

REFLECTIONS ON FREE RADICAL POLYMERIZATION

C. H. BAMFORD and G. C. EASTMOND

*Department of Inorganic, Physical & Industrial Chemistry,
University of Liverpool, England*

INTRODUCTION

When a subject has been investigated for so long a time, and so intensively, as free radical polymerization, we inevitably encounter the question "What are the prospects for future research in this field?", with the implication that we may have reached, or even passed, the boundary of diminishing return. There is no single answer to the question, since the reply is dependent on the interests of the questioner, who may be an academic scientist, a polymer manufacturer who already employs free radical polymerization, or a potential manufacturer who wishes to develop new products. The second case is the easiest to deal with, for the present manufacturer is forced to carry out some research to maintain or improve the position of his products with respect to his competitors. Frequently, apparently small improvements (*e.g.* in colour, stability) may be of decisive importance. It is perhaps surprising to find how little detailed published information there is about some polymerizations of great industrial importance, *e.g.* that of vinyl chloride. With regard to the third type of questioner (the potential manufacturer) it is probably true that, as far as can be seen at the moment, homopolymers with strikingly new properties are less likely to be obtained by simple free radical polymerization than by some other techniques, although, as grafting techniques improve, modification of the properties of polymers and other materials may become increasingly feasible and important. There may also be other possibilities involving *e.g.* complexing of radicals, as we shall see later. The former statement is intended to relate particularly to the polymerization of vinyl type derivatives; obviously it is inapplicable to new types of monomers (such as CSF_2) which may polymerize by radical mechanisms.

The purpose of this talk is mainly to discuss some kinds of new chemical information which we may hope to derive by studying free radical polymerizations, *i.e.* to try to provide a partial answer for the first type of questioner, the academic scientist. The pattern of these polymerizations is established: initiation, propagation, chain transfer and termination with, perhaps, retardation or inhibition. We may consider the information available at three levels, of increasing precision. First, many monomers have not received any detailed kinetic study and little, if anything, is known about³ the component reactions. In some cases the existence of some types of component reaction (such as thermal initiation) is doubtful. Secondly, even with common monomers, there is often (or generally) uncertainty as to the values of the kinetic parameters, as anyone who has searched

the literature for these quantities will appreciate. It may be argued that this is not very important, so long as orders of magnitude are known. This, however, is debatable, since in many cases errors in kinetic parameters are exaggerated in subsequent calculations, so that the results become too crude to allow any useful quantitative deductions to be gained. Thirdly, there is little information of a physical kind (*e.g.* ESR spectra) relating to active species while they are actually taking part in the reaction. Recently Fischer¹ has been able to record the ESR spectrum of methacrylic acid radicals during polymerization in the liquid phase; the spectrum showed a high degree of resolution (since anisotropic broadening was reduced) and consisted of 18 lines. (These are not all resolved under normal conditions). More work of this kind on other systems is clearly desirable. Finally, in no case do we have any reasonably well-based views about the detailed nature of the transition states of the component reactions. We are, therefore, very far from a basic understanding of the factors which govern the rates of the component reactions, although semi-empirical approaches have been of value.

In the following paper we discuss some topics which are of current interest to the authors; the choice of topic is ultimately a personal one, and it would be unwise, as well as presumptuous, to attempt to predict future developments in our subject.

FREE RADICAL POLYMERIZATIONS

Uncatalysed polymerizations

Uncatalysed polymerizations are remarkably difficult to study experimentally on account of the high degree of monomer purity required to ensure reproducible results. Many monomers, apparently well purified, will readily undergo thermal polymerization; in no case does an established mechanism exist.

Methyl methacrylate is a notorious example of a monomer of which the uncatalysed reaction has been studied by several groups of workers, without the emergence of an accepted mechanism². To explain the observed behaviour it has been necessary to postulate unusual phenomena such as the thermal formation of an inhibitor and photochemical formation of a catalyst of comparatively long life.

Styrene has given more reproducible results. The rates of thermal polymerization are much higher than those observed with methyl methacrylate. After a series of conflicting results Mayo³ carried out a careful study of the thermal polymerization of styrene and suggested that the main chain-starting process was third order in monomer. More recent work by Mayo⁴ suggests that the mechanism of thermal initiation involves the initial formation of a dimer which then interacts with a further molecule of styrene to give radicals capable of initiation. This process is considered to be much more likely than a simple bimolecular interaction of monomer molecules to give radicals; Mayo suggests further that a number of monomers may not polymerize thermally on account of their inability to form suitable reactive dimer intermediates.

This suggestion is particularly interesting in view of recent observations of Leeming, Lehrle and Robb⁵, who are currently investigating the thermal

polymerization of chloroprene. They find that reproducible dilatometric rates of thermal polymerization can only be achieved if the monomer is isolated from the vapour phase by a mercury plug. Polymerization is complicated by the simultaneous formation of significant amounts of dimers. Four different dimers may arise. In experiments carried out in the presence of inhibitors it was shown that the rate of dimer formation equals the rate of polymer formation in the uninhibited reaction. Analysis of the contents of the reaction vessel in the absence of inhibitor at various stages of the polymerization showed that an approximately stationary concentration of dimer is present throughout. These results suggest that the rate of thermal polymerization is controlled by the rate of dimer formation. Experiments on the bulk polymerization of the dimers showed that the presence of small concentrations of monomer (~ 5 per cent) is necessary for significant rates of polymer formation to be achieved. It would appear from the work of Leeming *et al.* that the bulk thermal polymerization of chloroprene at 35°C is the result of the polymerization of dimers formed spontaneously by Diels-Alder type reactions; possibly trace impurities in the monomer may catalyse polymerization of the dimers, so that with very pure monomer dimers alone may be formed. The structure of the polymer does not appear unusual, and the formation of a single polymer from dimers of quite different structure is remarkable and so far unexplained.

