl acetate and acrylonitrile has not yet been assessed. The remarkably low rate of polymerization of acrylonitrile initiated by $Mn(acac)_3$ is of interest. It cannot be attributed solely to retardation by Mn^{III}, since this would be greater with $Mn(facac)_3$, but must imply that $Mn(acac)_3$ is an extremely slow initiator compared to $Mn(facac)_3$. The central carbon atom in the radical $CH_3CO\dot{C}HCOCH_3$ derived from $Mn(acac)_3$ carries a partial positive charge, so that reaction with acrylonitrile would be relatively slow[9a], while initiation by $Mn(facac)_3$, being anionic in character, would take place relatively rapidly. The different behaviour of the two chelates towards acrylonitrile therefore implies, in our opinion, a difference in the mechanism of initiation, in particular the existence of a more polar transition state with $Mn(facac)_3$ in which the monomer acquires a negative charge.

A few experiments on the copolymerization of methyl methacrylate and styrene initiated by $Mn(facac)_3$ have been carried out. True copolymers are formed, as would be expected from the free-radical character of the reaction, but molecular weights are low, on account of the retardation reaction between styryl radicals and $Mn(facac)_3$. The kinetic behaviour of these systems may readily be calculated. Thus, for the reduced rate of copolymerization we may deduce Eq. (14)

$$\frac{\omega}{\omega_0} = \frac{1}{\Sigma} \left[\left\{ 1 + \Sigma^2 \left(1 + \frac{a[C]}{I} \right) \right\}^{\frac{1}{2}} - 1 \right] \qquad (14)$$

in which

$$\Sigma^2 = 4Ik_{pAA}/(b^2 r_A^2[A]^2[C]^2) \times$$

$$\{r_A^2 \delta_A^2[A]^2 + 2\phi r_A r_B \delta_A \delta_B[A][B] + r_B^2 \delta_B^2[B]^2\}. \tag{15}$$

Equation (14), identical in form with Eq. (9), applies to the copolymerization of monomers A, B, in which the radical derived from A reacts with the chelate C (velocity-coefficient b), thus introducing retardation. The quantity $a[C]$ in Eq. (14) represents the total rate of initiation by the chelate, and, as before, I is the rate of initiation by an additional initiator, e.g. benzoyl peroxide. The remaining symbols in Eq. (15) have their conventional significance. Satisfactory agreement with Eqs. (14) and (15) has been obtained in the experiments so far carried out.

The phenomenon of selective free-radical initiation depends, according to the views expressed above, on the existence in the initiating molecule of two different types of functionality, and it is possible that other systems might be devised which show this property.

We may note that our observations are, in a sense, complementary to those of Professor Okamura, described in his General Lecture at the Prague Symposium (1965)[9(b)]. Okamura was concerned with trioxan radicals T·, which by loss of an electron (to maleic anhydride) form T+ and initiate cationic trioxane polymerization; in our case an anion loses an electron and subsequently initiates free-radical polymerization.

THE PROPAGATION REACTION

A number of instances are known in which the rate of free-radical polymerization is different from that expected in the presence of substances which are not normally initiators or retarders. We shall now turn our attention to phenomena of this type, particularly with the object of appraising the evidence for a change in the nature of the propagation reaction brought about by the additive.

Metal salts can produce marked increases in the rate of polymerization. The earliest example in the literature appears to be effect of some lithium salts, particularly the chloride, on the free-radical polymerization of acrylonitrile in N,N-dimethylformamide solution[10]. A concentration of LiCl of 0.3 mole l.$^{-1}$, approximately, was found to increase the rate by nearly a factor of two at $60°C$. (Initiation was by azo-bis-isobutyronitrile.) Measurements of absolute rate coefficients by the rotating sector technique revealed that the whole effect arises from an increase in the propagation coefficient k_p, the termination coefficients k_t remaining essentially unaffected. The absolute coefficient for transfer to triethylamine and carbon tetrabromide also increased, but to a rather smaller extent, on addition of lithium chloride. These results were interpreted[10] in terms of complex formation between salt and propagating radicals giving species (I) and (II).
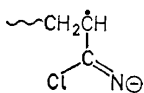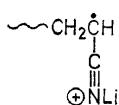
(I)   (II)

