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NEW POSSIBILITIES OF INITIATING RADICAL REACTIONS*

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DURING the last few years we have been exploring new types of free-radical sources which can function as initiators of polymerization, and in this lecture I should like to summarise some aspects of our work. We shall be concerned with initiation by two kinds of systems, one a derivative of a metal in a low oxidation state in association with an organic halide, and the other a metal chelate. It is my intention to consider topics of chemical interest in the initiation processes, without entering into detailed kinetics, and also to give information of a more practical kind which will indicate the potentialities of these systems as initiators of free-radical reactions in polymers.

1. INITIATING SYSTEMS CONSISTING OF ORGANO–METALLIC DERIVATIVES WITH ORGANIC HALIDES

(*a*) *Thermal initiation*

(*i*) Many of these systems have been studied in the last few years. In the majority, the metal is in its zero-valent state, and the ligands include carbonyl,(1) phenyl isonitrile,(2) triphenyl phosphine,(1, 3) triphenyl and trialkyl phosphites,(4) and pyridine.(5) Some compounds with the metal in other low-valence states, mainly with PR_2 ligands, have also been investigated.(6) The halides most frequently used include carbon tetrachloride and tetrabromide, ethyl trichloracetate and polyvinyl trichloracetate. Typically, the concentrations of the organo–metallic derivative and halide lie in the range 10^{-4}–10^{-3}, and 10^{-2}–10^{-1} mole l^{-1}, respectively. In the simplest cases, reaction occurs in homogeneous liquid systems; a few examples we shall consider involve solid halogen derivatives, but this does not introduce any special features other than those generally encountered in heterogeneous free-radical polymerizations.(7) The radical-forming process in these systems is essentially an electron-transfer from the metal to the halide. The former thus assumes a higher oxidation state while the latter generally undergoes scission into a halide ion (which becomes associated with the metal) and a radical fragment which is the initiating species. For example, carbon tetrachloride yields $\dot{C}Cl_3$ radicals while ethyl trichloracetate forms $C_2H_5OOC\dot{C}Cl_2$.

All the systems show similar kinetic behaviour. No polymerization occurs in the absence of halide. As the concentration of the latter is increased the rate of polymerization increases initially, but eventually reaches a plateau value which is unaffected by further increase in halide concentration. This limiting rate, which is effectively independent of the nature of the halide, has been taken to indicate the

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* Main lecture.

occurrence of a potentially rate-determining process preceding reaction involving the halide. Thus the electron-transfer mentioned above does not take place directly between the metal derivative and the halide; the former must first undergo a reaction leading to a more reactive species. Such a reaction, which constitutes the first step in the initiation mechanism, may be either a replacement of a ligand by another suitable molecule (often the monomer) (S_N2) or a simple dissociation (S_N1). Molybdenum(8, 9) and manganese(10) carbonyls are examples of the two types, the primary reactions being:

$$\mathrm{Mo(CO)_6} + \left\{\begin{matrix}\mathrm{M}\\ \mathrm{S}\end{matrix}\right. \rightleftarrows \underset{\text{(I)}}{\mathrm{Mo(CO)_5}\cdots\left\{\begin{matrix}\mathrm{M}\\ \mathrm{S}\end{matrix}\right.} + \mathrm{CO} \qquad (1)$$

$$\mathrm{Mn_2(CO)_{10}} \rightarrow \underset{\text{(I)}}{\mathrm{Mn_2(CO)_9}} + \mathrm{CO}. \qquad (2)$$

Here M,S represent monomer and solvent molecules respectively. It has also been suggested that dissociation of the Mn–Mn bond contributes to the process in the case of manganese carbonyl.(11) As indicated in (1), a solvent with electron-donating powers (e.g. ethyl acetate) can replace monomer in the S_N2 type of reaction. The occurrence of the S_N2 substitution is inferred from the dependence of the rate of polymerization on $[M]^{3/2}$ in an inert solvent such as benzene, which shows that monomer must be involved in the initiation process. On the other hand, in an "active" solvent, the order in [M] is less than 1·5 on account of the contribution from the solvent. The information which is currently available about the nature of the primary reactions for the organo–metallic derivatives studied is summarized in Table 1.