Initiators based on metal carbonyls

In an earlier report⁶ we described some of the characteristic properties of metal carbonyl-organic halide systems as free radical initiators, and we now continue with an account of more recent developments. The main kinetic features encountered are the following; some of these have been recognized since the earlier paper was written.

(i) The rate of polymerization at constant [halide] is proportional to the square root of the carbonyl concentration provided the latter is sufficiently low. This would be expected for a free radical reaction. At higher carbonyl concentrations inhibition is encountered, the rate of polymerization increasing less rapidly than [carbonyl]^{1/2}. Under these conditions some species is interfering with the initiation process (not the propagation); the magnitude of the effect varies markedly from one carbonyl to another, being large^{7,8} with $\text{W}(\text{CO})_6$ and $\text{Ni}(\text{CO})_4$ and small^{9,10} with $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$.

(ii) In all cases the dependence of the rate of polymerization on halide (*e.g.* CCl_4) concentration is of the same form; the rate is nearly zero for [halide] = 0, increases rapidly with halide concentration and, finally, becomes almost independent of the latter. The sharpness of the dependence is a function of the natures of the carbonyl, halide and solvent¹¹ present.

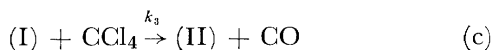
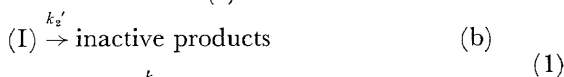
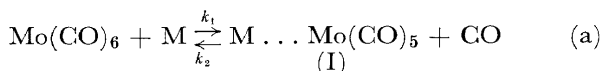
(iii) By using carbon tetrachloride labelled with ^{14}C it has been shown that radioactivity is incorporated into the polymer to an extent which indicates that the initiating radicals are $\dot{\text{C}}\text{Cl}_3$ (or perhaps the equivalent MCCl_3 , M representing a monomer molecule)¹². A similar conclusion has been drawn from the use of polymers containing $-\text{CCl}_3$ groups as the halide components, in which case polymer networks are formed if the radicals of the vinyl monomer undergo combination to some extent in the termination reaction. The initial radicals in this case must be derived from the $-\text{CCl}_3$ groups by

abstraction of chlorine atoms, so that the new polymer chains grow from the $-\dot{\text{C}}\text{Cl}_2$ residues. The formation of networks in this way, which is perhaps one of the more important practical aspects of the use of these initiators, is the subject of a separate communication to this conference.

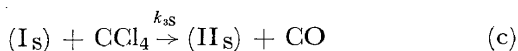
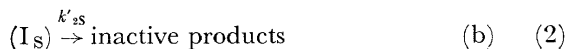
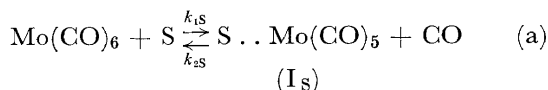
(iv) Carbon monoxide inhibits the polymerization. The magnitude of this inhibition seems to be a characteristic of the periodic group of the metal, the order being



We remarked earlier that the form of the halide dependence could imply the existence of a potentially rate-determining step in the process which does not involve the halide, and we suggested⁶ that this might be a reaction with monomer(M) represented by equation (1a) for molybdenum carbonyl.



The simple kinetic scheme based on (1a) and the subsequent reactions (1b, c, d) was shown to be in good agreement with the available observations for a number of carbonyls. According to (1), the overall order in [M] for the polymerization reaction should be 1.5, and this has been shown to hold accurately when benzene is used as diluent¹¹. Under these conditions all the kinetic features can be derived from (1) on the assumption that benzene is merely an inert diluent. Such is by no means true when ethyl acetate is used as diluent. In this case the reaction is of first order in [M], and the halide dependence becomes much sharper. We believe these findings are best explained by postulating that ethyl acetate (and some other solvents, but not benzene) can replace monomer in reaction (1a), *i.e.* that we now have the additional processes shown in (2a-d), in which S represents an active solvent.



Other solvents which have sufficient electron-donating power behave like ethyl acetate; among those we have studied are dioxan and acetic anhydride. In each case, the rate of initiation I at constant [M] and "high" [halide] is linear in [S], as would be anticipated from (2). (To obtain this result a further component must be added as diluent; benzene, being inactive, was used for this purpose). Thus we have in general at "high" [halide]:

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$$I = \{k_1[M] + k_{1S}[S]\} [\text{Mo}(\text{CO})_6] \quad (3)$$

From kinetic observations (at zero CO pressure) the parameters k_{1S} , k_{3S}/k'_{2S} may be evaluated, with the results^{11, 13} shown in *Table 1*. We do not think these results are complicated by any dielectric effects; thus the dielectric constants of benzene and dioxan are similar, but the two liquids behave quite differently.