Of these, complex (I), carrying a negative charge, might react more rapidly than the uncomplexed radical with the positive double bond in acrylonitrile. It was assumed that only a small fraction of the radicals forms complexes, so that although the species (II) might propagate relatively slowly, the resulting decrease in rate of polymerization would not be observable experimentally. According to this view, only increases in rate coefficients of any reaction, whether propagation, transfer or termination, which arise from complex formation involving a small fraction of the radicals, should be experimentally observable. Complex (I) could also explain the increase in the rate coefficient of chain transfer to CBr_4, since the latter behaves as an electron-acceptor in these reactions[9(a)], while the increased rate of transfer to NEt_3 was ascribed to the participation of (II). The latter reaction would be facilitated[9(a)] by the positive charge on (II). It was also found that changes in reactivity ratios in the expected sense were brought about by the addition of lithium chloride in the copolymerization of acrylonitrile and vinyl acetate. (The polymerization of vinyl acetate is unaffected by salts.)

The experimental results on this system can therefore be explained satisfactorily in terms of radical complexing. However, it may be enquired whether this explanation is necessary, and, in particular, whether other kinds of complex formation could be invoked. There seems little evidence for the formation of lithium chloride–acrylonitrile complexes, and some against it[10]. The existence of salt complexes with CBr_4 and NEt_3 would also have to be assumed to account for the observations on chain-transfer.

Imoto, Otsu and their colleagues have studied the effect of zinc chloride on the polymerization of several vinyl monomers[11-13]. The photopolymerizations of methyl methacrylate, methyl, ethyl and butyl acrylates and acrylonitrile were shown to be accelerated by the addition of zinc chloride (2–6 per cent w/v) while the photopolymerization of vinyl chloride was unaffected. The thermal polymerizations of methyl methacrylate and acrylonitrile initiated by azo-bis-isobutyronitrile were also accelerated by zinc chloride, and it was established that the salt is without effect on the rate of thermal decomposition of the initiator, so that it is unlikely to increase the rate of initiation.

Imoto, Otsu and Harada[12] showed that $k_p k_t^{-\frac{1}{2}}$ is increased by the presence of zinc chloride and suggested that this is brought about by augmentation of k_p; in an earlier paper Imoto, Otsu and Shimizu[11] provided some evidence that decrease in k_t (arising from increased viscosity) is not the main reason for the increased rate of polymerization. In the copolymerization of methyl methacrylate and vinylidene chloride, the reactivity ratios changed on addition of $ZnCl_2$ in a manner consistent with an increase in the reactivity of MMA towards both the methyl methacrylate and vinylidene chloride radicals[12].

The Japanese authors[12,13] established that both methyl methacrylate and acrylonitrile form 1:1 complexes with zinc chloride which are polymerized rapidly by free-radical initiators; polymerization of $AN \cdot ZnCl_2$ occurs even in the solid state at $-30°C$ on illumination. These findings provide an explanation for the suggested increase in the effective value of k_p, and there is no need to invoke complexing of radicals.

Although the above evidence for variations in k_p is strong, the most direct indication of changes in the velocity coefficients is provided by

measuring their absolute values. These measurements were made for the MMA–ZnCl₂ system by Bamford, Brumby and Wayne[14] (using the rotating sector technique) with results shown in *Table 3*.

Table 3. Absolute rate coefficients in the polymerization of methyl methacrylate at 25°C.

[ZnCl₂] (mole l.$^{-1}$)	$10^{-2}k_p$ (mole^{-1}l. sec^{-1})	$10^{-7}k_t$ (mole^{-1}l. sec^{-1})
0	2·5 ± 0·3	2·3 ± 0·6
1·42	6·1 ± 1·0	2·2 ± 0·6

It is clear from these observations that, as suggested by Imoto, Otsu *et al.*, zinc chloride brings about an increase in the effective value of k_p, while leaving k_t unchanged. The Japanese workers concluded that considerable chain transfer occurred in these systems, but this was not confirmed by Bamford *et al.*

Burnett and his colleagues[15,16] have made interesting observations on the rates of polymerization in several aromatic solvents, notably halogeno-benzenes. The work was carried out at 60°C, mostly with methyl metha-crylate as monomer and azo-bis-isobutyronitrile as initiator. The rates of polymerization are considerably higher in these solvents than would be expected if the solvents act as inert diluents. However, the increase in rate is not accompanied by an increased incorporation of initiator fragments in the polymer (except in the case of naphthalene), and there is no incorporation of solvent residues. Burnett *et al.* report similar results for the mono-halogeno-benzenes with other initiators, although in the case of the naphthalene–methyl methacrylate system enhanced rates are not found with benzoyl peroxide. Burnett *et al.* propose that the solvent increases the rate of initiation. The initiator radicals are supposed to react with solvent to give radicals which can initiate in the manner exemplified by Eq. (16) below.