The rate of initiation by derivatives which undergo (1) would be expected to depend on the nature of the monomer, so that initiation would be to some extent selective. (Such selectivity is quite distinct from any effects which may arise from differences in the reactivities of monomers towards free-radicals.) On the other hand, if (2) represents the primary step, no selectivity would be anticipated, since monomer is not involved in any rate-determining step in initiation. The relevant data are not extensive; in Table 2 we compare the behaviour of molybdenum and manganese carbonyls towards styrene and methyl methacrylate.(10) Clearly $Mo(CO)_6$ initiates polymerization of the latter monomer more readily, while $Mn_2(CO)_{10}$ does not discriminate (within limits of experimental error).

Since initiating radicals are formed by reaction between the organic halide and the metal derivative arising from (1) or (2) this latter derivative must be more reactive than the original complex. Studies of the rate of initiation by molybdenum carbonyl in a variety of solvents have provided information on this point.(8, 9) The solvents include ethyl acetate, dioxan, acetic anhydride. If the organo–metallic compound formed in (1) is denoted by $Mo(CO)_5L$ we find that if L is one of the above molecules, $Mo(CO)_5L$ is not sufficiently stable to allow isolation; these complexes react directly with CCl_4. Where L is pyridine, or a phosphine derivative, the complex is isolatable, and then requires activation (e.g. by reaction with monomer) before reaction with CCl_4 is possible. Considerations of this kind have suggested that the reactivity of the compound $Mo(CO)_5L$ towards CCl_4 depends on the nature of the ligand L as indicated in the sequence:(5)

O-compound > nitrile > N-base > P-compound > CO.

TABLE 1. PRIMARY REACTIONS IN THERMAL INITIATION

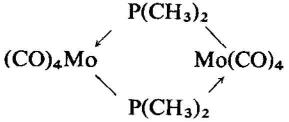
S_N1	Ref. no.	S_N2	Ref. no.	Unknown	Ref. no.
$Mn_2(CO)_{10}$	10	$Mo(CO)_6$	8, 9	$Co_4(CO)_{12}$	15
		$Mo(CO)_5Py$	5	$Co_2(CO)_6PhC_2COOCH_3$	15
		$Cr(CNPh)_6$	13	$Co_3(CO)_9H(PhC_2H)$	15
	12	$Mo(CNPh)_6$	13	$Re_2(CO)_{10}$	16
		$W(CNPh)_6$	13	$Re_2(CO)_8(PPh_3)_2$	16
		$Ni(CO)_4$ (?)	14	$Re(CO)_3(PPh_3)_2$	16
$(CO)_5Mo \leftarrow P(C_2H_5)_2-P(C_2H_5)_2 \rightarrow Mo(CO)_5$	12	$Ni(CO)_2(PPh_3)_2$	1	$C_5H_5Mn(CO)_3$	17
		$Ni\{P(OPh)_3\}_4$	4		
		$Pt(PPh_3)_4$	3		

TABLE 2. SELECTIVITY IN INITIATION[10]

Values of initiating activities (i.e. rate of initiation/[carbonyl]) at 80°C, $sec.^{-1}$	$Mn_2(CO)_{10}$	$Mo(CO)_6$
Styrene	$5{\cdot}2 \times 10^{-6}$	$22{\cdot}5 \times 10^{-6}$
Methyl methacrylate	$3{\cdot}7 \times 10^{-6}$	$94{\cdot}6 \times 10^{-6}$

It is of interest that Strohmeier[18] has proposed the reverse order for the *stability* of the complexes, on entirely different grounds, so that our conclusions are in agreement.

The usefulness of these systems as initiators naturally depends on their ability to produce free radicals at a convenient rate at the required temperature. Three characteristics are important in this connection:—the activity of the complex as initiator at low concentrations, the extent of inhibition by the complex and the concentration of the organic halide which is required to obtain desirably high rates of initiation. We shall consider these separately.

(*ii*) Although the rates at which many organo-metallic derivatives initiate polymerization have been measured at a single temperature, data extending over ranges of temperature are much less numerous. Figure 1 sets out most of the information available in the form of Arrhenius lines, and may be employed in assessing the activity of a particular initiator at a given temperature in bulk methyl methacrylate. The line referring to azo-*bis*-isobutyronitrile is given in Fig. 1. for comparison.