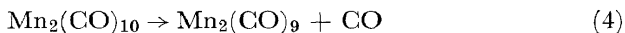
The magnitude of k_{1S} (together with k_1) determines the maximum rate of initiation which is obtainable with a given reaction mixture (through the relation (3)) while k_{3S}/k'_{2S} determines the sharpness of the dependence of the rate on $[\text{CCl}_4]$. Clearly from the results in *Table 1* this dependence is extremely sharp for ethyl acetate compared to monomer. This is further

Table 1. Kinetic parameters at 80°C for systems containing $\text{Mo}(\text{CO})_6$

<i>Solvent:</i>	<i>None</i>	<i>Ethyl acetate</i>	<i>Dioxane</i>	<i>Acetic anhydride</i>	<i>Benzene</i>
$10^5 k_{1S}$	1.3 (= $10^5 k_1$)	1.4	0.75	1.87	0
k_{3S}/k'_{2S}	33.3 (= k_3/k'_2)	355	163	230	0
$10^5 k_{CO}$ ($[\text{CCl}_4] = 0$)	1.2	1.0	0.56		
Overall order in $[\text{M}]$ at constant $[\text{S}]$ (37.5% v/v):			1.25	1.20	1.5

evidence for the formation of a separate species (I_S) from the solvent, since ethyl acetate and monomer are not very dissimilar chemically, and it would, therefore, be surprising if there were a marked medium effect (see below). It would be of interest to determine the values of k_{3S}/k'_{2S} for a series of different solvents of related constitution (*e.g.* a group of esters) for a given halide, and also for a series of different halides for a given monomer-solvent mixture. In this way one should obtain interesting information about the effects of the structures of these components on the relative rates of (2b) and (2c). Unfortunately such results are not available at present.

The above results apply to molybdenum carbonyl. With manganese carbonyl¹⁴ the situation is different. The polymerization with this initiator is always first order in monomer concentration, showing that monomer does not enter into the initiation in a rate-determining manner. Further, the rate of reaction at constant $[\text{M}]$ is not much affected by the nature of the solvent. Probably the first step is the direct scission of CO



It is interesting that the dependence of the rate on halide concentration is likewise unaffected by changing the solvent. This would be expected if $\text{Mn}_2(\text{CO})_9$ reacts directly with the halide without solvent intervention. The contrast between the behaviour of $\text{Mo}(\text{CO})_6$ and $\text{Mn}_2(\text{CO})_{10}$ in this respect is shown in *Figure 1*.

Manganese carbonyl in the presence of a suitable halide is an active photosensitizer of polymerization, even in visible light. Bamford, Crowe and Wayne¹⁵ have shown that the kinetics are similar to those of the thermal

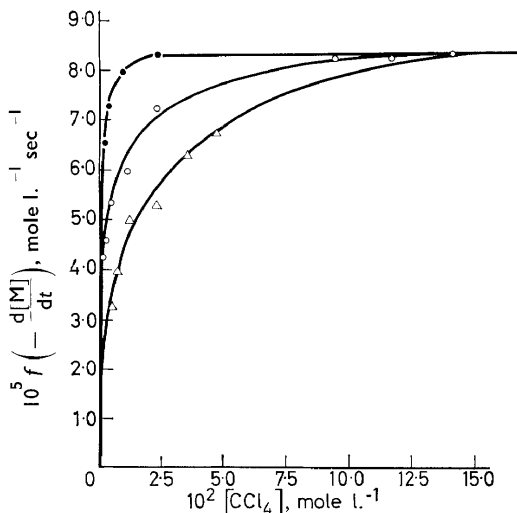


Figure 1. Dependence of the initial rate of polymerization of methyl methacrylate at 80°C on the concentration of carbon tetrachloride. All curves normalized (factor f) at 'high' $[\text{CCl}_4]$, $[\text{Monomer}] = 3.3$ mole l.^{-1}

- $[\text{Mn}_2(\text{CO})_{10}] = 1.5 \times 10^{-3}$ mole l.^{-1} using benzene or ethyl acetate as solvents, $f = 2.33$
- $[\text{Mo}(\text{CO})_6] = 3.49 \times 10^{-4}$ mole l.^{-1} , ethyl acetate as solvent, $f = 1.0$
- △ $[\text{Mo}(\text{CO})_6] = 3.49 \times 10^{-4}$ mole l.^{-1} benzene as solvent, $f = 1.55$

reaction, except for points of detail. The quantum yield γ for initiation ($\lambda = 4358\text{\AA}$) is close to unity, hence it has been suggested that (4) represents the primary act. If the metal-metal bond were dissociated the value $\gamma = 1$ would, of course, be fortuitous, unless two dissimilar fragments, one of them unreactive, were formed.