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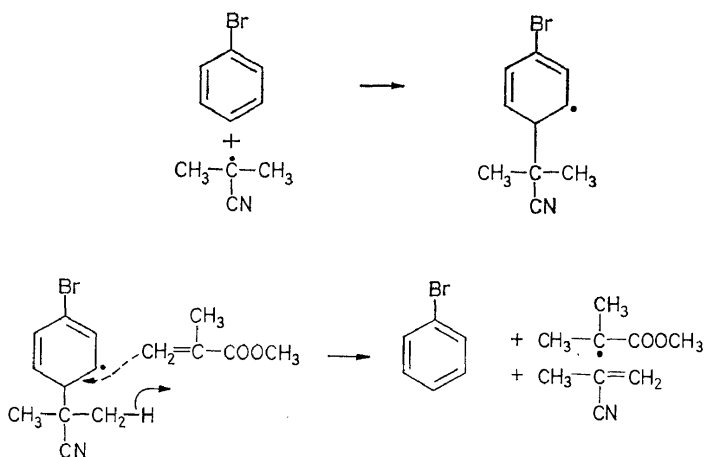
Such reactions can only increase the rate of initiation if they are able to compete with radical-destroying processes, e.g. combination of initiating radicals as suggested by Burnett et al.[16], hence it must be assumed that the initiating radicals enter into the reaction (16) at a rate comparable to, or higher than, that of reaction with monomer. To the present author this seems most unlikely to be so.

Bamford and Brumby[17] have measured the absolute rate coefficients of propagation and termination in systems of this type at 25°C, using azo-bis-isobutyronitrile (AZBN) as photosensitizer. During the course of the work it was found that enhanced rates are observed in chloro- and bromo-benzene solutions, as reported by Burnett et al.[15,16] for thermal initiation, and also in anisole and benzonitrile. The results are given in *Table 4*.

Table 4. Effect of solvents on the rate coefficients for the polymerization of methyl metha-crylate at 25°C. [MMA] = 4·69 mole l.$^{-1}$ [AZBN] = 6×10^{-3}mole l.$^{-1}$

Solvent	$10^4 R_p$ (mole l.$^{-1}$ sec^{-1})	$k_p/k_t^{-\frac{1}{2}}$ (mole$^{-\frac{1}{2}}$ l.$^{\frac{1}{2}}$ sec$^{-\frac{1}{2}}$)	$10^7 I$ (mole l.$^{-1}$ sec^{-1})	$10^6(k_p/k_t)$	$10^{-2}k_p$ mole^{-1} l. sec^{-1}	$10^{-7}k_t$ (mole^{-1} l. sec^{-1})
Benzene	0·540	0·0567	0·412	12·3	2·6	2·1
Fluorobenzene	0·566	0·0590	0·419	12·9	2·7	2·1
Chlorobenzene	0·615	0·0638	0·422	14·45	2·8	1·95
Anisole	0·647	0·0679	0·413	16·2	2·85	1·75
Bromobenzene	0·727	0·0749	0·428	18·2	3·1	1·7
Benzonitrile	0·785	0·0803	0·434	19·5	3·3	1·7

The rates of initiation, I, calculated from the values of the rate of polymeriza-tion R_p and $k_p k_t^{-\frac{1}{2}}$, do not appear to depend on the nature of the solvent, in contradiction to the proposals of Burnett et al.[15,16]. On the other hand, the increases in rate arise from variations in $k_p k_t^{-\frac{1}{2}}$. Both k_p, k_t are sensitive to the nature of the solvent. The changes in the termination coefficient appear to be close to those expected from the relation $k_t \propto \eta^{-1}$ (η being the viscosity of the reaction mixture) which arises from diffusion control of the termination process[18], and thus do not require any special explanation. The reasons for the changes in k_p, however, are by no means obvious. The formation of a complex between monomer and solvent seems unlikely; this would lead to negative deviations from Raoult's law, whereas in fact the mixture of bromobenzene and monomer behaves ideally.