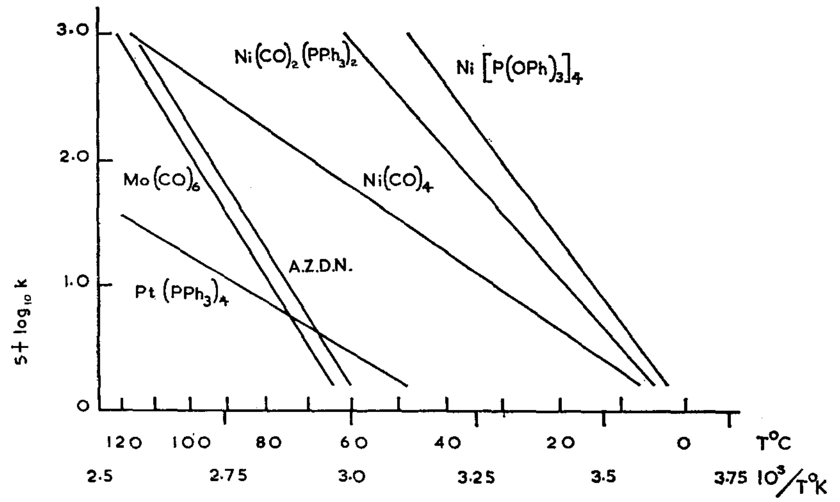


FIG. 1. Dependence of first-order velocity constant for initiation k on temperature. (Rate of initiation at limiting halide concentration = k[metal derivative].) Monomer—methyl methacrylate.

(*iii*) Inhibition is generally encountered with simple carbonyls as the concentration of the carbonyl is increased; the rate then falls progressively below that predicted from the square-root dependence observed at lower concentrations. $Co_4(CO)_{12}$, which is very active at low concentrations, shows marked inhibition(15) at concentrations higher than 10^{-5} mole l^{-1} and $Mo(CO)_6$ behaves similarly at concentrations exceeding 5×10^{-4} mole l^{-1}, approximately, (with CCl_4 as halide).(19, 20) The nickel(1, 4) and platinum(3) derivatives in Fig. 1 do not show inhibition at concentrations below 3×10^{-3} mole l^{-1} approximately; above this value $Ni(CO)_4$ begins to inhibit.(14) (The much more pronounced inhibition by $Ni(CO)_4$ noted in earlier work(21) is probably attributable to the presence of carbon monoxide, to which this initiator is remarkably sensitive.) $Ni(CO)_2(PPh_3)_2$, $Ni\{P(OPh)_3\}_4$ and $Pt(PPh_3)_4$ have not been examined at concentrations greater than 3×10^{-3} mole l^{-1}. In the presence of this concentration of $Ni\{P(OPh)_3\}_4$ (with $[CCl_4] = 0{\cdot}05$ mole l^{-1}, approximately) methyl methacrylate polymerizes at 25°C at a rate of $5{\cdot}6 \times 10^{-4}$ mole l^{-1} sec^{-1} or nearly 22 per cent per hr.

(*iv*) In some circumstances, e.g. when it is desired to prepare a block copolymer of high molecular weight (see Section *cii*), chain transfer must be kept to a minimum. Since halides are active transfer agents, it is clearly desirable to use the lowest concentration of halide consistent with practicable rates of initiation. Table 3 shows the halide concentrations necessary to achieve 90 per cent of the limiting rates for a number of metal derivatives. Manganese carbonyl appears to require only relatively low carbon tetrachloride concentrations, and hence should be particularly useful when transfer to halide must be avoided. If halides more active than carbon tetrachloride are employed (e.g. ethyl trichloracetate, carbon tetrabromide) the concentrations required are naturally lower than those indicated in Table 3.

TABLE 3. CCl_4 CONCENTRATION REQUIRED TO OBTAIN 90 PER CENT OF MAXIMUM RATE OF POLYMERIZATION. METHYL METHACRYLATE AS MONOMER

Complex	Temperature (°C)	$[CCl_4]$, mole l^{-1}
$Ni(CO)_4$	25	0·044
	0	0·032
$Ni(PPh_3)_2(CO)_2$	25	0·096
$Ni\{P(OPh)_3\}_4$	25	0·086
$Pt(PPh_3)_4$	60	0·029
$Mo(CO)_6$	80	0·13
$Mn_2(CO)_{10}$	80	0·0058

(*v*) As a general rule, the activity of the halide component in initiation increases with the number of chlorine or bromine atoms joined to a single carbon atom, or on the introduction of an electron-attracting group, such as carboxyl, into the molecule.(22, 23) Thus for the simple halides we have the order of decreasing activity, $CCl_4 > CHCl_3 > CH_2Cl_2 > CH_3Cl$ while CCl_3COOH is considerably more active than CCl_4. Methylene chloride is only feebly active and fluorine and iodine derivatives are usually inactive. These findings are easily understandable, since the radical-forming process involves an electron-transfer from the active species (I) produced in reactions (1) or (2) to a halogen atom of the halide. An addition (charge-transfer) complex (II) is probably an intermediate—

$$(I) + Cl\text{-}X \rightarrow (II) \rightarrow \overset{\ominus}{Cl} + \dot{X} + \;.\;\; . \qquad (3)$$