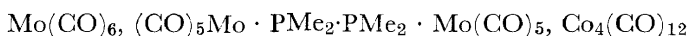
Further information about the nature of the primary processes in these reactions may be obtained by studying the rate of evolution of carbon monoxide. It appears that the initial rate of formation of carbon monoxide from molybdenum carbonyl in solution in different media, in the absence of halide, is quite close to the rate of initiation deduced from the rate of polymerization, measured at "high" halide concentration. This would be expected from the mechanism already proposed; the initial rate of evolution of carbon monoxide is the rate of the forward reaction (1a) or (2a) and this represents the maximum rate of chain starting. It is assumed that (1b), (2b) neither evolve nor absorb carbon monoxide. The values of k_{CO} calculated from the equation

$$\frac{d[\text{CO}]}{dt} = k_{\text{CO}}[\text{Mo}(\text{CO})_6][\text{S}] \quad (5)$$

are shown in Table 1 for monomer, ethyl acetate and dioxan solutions, and are satisfactorily close to the corresponding values of $k_{1\text{S}}$. In benzene and cyclohexane solutions no carbon monoxide is evolved, in agreement with the observed absence of an initiation process involving these hydrocarbons. Further, the rate of evolution of carbon monoxide from solutions of $\text{Mo}(\text{CO})_6$ in CCl_4 is extremely slow. This is clear evidence against the occurrence of a

direct reaction between molybdenum carbonyl and carbon tetrachloride during initiation. Again the situation with manganese carbonyl is different¹⁴. The rate of evolution of carbon monoxide is still equal, within experimental error, to the maximum rate of initiation for the same carbonyl concentration (*i.e.* at high [halide]), but it is independent of the nature of the medium. This obviously supports the idea already put forward that the rate determining process in initiation does not involve the intervention of a monomer or solvent molecule and may be represented by (4).

A few determinations have been made of the efficiency of initiation *i.e.* the number of chains started per carbonyl molecule decomposed¹⁶. In the three cases which have been examined it turns out that when CCl_4 is the halide one chain is initiated for each metal atom in the carbonyl decomposed. The carbonyls which have been studied in this way are



The oxidation number of the metal thus appears to increase by unity as a result of initiation. A paramagnetic species¹¹ giving a strong ESR signal in solution is formed from $\text{Mo}(\text{CO})_6$, and may be derived from $\text{Mo}^{(I)}$, although this has not been established with certainty. Efforts have been made to characterize the products of reaction in systems containing $\text{Mo}(\text{CO})_6$, CCl_4 and a reactive solvent such as ethyl acetate or dioxan. So far characterization has not been possible; it appears that radical attack on the solvent produces a mixture of substances which act as ligands and produce a complex mixture of molybdenum derivatives¹⁶. No ESR spectrum can be obtained from the reaction products from $\text{Cr}(\text{CO})_6$ and $\text{W}(\text{CO})_6$. This may indicate the formation of final oxidation states of these metals which are different from that of molybdenum, or alternatively it may merely be a result of the magnitude of the relaxation times.

We have already referred to the inhibition which generally occurs at high carbonyl concentrations. Recently an indication of the reactions which are responsible for this has been obtained¹⁶. As already explained, the activity of a halide is measured by the sharpness of the rate-[halide] curve, *i.e.* by the ratio k_3/k'_2 in systems containing no added solvent. It has been found that with $\text{Mo}(\text{CO})_6$ the importance of inhibition depends inversely on the activity of the halide. This is apparent from *Figure 2*: with chloroform, which is rather inactive, there is very strong inhibition, carbon tetrachloride, with greater activity shows less, while with the very active ethyl trichloroacetate there is no inhibition at the higher concentration. Inhibition is observed at a very low concentration of ethyl trichloroacetate. These observations suggest that inhibition arises from the interaction of species (I) and (II) in (I); in the presence of a sufficiently high concentration of an active halide the concentration of (I) would be very small, consistent with the absence of inhibition. It is not known how far this observation may be extended to other carbonyls; if the effect is general the use of very active halides will be of considerable practical importance in allowing much higher rates of polymerization to be obtained with the aid of higher carbonyl concentrations.

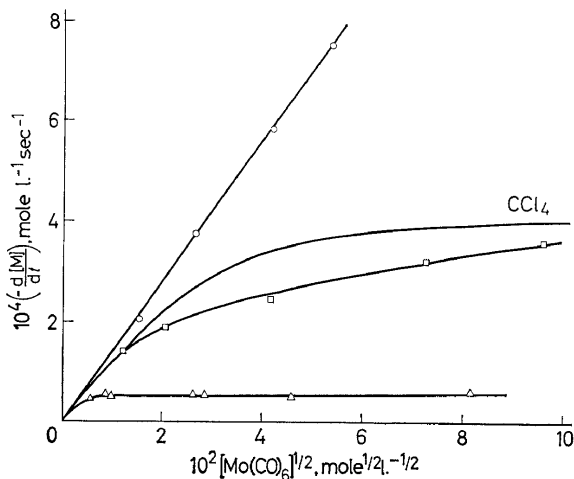


Figure 2. Variation of initial rate of polymerization of methyl methacrylate at 80°C with molybdenum carbonyl concentration in the presence of various halogen compounds

△ $[\text{CHCl}_3] = 0.192 \text{ mole l.}^{-1}$

○ $[\text{CCl}_3\text{CO}_2\text{C}_2\text{H}_5] = 0.192 \text{ mole l.}^{-1}$

□ $[\text{CCl}_3\text{CO}_2\text{C}_2\text{H}_5] = 0.0143 \text{ mole l.}^{-1}$

Carbon tetrachloride curve, $[\text{CCl}_4] = 0.192 \text{ mole l.}^{-1}$

We conclude this section by providing some comparative data on the relative reactivities of the carbonyls as initiators. For this purpose we show in Table 2 the values of 10^6a at 60°C, where a , defined by the relation

$$I = a[\text{carbonyl}],$$

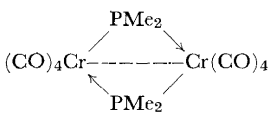
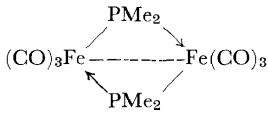
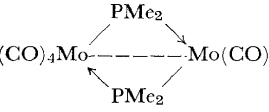
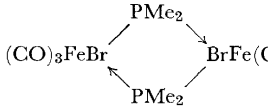
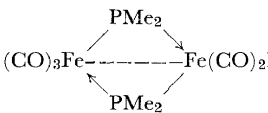
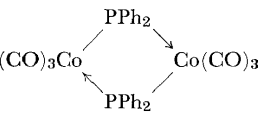
is a measure of the rate of initiation at limiting halide concentration in effectively bulk methyl methacrylate.