It has been pointed out by Henrici-Olivé and Olivé[19-22] that the electron-affinities of typical polymer radicals are of the same order as those of such molecules as tetracyanoethylene and chloranil, which are known to form charge-transfer complexes with typical solvents used in vinyl polymer-ization. These authors assume that a polymer radical R_n can form a complex with either a monomer or a solvent molecule S, but that only the complex with monomer leads to propagation (see Eq. 17). (It will be recalled that complex formation between polystyryl radicals and bromobenzene was originally postulated by Mayo[23] to account for his observations on chain transfer by bromobenzene.)

$$(K_m) \ R_n \cdot M \overset{M}{\rightleftharpoons} R_n \cdot \overset{S}{\rightleftharpoons} R_n \cdot S \ (K_s) \qquad (17)$$
$$\downarrow$$
$$R_{n \cdot +1}$$
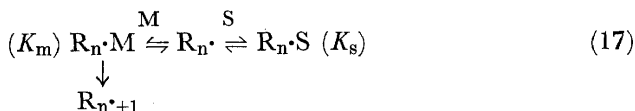
The rate of polymerization is therefore given by

$$-\frac{d[M]}{dt} = k[R \cdot M], \qquad (18)$$

$[R \cdot M]$ being the total concentration of radical–monomer complexes and k a constant. If K_m, K_s are the equilibrium constants of the reaction of the radicals with monomer and solvent, respectively, (Eq. 17) and effectively all radicals are complexed, it may easily be shown that

$$-\frac{d[M]}{dt} = k_p' M[R_t \cdot] \left\{ \frac{[M]_0}{(K_s/K_m)[S] + [M]} \right\} \qquad (19)$$

where $[R_t \cdot]$ is the total radical concentration, $[M]_0$ the bulk monomer concentration and k_p' a constant which is related to the conventional propagation coefficient by the equation

$$k_p = k_p' \left\{ \frac{[M]_0}{(K_s/K_m)[S] + [M]} \right\} . \qquad (20)$$

If we assume that $[S] + [M] = [M]_0$, then, on this view, a solvent will only be an inert diluent if $K_s = K_m$. If $K_s > K_m$, rates of polymerization in the solvent S will be lower than in an inert diluent, while if $K_s < K_m$ they will be higher. (Clearly if the propagating radicals do not form complexes with a given solvent, but enter into extensive complex formation with monomer, dilution of the reaction mixture with this solvent will have no significant effect on the rate). The order of reaction in $[M]$ may, therefore, depart from unity, even if monomer is not involved in the initiation step. Henrici-Olivé and Olivé have shown that their hypothesis is in agreement with many experimental results. In the case of the enhanced rates observed by Burnett et al.[15,16] for the polymerization of methyl methacrylate in bromobenzene solution, they claim that their hypothesis is consistent with the experimental findings, while that of Burnett et al. is not. The latter conclusion is, of course, in agreement with our own observations described earlier.

However, the mechanism of Henrici-Olivé and Olivé appears, to us, to run into difficulties. For example, the behaviour of anisole seems anomalous. Two kinds of complex between anisole and the polymer radical can be envisaged; a π-complex in which electron-donation from the π-orbitals of the aromatic nucleus of anisole occurs, and a σ-complex, in which donation is from the σ lone-pairs of the oxygen atom. Presumably the complex formed will be the more stable of these, and must, therefore, be more stable than the π-complex formed with benzene (since the methoxy substituent increases the availability of π-electrons in the nucleus). However, the rates of polymerization observed are *higher* in anisole than in benzene; in terms of the hypothesis we are discussing this must imply that anisole forms with polymer radicals a complex which is *less* stable than that of benzene.

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The solvents giving rise to unexpectedly high rates of polymerization are generally polar in character. Nevertheless, the possession of a comparatively high dielectric constant (ϵ) is not a sufficient condition for a solvent to be active in producing enhanced rates. Thus ethyl acetate ($\epsilon = 6\cdot0$), benzene ($\epsilon = 2\cdot3$) and acetonitrile ($\epsilon = 38\cdot8$) behave as ideal diluents, while methyl benzoate ($\epsilon = 6\cdot5$) gives high rates.