N-chlorinated and N-brominated imides and amides have recently⁽²⁴⁾ been shown to be very active when used with organo–metallic compounds in initiating systems. The N–Cl bond is relatively weak, and the CO group in –CONCl– is strongly electron-attracting, so that the activity of these halides is not surprising. Tracer experiments have confirmed⁽²⁴⁾ that initiation occurs through the formation of $RCO\dot{N}R'$ radicals. The application of these reactions in polymer grafting will be mentioned later (Section 1 *cii*).

(*vi*) The nature of the metal derivatives formed in these initiation reactions has not yet been elucidated. However, a fair amount of evidence is now available for $Mo(CO)_6$ systems. Each $Mo(CO)_6$ reacting gives rise to a single radical,⁽²⁰⁾ hence reaction⁽³⁾ would be expected to lead to a derivative of Mo^I. Recent investigations⁽²⁵⁾ with electron resonance spectroscopy have shown that the molybdenum does not remain in this oxidation state, but appears to be oxidized further to Mo^V. Experiments on model compound indicate that the oxidation $Mo^I \rightarrow Mo^V$ effected by CCl_4 does not involve free-radical formation; perhaps two double electron transfer processes occur. Thus, as stated earlier, the radical-forming reaction in initiation involves the oxidation $Mo^O \rightarrow Mo^I$.

(*b*) *Photo-initiation by carbonyls*

Manganese and rhenium carbonyls ($Mn_2(CO)_{10}$, $Re_2(CO)_{10}$) in the presence of halides are active photo-initiators of polymerization.⁽²⁶⁻²⁸⁾ The long-wave limits of absorption are approximately 4600 and 3800 Å, respectively, and photosensitization occurs up to these wavelengths.

With manganese carbonyl, the general form of the dependence of the rate of polymerization on halide concentration is similar to that already described for thermal reactions, but the exact relation depends on the light intensity. At higher absorbed intensities the dependence is less sharp. The halide dependence with rhenium carbonyl has not been studied in detail; the concentration of carbon tetrachloride required to give the limiting rate of polymerization is remarkably low—less than 2×10^{-5} mole l^{-1}—and extremely rigorous purification of monomer is necessary if meaningful results are to be obtained.⁽²⁸⁾

Polymerizations photoinitiated by rhenium carbonyl show an unusual feature—viz. a long-lived after-effect.⁽²⁸⁾ This continues for several hours at room temperature after the light has been cut off; it is therefore distinct from after-effects associated with normal free-radical decay and it is not connected with thermal initiation of polymerization by rhenium carbonyl. No comparable effect is found with manganese carbonyl. These observations have been interpreted in terms of a primary photochemical process producing two dissimilar fragments from the metal carbonyl. One of these reacts rapidly with carbon tetrachloride to form initiating radicals, while the other reacts slowly when it is derived from $Re_2(CO)_{10}$, or not at all when formed from $Mn_2(CO)_{10}$. In support of this mechanism it has been shown⁽²⁷⁾ that a solution of $Re_2(CO)_{10}$ in methyl methacrylate, after irradiation and subsequent standing in the dark for 1 hr, produces polymer when added to a mixture of monomer and carbon tetrachloride. (No significant polymerization occurs during the irradiation.) With manganese carbonyl the intermediates formed on irradiation were found to decay much more rapidly.

The quantum yield for initiation at 25° has been determined with methyl methacrylate as monomer and $[CCl_4] = 0 \cdot 1$ mole l^{-1}, approximately. Wavelengths used were 4358 Å ($Mn_2(CO)_{10}$) and 3650 Å ($Re_2(CO)_{10}$). For both carbonyls, values close to unity were obtained. Clearly both compounds are very efficient photosensitizers. The value quoted for $Re_2(CO)_{10}$ refers to the reaction occurring in the light; if the subsequent dark reaction were included the quantum yield would exceed unity. The value of the quantum yield has been taken to support the view that the initial primary process is unlikely to be rupture of the metal–metal bond with production of two identical fragments. If this were so, a quantum yield of unity would be obtained only if the succeeding processes for both carbonyls were 50 per cent efficient. Bamford, Crowe, Hobbs and Wayne(28) therefore suggested that (4) represents the primary dissociation—