One of the most interesting features of these results is the high activity of dinuclear carbonyls carrying phosphine bridges. This is apparent for the chromium, molybdenum and iron compounds listed in the Table. In the mononuclear iron compounds, substitution of CO by PPh_3 increases the activity, and the same has been found¹⁰ for the binuclear rhenium derivatives $\text{Re}_2(\text{CO})_{10}$, $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$. Replacement of CO by PR_3 would be expected to increase the strength of the bonding of the remaining CO groups by increasing the extent of back-donation from the metal, and so to decrease the rate of initiation, if this process involves displacement of CO. Accordingly, it has been suggested that the primary process in initiation in these cases is the rupture of a metal-phosphine bond, rather than a metal-carbonyl bond¹⁰. An indication that this also occurs in the case of the bridged phosphine derivatives has been found, since the rate of evolution of carbon monoxide from the molybdenum compounds (in the absence of halogen compound) is very much smaller than the rate of initiation. At high carbon tetrachloride concentrations in monomer solution, two molecules of CO are evolved per molecule of carbonyl decomposed (*i.e.* one CO per molybdenum atom),

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consistent with a reaction scheme similar to (1), but with (1a) replaced by a step in which a metal-phosphine bond is broken without evolution of CO. Similar results are obtained in inert solvents such as benzene, cyclohexane, suggesting that the primary scission does not require the intervention of a monomer or solvent molecule.

 Table 2. Values of 10^6a (sec^{-1}) at 60°C

$\text{Cr}(\text{CO})_6$	0.10	$\text{Fe}(\text{CO})_5$	0.7
	72	$\text{Fe}(\text{CO})_4(\text{PPh}_3)$	3.0
$(\text{CO})_5\text{Cr}.\text{PMe}_2.\text{PMe}_2.\text{Cr}(\text{CO})_5$	0.50	$\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$	6.4
$\text{Mo}(\text{CO})_6$	5.0		18
	1,200		350
$(\text{CO})_5\text{Mo}.\text{PMe}_2.\text{PMe}_2.\text{Mo}(\text{CO})_5$	2.5	$(\text{CO})_4\text{Fe}.\text{PMe}_2.\text{PMe}_2.\text{Fe}(\text{CO})_4$	22
$(\text{CO})_5\text{Mo}.\text{PEt}_2.\text{PEt}_2.\text{Mo}(\text{CO})_5$	12		10
	2,250	AZDN	7.9

A further noteworthy feature of *Table 2* is the remarkable increase in activity in the bridged phosphine derivative of iron carbonyl brought about by introduction of two bromine atoms into the molecule. It is not yet clear whether this is a result of steric or electronic effects*. Finally, we may note that the linear phosphine derivatives listed show little, if any, inhibition at high concentrations, and thus differ from the majority of carbonyl derivatives.

It is clear that much further investigation will be required before we possess a complete picture of the factors which influence the activity of the carbonyls and their derivatives in the type of reaction we are considering. Clearly the intervention in the primary process of monomer, or electron-donating solvent, depends on the nature of the metal atom, but for a given metal it is also affected by the chemistry of the ligands. Elucidation of this behaviour seems essential to an understanding of the relative activities of the carbonyl derivatives.

* Recent work has shown that the high activity results from the decrease in electron density on the metal atoms produced by the introduction of halogen.

Initiators based on phenyl isocyanide derivatives

The hexaphenylisocyanide derivatives of the Group VI metals, with general formula $M(\text{CNC}_6\text{H}_5)_6$, were first prepared by Malatesta and Sacco¹⁷. They are bright red solids, of rather limited solubility but with reasonable thermal stability.

As a ligand, phenyl isocyanide resembles carbon monoxide, except that the extent of back-donation from the *d*-orbitals of the metal to the ligand is less important, so that the double bond character of the metal-carbon bond is reduced and the ligand is less firmly held. The derivatives initiate polymerization in a manner remarkably similar to that of the carbonyls, but, as would be expected, they are rather more active¹⁸. No initiation can be obtained in the absence of a suitable halide; the relation between the rate of polymerization and the halide concentration is of the familiar form already described.