We do not yet know enough about the effects of structural features in the additives to make other than tentative suggestions. It seems probable that a π-system containing a heteroatom is necessary to give enhanced rates[24]. An interesting comparison is provided by the two esters

—COOEt   and   —CH₂COOEt
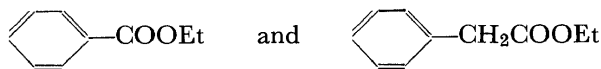
of which the former alone has a π-system with a heteroatom, and is effective in giving "high" rates of reaction. A propagating radical may form a complex with a molecule containing such a π-system, and then a collision between any part of the π-system and a monomer molecule may have a finite probability of leading to reaction. In other words, the complex and monomer enter into a "sticky collision", both the radical and the monomer molecule being held by the polarizable π-system, and ultimately achieving a configuration suitable for reaction. Thus the collision diameter of the radical, and hence the propagation coefficient, may be effectively increased by complex formation.

E.S.R. investigations, particularly under conditions of high resolution such as were employed by Fischer[25] in his elegant experiments, should provide useful information of the nature of the propagating radicals. If the radicals are extensively complexed as postulated by Henrici-Olivé and Olivé their e.s.r. spectra should be sensitive to the nature of the medium. Although changes have been noted in the presence of salts[26], there is a lack of suitable high-resolution experimental data for examining the general proposal. The tentative hypothesis we have advanced does not necessitate the existence of a large fraction of the radicals in complexed form, and would therefore be more difficult to test with the aid of e.s.r. spectra.

NEW INITIATORS BASED ON ORGANIC DERIVATIVES OF METALS

The radical-forming reactions of metal carbonyls in association with organic halides have been extensively reported[27]. In this final section I wish to draw attention to an organic derivative of a metal in its zeroth oxidation state, viz. tetrakis triphenyl phosphite nickel (0), $Ni\{P(OPh)_3\}_4$. This compound is readily prepared by refluxing freshly sublimed nickelocene with excess triphenyl phosphite in benzene solution under an atmosphere of nitrogen[28].

$Ni\{P(OPh)_3\}_4$ resembles the metal carbonyls in its radical-producing reactions, but is of special interest because of its unusually high activity, and also since it is free from the disadvantage of giving rise to inhibition at relatively high concentrations. (Initiators which inhibit in this way are of

limited practical use, since, although they may be very active at low concentrations, they cannot be used to obtain rapid polymerization at higher concentrations.) Tetrakis-triphenyl phosphite nickel (0) initiates[29] the free-radical polymerization of bulk methyl methacrylate readily at 25°C, although in the pure solid state the compound is stable, melting at 146°C. The rate of polymerization at 25°C is given by Eq. (25)

$$- \frac{d[M]}{dt} = 1 \cdot 02 \times 10^{-2} [\text{Ni}\{\text{P(OPh)}_3\}_4]^{\frac{1}{2}} \text{mole l.}^{-1} \text{sec}^{-1} \qquad (25)$$

$$([\text{CCl}_4] = 0 \cdot 153 \text{ mole l.}^{-1})$$

and some values of the rate of conversion of bulk methyl methacrylate at 25°C are given in Eq. (26) for purposes of illustration.

Conversion $= 400[\text{Ni}\{\text{P(OPh)}_3\}_4]^{\frac{1}{2}}$, per cent per h
Initiator concentration 10^{-2} mole l.$^{-1}$ (13 g l.$^{-1}$) gives a conversion 40 per cent per h. (26)

From Eq. (25) we may deduce that tetrakis-triphenyl phosphite nickel (0) initiates the polymerization of methyl methacrylate at 25°C, nearly 30 times as rapidly as an equimolar concentration of azo-bis-isobutyronitrile at 60°C.