$$Me_2(CO)_{10} + h\nu \rightarrow Me(CO)_4 + Me(CO)_6, \tag{4}$$

Me representing the metal atom. $Me(CO)_4$ was supposed to give rise to rapid initiation—

$$\begin{array}{l} Me(CO)_4 + CCl_4 \rightarrow (III) \rightarrow \dot{C}Cl_3 + Me(CO)_4Cl \\ \hspace{9em} \downarrow \\ \hspace{8em} \{Me(CO)_4Cl\}_2 \end{array} \tag{5}$$

while the following reactions of $Me(CO)_6$ were postulated—

$$Me(CO)_6 \rightleftharpoons Me(CO)_5 + CO \tag{6}$$

$$Me(CO)_5 + CCl_4 \rightarrow Me(CO)_5 \cdots CCl_4 \begin{array}{l} \nearrow Me(CO)_5Cl + \dot{C}Cl_3 \\ \qquad (Me{=}Re) \\ \underset{Me(CO)_5}{\searrow} Me_2(CO)_{10} + CCl_4. \\ \qquad (Me{=}Mn) \end{array} \tag{7}$$

Thus with $Mn_2(CO)_{10}$ all the initiation arises from (5), but with $Re_2(CO)_{10}$ (6), (7) are responsible for the prolonged after-effect. A further process, of second order in the concentration of active intermediates, is necessary in the case of manganese carbonyl to account for the dependence of the halide curve on the absorbed intensity. Such a reaction might be of the form:

$$(III) + Mn(CO)_4 \longrightarrow \text{inactive products.} \tag{8}$$

We conclude this section by noting that, on account of the efficient photosensitization by these carbonyls, relatively high rates of photopolymerization may easily be obtained. For example, in the work of Bamford, Crowe and Wayne(26) referred to, the light source was a 125 W high pressure mercury arc and a parallel beam was obtained with the aid of two pyrex lenses. Light of wavelength 4358 Å was isolated by the pair of Wratten filters 2E and 98. Rates of polymerization of methyl methacrylate at 25°C approaching 10 per cent per hr could be obtained with this arrangement with $[Mn_2(CO)_{10}] = 2 \cdot 57 \times 10^{-4}$ mole l^{-1}. The photosensitizing action of $Mn_2(CO)_{10}$ in visible light is a further feature which makes this carbonyl a very useful practical photosensitizer.

(*c*) *Practical applications*

We shall discuss three applications of systems composed of organo-metallic derivatives and organic halides—as initiators, in the synthesis of block and graft copolymers, and in providing a technique for investigating the nature of the termination reaction in free-radical polymerization.

(*i*) The data in Fig. 1 refer to initiation of the polymerization of methyl methacrylate, and since initiation may be selective (Section *ai*) they will not necessarily apply to any other bulk monomer. However, they should be more closely applicable to solutions of other monomers in solvents resembling methyl methacrylate in electron-donating power, e.g. ethyl acetate.

Figure 1 illustrates that some of the systems may be employed as free-radical initiators at temperatures down to about 0°, or perhaps somewhat lower. Nickel derivatives are clearly particularly active, and indeed initiate almost as rapidly at 0° as does azo-*bis*-isobutyronitrile at 60°. $Ni\{P(OPh)_3\}_4$ appears to have advantages in that it is easy to prepare, comparatively stable in the solid state (m.p. 146°) and does not evolve any gas during reaction. Although $Ni(CO)_4$ initiates rather more rapidly below 0° it is much less convenient to use, and has the additional disadvantage that initiation is strongly inhibited by carbon monoxide, which is a product of reaction.

The use of manganese carbonyl as a photoinitiator in visible light has been described in Section b.

(*ii*) If the halide component of the initiator is written as X-hal, the initiating radical will generally be $\dot{X}$ (Eqn. 3), so that the residue X becomes incorporated in the polymer as a terminal group. This provides a useful method of controlling the nature of the terminal group, since the nature of X may be varied over a fairly considerable range, subject to the limitations on activity discussed in Section *av*. If the termination reaction in the polymerization is radical combination, the resulting polymer will have X as terminal group at both ends. For example, polystyrene chains with $-CBr_3$ or $-CHClCOOH$ terminations may be prepared in this way.