Inhibition is generally less marked than with the carbonyls; *Figure 3* shows plots of rate of polymerization against the square root of the concentration for several chromium derivatives, for constant $[\text{CCl}_4]$, and it will

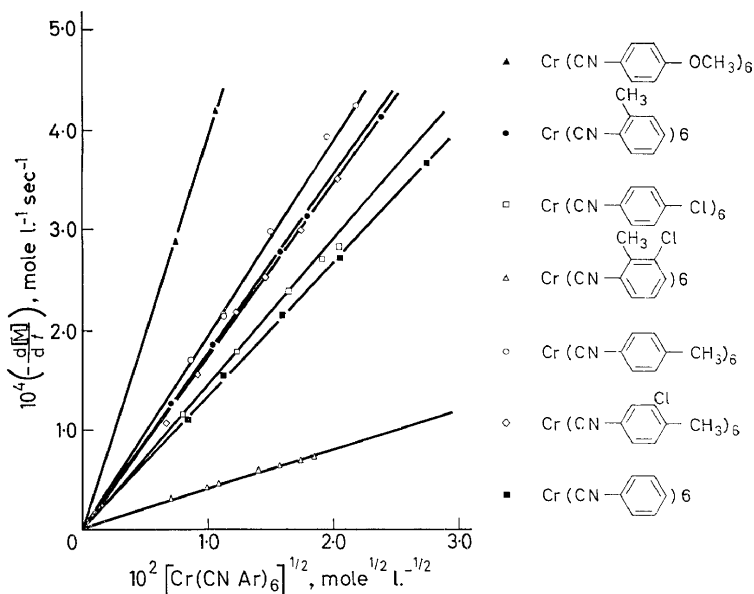


Figure 3. Initial rates of polymerization of methyl methacrylate at 80°C initiated by various chromium hexaphenylisocyanide derivatives in the presence of carbon tetrachloride, $[\text{CCl}_4] = 0.142 \text{ mole l.}^{-1}$

be seen that inhibition is virtually absent. The rates of initiation are affected by the introduction of substituents into the benzene rings¹⁹. It seems that those groups leading to an increase in electron density in the isocyanide group increase the rate of initiation. This is very marked for the *p*-methoxy derivative shown in *Figure 3*, for which $10^6a = 1600$ at 80°C, compared

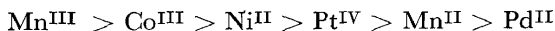
to a value of 93 for the unsubstituted isocyano-derivative. Possibly the increase in electron density reduces the extent of back-donation from the filled *d*-orbitals of the metal, and so reduces the stability of the compound. The low activity of the derivative carrying *o*-Me and *m*-Cl substituents is not easy to understand, particularly in view of the much higher activity obtained with closely related derivatives.

There is at present no evidence as to whether the primary process in initiation is a dissociation of the isocyanide, or involves a reaction with monomer. The overall process seems similar to that found with the carbonyls *viz.* extraction of a halogen atom from the halide molecule. In agreement with this, networks are formed when polymers carrying $-\text{CCl}_3$ groups are used as the halide component of the initiators, as with the carbonyls. The products of the initiation reaction with $\text{Mo}(\text{CNPh})_6$ give an ESR spectrum similar to that which arises from reaction of $\text{Mo}(\text{CO})_6$, while no spectra can be obtained from the corresponding chromium and tungsten compounds.

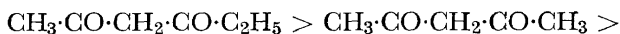
The relatively high activity of the isocyano derivatives and the possibility of modifying this by introducing substituents into the molecules make these compounds attractive for further study.

Initiation by metal chelates

In the course of their work on the mechanism of oxidation of metal chelates by oxygen, Arnett and Mendelsohn²⁰ noted that certain chelates, particularly $\text{Mn}(\text{acac})_3$, were able to accelerate the thermal polymerization of styrene at 100°C. Kastning, Naarmann, Reis and Berding²¹, and also Bamford and Lind²² have subsequently studied polymerizations initiated by a number of metal chelates. Kastning *et al.* compared the activities of a series of acetylacetonates by heating 0.5 per cent w/w solutions in styrene for one hour at a constant temperature, generally in excess of 100°C, and noting the temperatures at which "active" initiation occurred. The order of reactivity was found to be:



By using various ligands with Mn^{III} , Kastning *et al.* observed the following order of activity:



Bamford and Lind²², working with methyl methacrylate at 80°C, with chelate concentrations of the order of 10^{-3} mole l.⁻¹, confirmed that $\text{Mn}(\text{acac})_3$ is an active initiator, and found $\text{Ni}^{\text{II}}(\text{acac})_2$, $\text{V}^{\text{III}}(\text{acac})_3$ and $\text{Cr}^{\text{III}}(\text{acac})_3$ to be weak initiators, and $\text{Co}^{\text{III}}(\text{acac})_3$, $\text{TiO}(\text{acac})_2$ and $\text{Pb}(\text{acac})_2$ to be devoid of activity. The rate of polymerization initiated by $\text{Mn}(\text{acac})_3$ is proportional to $[\text{Mn}(\text{acac})_3]^{\frac{1}{2}}$ over the whole concentration range studied, and at 80°C is given by

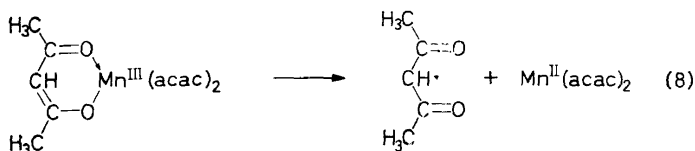
$$\omega = 1.0 \times 10^{-2} [\text{Mn}(\text{acac})_3]^{\frac{1}{2}} \text{mole l.}^{-1} \text{sec}^{-1}. \quad (6)$$

The square root relation suggests a free radical polymerization, and this is confirmed by molecular weight data, which allow calculation of $k_p/\sqrt{k_t}$.