Figure 2 indicates the dependence of the rate of polymerization on the halide concentration. The curves referring to carbon tetrachloride and ethyl
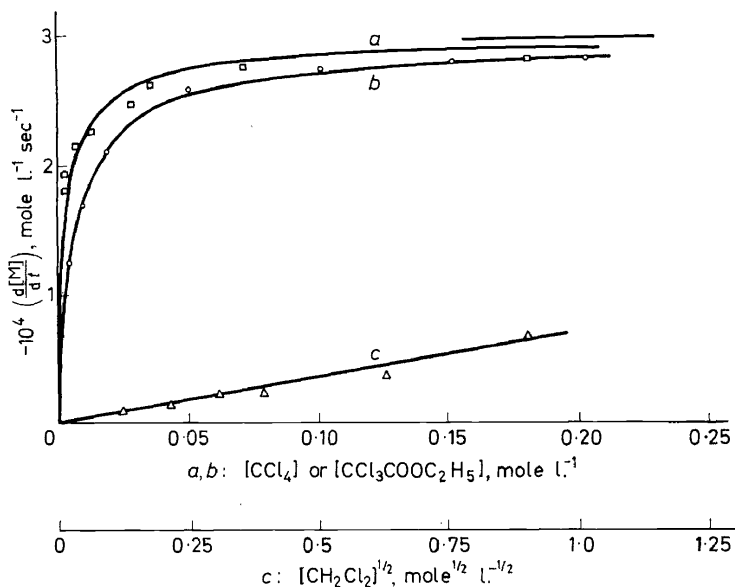

Figure 2. Initiation of the polymerization of methyl methacrylate at 25°C by Ni{P(OPh)₃}₄– halide systems. Dependence of rate on [halide]. [Ni{P(OPh)₃}₄] $= 7 \cdot 62 \times 10^{-4}$ mole l.$^{-1}$ (*a*) Ethyl trichloracetate; (*b*) carbon tetrachloride; (*c*) methylene chloride.
The (hypothetical) limiting rate ([halide] → ∞) is shown. The curves are those calculated from the kinetic scheme (27), with the parameters given in ref. 29.

trichloracetate closely resemble those found in the corresponding metal carbonyl systems, the rate tending to reach a limiting value as the concentration of halide is increased. Clearly these two active halides give limiting rates of polymerization which are closely similar. With the relatively inactive methylene chloride, the rate of polymerization is seen to be proportional to $[CH_2Cl_2]^{\frac{1}{2}}$ over the concentration range studied.

In the presence of carbon monoxide the rate of polymerization is depressed (*Figure 3*), corresponding to a decrease in the rate of initiation. The shape of the rate–[halide] curve is not changed by addition of carbon monoxide. On the other hand, addition of triphenyl phosphite, which also causes a reduction in the rate of polymerization, greatly reduces the "sharpness" of the curve (*Figure 3*).
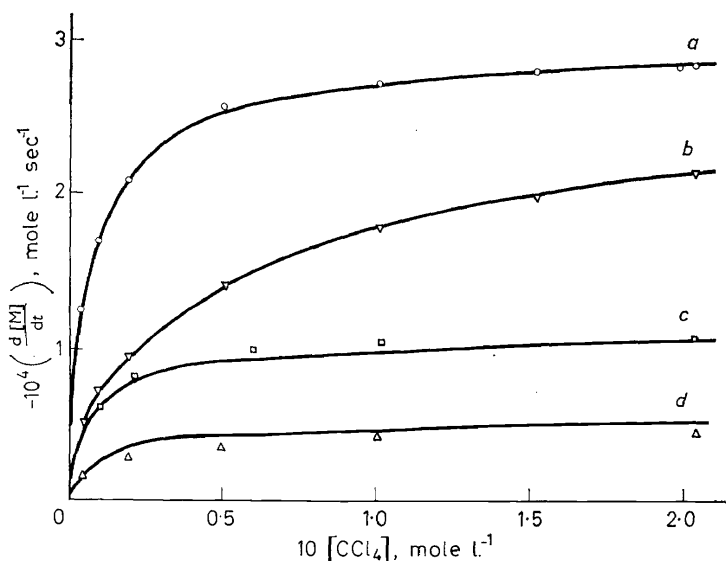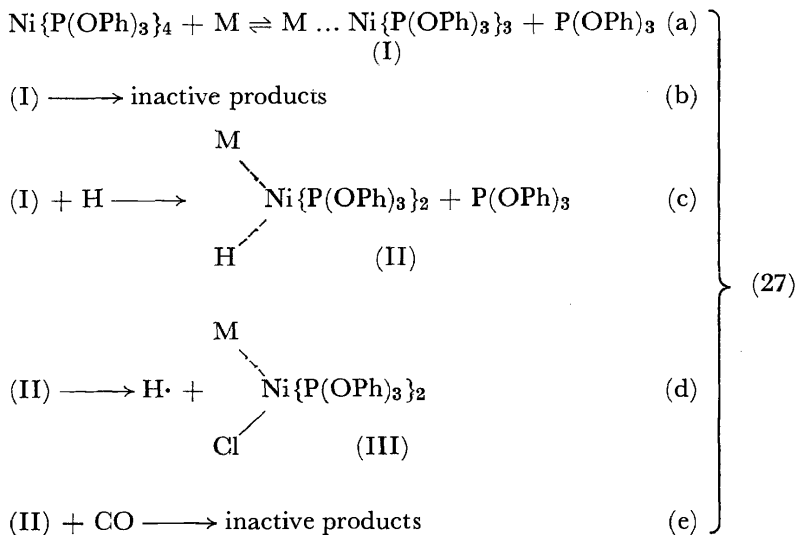