Where X is part of a polymer chain the reaction will lead to a block or graft copolymer. Let us suppose that a polymer of monomer A with CBr_3 end-groups, prepared as above, is used as the halide component of the initiator in polymerizing monomer B. The initiating radicals will be $Br_3CA_p\dot{C}Br_2$ and the propagating chains $Br_3CA_pCBr_2$ $B_q\dot{B}$. If $\dot{B}$ radicals terminate by combination, the resulting polymer will be Br_3CA_p $CBr_2B_rCBr_2A_pCBr_3$. Further initiation will activate terminal CBr_3 groups of this polymer (in preference to CBr_2 groups, which are less reactive) and a copolymer containing seven blocks–4A and 3B–will be the next product, and so on. A simpler system would be obtained if the initial halide component had the structure Br_3CA_p, in which case a single three-block product $A_pCBr_2B_mCBr_2A_p$ should predojminate. Syntheses of these types, in which A is styrene and B acrylonitrile or vinyl chloride, are in progress in our laboratories. Photoinitiation by manganese carbonyl is particularly convenient here, since it is effective with a relatively low concentration of halide groups.(26)

Graft polymers are produced when the halide component of the initiator for the polymerization of monomer B is a pre-formed polymer carrying side chains with active halide groups. In such a case a network will be built up if there is a combination component of the termination reaction in monomer B. Networks of this type have been synthesized with polyvinyl trichloracetate as the initiating halide, and styrene(23) and methyl methacrylate(29) as the cross-linking monomer B. A very wide range of new network polymers may be constructed in this manner; the number and distribution of halide groups in the pre-polymer chains may be varied, as may the molecular weight of the pre-polymer, and the mean length of the cross-links between the pre-polymer chains is controllable by adjustment of the rate of initiation. The cross-link density is determined *inter alia* by the duration of the reaction. If a chain-transfer agent is added in sufficiently high concentration network formation will be suppressed, and the reaction products will then consist of the simple graft copolymer mixed with B homopolymer. Lower concentrations of transfer agent would give rise to a polymer in which the preformed chains are cross-linked and also carry branches of poly-B. We believe that exploration of the possibilities offered by these reactions might lead to materials with interesting properties.

The initiating activity of N-halogenated amides described in Section *av* has been utilized in grafting to polymers containing amide groups.(24) Polymers examined include the polypeptide poly-γ-methyl-L-glutamate, nylons 6, 66, 610, and the proteins wool, silk, gelatin. These materials were N-chlorinated or N-brominated by immersion in the corresponding sodium hypohalite solution acidified to pH 4–4·5. Nylons were also chlorinated by suspension in aqueous sodium carbonate and reaction with gaseous chlorine. The halogenated polymers were suspended in the monomer to be grafted and reacted with $Mo(CO)_6$ thermally at 70° or 80°, or with $Mn_2(CO)_{10}$ photochemically ($\lambda = 4358$ Å) at room temperature. Grafting of methyl methacrylate, methyl acrylate, acrylonitrile, styrene and vinyl acetate was effected by this technique. These reactions were, of course, heterogeneous, and grafting was confined to a surface layer of the initial polymer. In principle, the graft modifies the surface properties of the polymers without altering the mechanical properties significantly, since the bulk of the material is unaffected. However, the halogenation may cause considerable degradation if prolonged.

(*iii*) Experiments with a polymeric initiator such as polyvinyl trichloracetate may be used to determine the ratio of combination to disproportionation in the termination reaction in the free-radical polymerization of a vinyl monomer, since only the former reaction leads to cross-linking.(29) If all the initial radicals are attached to the chains of the polymeric initiator, and chain-transfer to monomer (and solvent, if present) is negligible, we may derive the following relation from simple gel theory:

$$\frac{1}{t_g} = \frac{\mathscr{I}\bar{P}_w}{c}\frac{k_{tc}}{k_{tc}+k_{td}}. \tag{9}$$

Here t_g is the gel time, $\mathscr{I}$ the rate of initiation, and $\bar{P}_w$, c are the weight-average degree of polymerization and base-molar concentration of the polymeric initiator, respectively. The velocity constants for termination by combination and disproportionation are denoted by k_{tc}, k_{td}, respectively. Values of $\mathscr{I}$ are known from kinetic observations on the polymerization. According to (9) a plot of $1/t_g$ against $\mathscr{I}$ should be linear, and from the slope of the line $k_{tc}/(k_{tc}+k_{td})$ may be evaluated. If chain-transfer to monomer or solvent is significant a correction must be applied to (9). Bamford, Dyson and Eastmond(29) have described observations of this kind, and have also specified the conditions which must hold for the simple relation (9) to be obeyed. The same workers(30) have subsequently studied a number of monomers and found that termination by combination is more widespread than was formerly believed to be the case. Apparently combination is effectively the sole termination reaction with styrene, acrylonitrile methyl, ethyl and *n*-butyl acrylates and vinyl acetate; methyl, ethyl and *n*-butyl methacrylates and methacrylonitrile alone among the monomers examined showed a mixed termination.