The value obtained ($0.17 \text{ mole}^{-1} \cdot \frac{1}{2} \text{sec}^{-1}$) is close to that observed in the polymerization of methyl methacrylate using conventional free radical initiators. From (6) we obtain

$$I = 4.6 \times 10^{-5} [\text{Mn}(\text{acac})_3] \text{ mole l.}^{-1} \text{ sec}^{-1} \quad (7)$$

This chelate is, therefore somewhat less active, as an initiator than is molybdenum carbonyl at 80°C . The rate of polymerization is first order in monomer concentration, showing that the monomer does not participate in the radical forming process in a rate determining manner. The suggested initiation reaction is



a type of decomposition previously postulated by Arnett and Mendelsohn²³. However, Kastning *et al.*²¹ state that they could not observe any valency change in the metal resulting from initiation, although they do not provide any details of the technique used.

At low concentrations the derivatives $\text{Mn}(\text{C}_6\text{H}_5\text{CO}\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_5)_3$ and $\text{Mn}(\text{ClC}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Cl})_3$ behave like $\text{Mn}(\text{acac})_3$, but at higher concentrations the rates are less than would be anticipated from square root dependence²². Furthermore, the apparent values of $k_p/\sqrt{k_t}$ are low, suggesting that some retardation process must be operative. Retardation might be responsible for the much lower activity of $\text{Mn}(\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_5)_3$ found by Kastning *et al.* at the relatively high concentrations used in their work²¹.

Kastning *et al.*²¹ reported an increase in the rate of initiation at 100°C brought about by the presence of various additives, notably organic halides and unsaturated hydrocarbons (dienes, trienes and tetraenes). Bamford and Lind²² did not observe a comparable effect with carbon tetrachloride at 80°C . However, particularly active halides, *e.g.* ammonium trichloroacetate, together with some metal chelates (particularly $\text{Cu}^{\text{II}}(\text{acac})_2$) have been observed^{22a} to initiate readily at 80°C , although $\text{Mn}^{\text{III}}(\text{acac})_3$ does not appear to be active in this respect.

RADICAL REACTIVITY IN COPOLYMERIZATION

In recent years interest in the reactivities of radicals in copolymerization has been maintained. Two particular lines may be discerned (*a*) attempts to revise the base-points in the *Q-e* scheme, and (*b*) efforts to produce

alternative semi-empirical treatments superior to the $Q-e$ scheme. We shall consider the latter of these.

In 1959, Bamford, Jenkins and Johnston²⁴⁻²⁶ published their treatment of radical reactivity (which we shall call the BJJ treatment) according to which the rate constant k_s for the reaction of a (polymeric) radical with any substrate S was expressed in the form:

$$k_s = k_{3,T} + \alpha_s \beta + \sigma_s \quad (9)$$

in which $k_{3,T}$ is the rate constant for the disproportionation reaction of the radical with toluene, σ is the Hammett σ -value for the substituent group of the radical (regarded as an α -substituted ethyl radical), and α_s, β_s are constants dependent only on the nature of the substrate. The use of σ is intended to allow for polar contributions to the transition state. Equation (9) was shown to apply both to transfer and addition reactions. It was pointed out²⁵ that, in a homopolymerization, a relation might be expected between α_s (in this case α_M , since the monomer is the substrate) and σ , since both these quantities result from the effect of the same substituent group, and from a survey of the data equation (10) was proposed:

$$\alpha_M = -5.3\sigma \quad (10)$$

If this is adopted, there is a formal similarity between the $Q-e$ scheme, and the BJJ treatment, which would be complete provided that the standard e -value selected for the H atom had been zero. However, the $\alpha_M - \sigma$ correlation is not an essential part of the theory, and indeed can lead to appreciable errors, *e.g.* with vinyl acetate. The correlation is really a makeshift, intended for use when σ has not been determined.

Quite recently Ham²⁷⁻²⁹ has presented a further empirical approach to the problem of predicting monomer reactivities in copolymerization, which, he claims offers "a more direct and possibly more precise means than the $Q-e$ scheme and rests on a logical and easily discernible concept". Ham gives the relation

$$P_{ab} P_{bc} P_{ca} = P_{ac} P_{cb} P_{ba} = P. \quad (11)$$

P is a constant and the P 's are the probabilities of addition of the monomers A, B, C to specific radicals; thus, with the ordinary terminology of copolymerization

$$P_{ab} = \frac{k_{ab} [A\cdot] [B]}{k_{aa} [A\cdot] [A] + k_{ab} [A\cdot] [B] + k_{ac} [A\cdot] [C]} \quad (12)$$

and so on. If $[A] = [B] = [C]$

$$P_{ab} = \frac{1/r_{ab}}{1 + 1/r_{ab} + 1/r_{ac}} \text{ etc.} \quad (13)$$

where the r 's represent reactivity ratios. The basis of Ham's equation (11) is the supposedly equal probability of occurrence of a sequence such as ABCA and its inverse ACBA. Similar considerations have been applied to longer sequences, extending to the length of a kinetic chain. It seems clear that if this principle is true, then the interactions between the various

radicals and monomers must be symmetrical. If (11) holds, it follows that

$$r_{ab} r_{bc} r_{ca} = r_{ac} r_{cb} r_{ba}. \quad (14)$$

Ham has proposed using these equations to predict reactivity ratios in binary systems. For example, if the four reactivity ratios for the systems A—B, B—C are known (*i.e.* r_{ab} , r_{ba} , r_{bc} , r_{cb}) then from (14) the ratio r_{ca}/r_{ac} for the system A—C may be calculated. If the value of P in (11) is known, then the separate reactivity ratios r_{ca} , r_{ac} may also be estimated. Ham²⁸ has provided values of P suitable for use in monomer systems of different kinds, depending on whether the monomers are conjugated or unconjugated.