Figure 3. Dependence of the rate of polymerization of methyl methacrylate at 25°C on [CCl₄] in the presence of carbon monoxide and triphenyl phosphite. [Ni {P(OPh)₃}₄] = 7·62 × 10⁻⁴ mole l.⁻¹
(*a*) [CO] = 0, [P(OPh)₃] = 0; (*b*) [CO] = 0, [P(OPh)₃] = 2 × 10⁻³ mole l.⁻¹; (*c*) [CO] = 7 mm, [P(OPh)₃] = 0; (*d*) [CO] = 35 mm, [P(OPh)₃] = 0.

When benzene is used as diluent the order of the overall reaction in [M] is 1·5, indicating that monomer is involved in the initiation step: this situation is exactly similar to that encountered with molybdenum carbonyl[27]. With stronger electron-donors as solvents the order in [M] is lower, although above unity—1·25 (ethyl acetate), 1·22 (dioxan), 1·03 (*N,N*-dimethylformamide). Similar results already reported for molybdenum carbonyl systems have been held to indicate that such solvents can enter into the initiation reaction in the same manner as monomer[27].

On the basis of the above results, the following mechanism is suggested for the initiation process in bulk monomer[29]. It is readily shown that this

scheme leads to kinetic predictions consistent with the experimental observations.

$$Ni\{P(OPh)_3\}_4 + M \rightleftharpoons M \ldots Ni\{P(OPh)_3\}_3 + P(OPh)_3 \quad (a)$$
$$(I)$$

$$(I) \longrightarrow \text{inactive products} \quad (b)$$

$$(I) + H \longrightarrow \begin{array}{c} M \\ \diagdown \\ Ni\{P(OPh)_3\}_2 + P(OPh)_3 \\ \diagup \\ H \end{array} \quad (c)$$
$$(II)$$

$$(II) \longrightarrow H\cdot + \begin{array}{c} M \\ \diagdown \\ Ni\{P(OPh)_3\}_2 \\ \diagup \\ Cl \end{array} \quad (d)$$
$$(III)$$

$$(II) + CO \longrightarrow \text{inactive products} \quad (e)$$

$$(27)$$

Here H, H· represent a halide molecule, and the radical derived from the latter by scission of a chlorine atom, respectively. It has been found[29] that each molecule of the nickel derivative which decomposes may start two chains, so that some initiation process additional to that in Eq. (27) is necessary. This probably involves complex (III), in which the nickel atom has an oxidation number of $+1$. In view of the comparative instability of this state, rapid reaction of (III) with H to give H· and Ni^{II} seems likely.

The activation energy for initiation in bulk methyl methacrylate is $25\cdot2$ kcal mole^{-1}, and the frequency factor 6×10^{13} mole^{-1}l. The latter is rather high for a bimolecular reaction, and may indicate that there is steric overcrowding in the molecule of the nickel derivative which is relieved on replacing a bulky triphenyl phosphite molecule by monomer. Some evidence of congestion in the molecule is provided by infra-red and x-ray observations[29]. It is interesting to note that nickel derivatives containing cyclohexyl residues in place of phenyl are much less active as initiators, the frequency factors being markedly lower[30]; in these molecules the flexible rings do not give rise to comparable congestion.

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