2. INITIATION BY CHELATE DERIVATIVES OF METALS

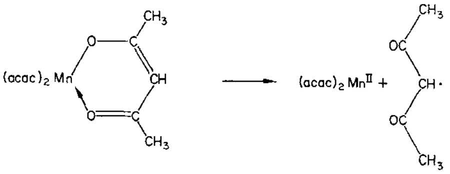
In 1962 Arnett and Mendelsohn(31) reported the ability of certain metal chelates to initiate polymerization and this type of initiation has subsequently been studied by Kastning *et al.*(32) and by ourselves.(33) In some cases the initiation process shows novel features, which we now discuss briefly. Of the simple chelates, those of Mn^{III} are particularly active. Manganic acetylacetonate readily initiates the polymerization of styrene and methyl methacrylate at 80°, the rates of initiation for both monomers being given approximately by the equation:

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

The activation energy and the frequency factor of the initiation reaction in methyl methacrylate have the values

$$\begin{aligned} E_i &= 26\cdot 2\ \mathrm{kcal\ mole^{-1}} \\ A_i &= 6\cdot 7 \times 10^{11}\ \mathrm{sec^{-1}}. \end{aligned} \tag{11}$$

It has been shown from measurements of magnetic susceptibility that initiation is accompanied by the reduction $Mn^{III} \rightarrow Mn^{II}$. The essential step is therefore the scission of a ligand as a free radical—



(12)

As would be expected from this, a ligand is incorporated into the polymer.(32) In reality the process is more complex than (12), since monomer participates in the initiation, but this need not concern us here.

Manganic 1,1,1-trifluoroacetylacetonate $Mn(facac)_3$ is an active initiator for the polymerization of methyl methacrylate(33) at 80°. Kinetic observations and examination of the tacticity of the polymer establish beyond doubt that the polymerization is free-radical in character. The rate of initiation is given by (13), which shows that in

$$\mathscr{I} = 3\cdot 8 \times 10^{-4}[\mathrm{Mn(facac)_3}]\ \mathrm{mole\ l^{-1}\ sec^{-1}} \tag{13}$$

bulk methyl methacrylate $Mn(facac)_3$ initiates more than seven times as rapidly as $Mn(acac)_3$. Both the activation energy and frequency factor of initiation given in (14) are significantly lower than for $Mn(acac)_3$

$$\begin{aligned} E_i &= 15\cdot 8\ \mathrm{kcal\ mole^{-1}} \\ A_i &= 2\cdot 9 \times 10^{6}\ \mathrm{sec^{-1}}. \end{aligned} \tag{14}$$

On the other hand, styrene polymerizes only very slowly in the presence of $Mn(facac)_3$—indeed the rate is lower than the spontaneous thermal rate. The chelate is a strong retarder of the polymerization of styrene; this is not surprising since styryl radicals are highly reactive towards oxidizing ions of transition metals, and the manganese atom in $Mn(facac)_3$ carries a positive charge resulting from electron-withdrawal by the CF_3 groups. Naturally, retardation interferes with the direct observation of initiation by $Mn(facac)_3$ in styrene, and a kinetic analysis is necessary to determine the rate of initiation. It turns out that this chelate initates the polymerization of styrene very slowly, if at all. The experimental evidence for this is presented in Fig. 2 (lower curve). In these experiments rates of polymerization in bulk styrene were measured in the presence of a constant concentration of benzoyl peroxide, with variable $[Mn(facac)_3]$. The ratio ω/ω_0 is shown in Fig. 2 as a function of $[Mn(facac)_3]^{-1}$ (ω, ω_0 are the rates of polymerization in the presence and absence of chelate, respectively).

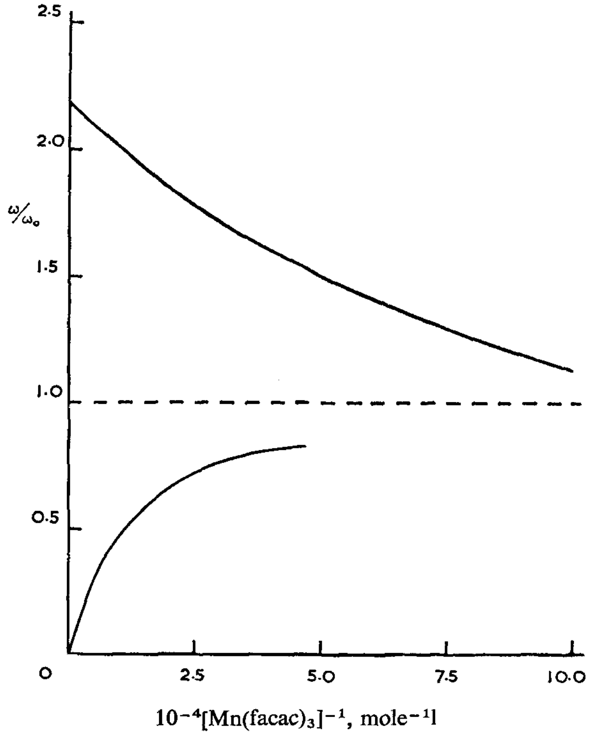


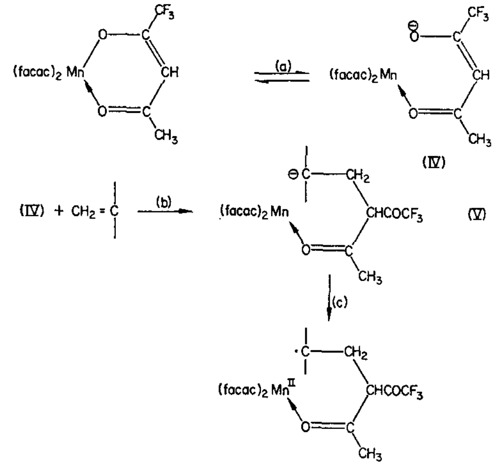
Fig. 2. Dependence of initial rate of polymerization ω on $[Mn(facac)_3]$; ω_0 is the rate with $[Mn(facac)_3] = 0$.

Lower curve: thermal reaction at 80°, [benzoyl peroxide] $= 2 \cdot 0 \times 10^{-3}$ mole l^{-1}.
Upper curve: photosensitized reaction, $\lambda = 3820$ Å. (No benzoyl peroxide present.)

The fact that the curve effectively passes through the origin indicates negligible initiation by the chelate[33].

Manganic 1,1,1-trifluoroacetylacetonate has been found to be an ineffective initiator of the polymerization of vinyl acetate, but to be very active with acrylonitrile.

This chelate is therefore a highly selective initiator, discriminating between monomers to a much greater extent than molybdenum carbonyl (Section *ai*). This behaviour, reminiscent of ionic polymerization, is understandable if initiation proceeds through a highly polar stage. The mechanism suggested⁽³³⁾ is shown in (15).



(15)

The first step (*a*) is the heterolytic fission of an Mn–O bond, encouraged by electron-withdrawal by CF_3. A monomer with a sufficiently high electron-accepting capacity (i.e. one readily susceptible to anionic polymerization) can add to the resulting active species (IV), to form the monomer anion (V). This is then oxidized by the Mn^{III} atom in the molecule to give an initiating free radical [reaction (15c)]. The anionic addition (15b) explains the selective nature of the initiation. Probably electron-attraction by the metal atom facilitates addition of the incoming monomer, but the polar properties of the latter will be of dominating importance. Thus, although the initiation is ultimately free-radical in character, the path through polar states imposes selectivity on the overall process.

Recent work⁽³⁴⁾ has shown that manganese chelates can act as photosensitizers of free-radical polymerization. It is interesting that photosensitized initiation by $Mn(facac)_3$ does not show monomer selectivity. This is indicated by the upper curve in Fig. 2 which refers to the polymerization of styrene photosensitized by $Mn(facac)_3$ with $\lambda = 3820$ Å. The finite intercept on the vertical axis made by the curve extrapolated from $10^{-4}[Mn(facac)_3]^{-1} = 0{\cdot}5$ mole^{-1}l., approximately, establishes that the chelate is initiating polymerization at a significant rate. Indeed, the rate of photo-initiation in styrene is at least equal to that in methyl methacrylate. Thus photoinitiation may involve the direct production of radicals from $Mn(facac)_3$, rather than the polar type of mechanism of equation (15).

It seems possible that further study of metal chelates, particularly in polar media, will reveal additional interesting features, and may also lead to the development of low-temperature initiators for the polymerization of some monomers.

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