Mayo³⁰ has pointed out that (14) follows directly from the equations of the $Q-e$ scheme, and also from the BJJ treatment, provided (10) is used. Further, he has criticised the choice of numerical data used by Ham to support his relations. Mayo concludes that for many systems the available data are not consistent with (14), the discrepancies being well outside the limits of experimental error. This naturally applies also to the results of the $Q-e$ and BJJ calculations. As Mayo says "All of these relations are based on the same underlying approximations: that monomer reactivity ratios for any pair of monomers are constant over a wide range of feeds at a given temperature, that steric and penultimate effects are negligible, and that any special (polar) interactions between A· and B and between B· and A (and so on) are symmetrical". He, therefore, proposes the use of (14) as a test of the adequacy of the theoretical approximations when experimental data for all three pairs of monomers are known. For this purpose (14) is rewritten in the form (15)

$$\frac{r_{ab} r_{bc} r_{ca}}{r_{ac} r_{cb} r_{ba}} = H, \quad (15)$$

and the departure of H from unity is used as a numerical measure of the inadequacy of the theoretical treatments.

Jenkins³¹ has noted very recently that the assumption of symmetrical polar interactions need not be invoked, and has consequently calculated H on the basis of (9) without the use of (10) for the fourteen systems for which the relevant parameters are known—actually most of those listed by Mayo³⁰. The relation derived from (9) is²⁶

$$-\log H = \sigma_a(a_b - a_c) + \sigma_b(a_c - a_a) + \sigma_c(a_a - a_b). \quad (16)$$

Jenkins finds that for the fourteen systems investigated the mean calculated value of H is 0.76 instead of unity; the observed value is 0.55. (Mayo's convention has been adopted here. H is always taken to be < 1 ; if the value calculated from (15) turns out to be > 1 the reciprocal is taken instead). Whereas the $Q-e$ scheme (which always gives $H = 1$) is sometimes in error by as much as a factor of 14, the maximum disagreement between (16) and experiment is always less than a factor of two. *Figure 4*, taken from Jenkins' paper, illustrates the comparative extents of agreement. Here observed values of H are plotted against those calculated from (16) (without the use of Mayo's convention), and the straight line of unit slope, representing perfect agreement, is also shown. The points are scattered in an apparently random

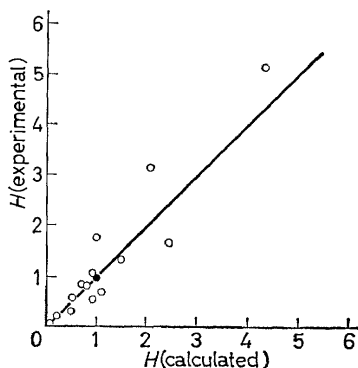


Figure 4. Comparison of experimental and calculated values of H , as defined in equation (15). The line drawn is that for $H(\text{exp.}) = H(\text{calc.})$. (After Jenkins³¹)
 • represents $H(\text{exp.}) = H(\text{calc.}) = 1$

manner about this line. Other methods of calculation predict $H_{\text{calc.}} = 1$ in all cases, and may thus be greatly in error.

It thus appears that relaxation of the symmetry restriction increases the value of the empirical scheme. Although more parameters are thus required (the σ values) it is important to realize that these are not at all empirical in the present sense, since they are determined by a completely different type of observation and cannot be adjusted to fit any polymerization data. The agreement between (16) and experiment is probably within experimental error at present. Mayo³⁰ has stressed the importance of obtaining better data. One point worthy of note is that homogeneous and heterogeneous systems are often used indiscriminately in evaluating reactivity ratios, and this is clearly unsatisfactory, at least in principle and probably in practice.

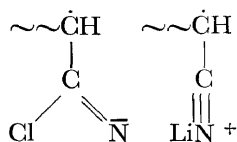
We believe that the accuracy of Ham's interesting postulate is not very different from that of the $Q-e$ scheme, but before this can be established a more rigorous statistical examination of the errors inherent in the measurements is necessary.

RADICAL COMPLEXES

A number of references in the literature refer to complex formation between propagating radicals and other species present in the reaction mixture. Complex formation has been invoked to explain (a) unexpected reaction paths and (b) changes in the microstructure of polymers brought about by additives.

One of the earliest instances was provided by Mayo's work³² on the transfer reaction between styryl radicals and bromobenzene. This showed that transfer occurred without incorporation of bromobenzene fragments into the polymer, and Mayo suggested that the halogen compound forms a complex with the growing chains (or alternatively with an abstracted hydrogen atom) which then reacts with the monomer by transferring a hydrogen atom to the latter and liberating bromobenzene and a dead polystyrene molecule. Clearly the process is kinetically equivalent to a transfer reaction. Mayo cites other evidence for complex formation between radicals

and aromatic substances. It is possible that complex formation between polyvinylacetate radicals and benzene may be responsible for the recent findings of Bengough, Brownlie and Jerguson³³. Burnett and co-workers have also postulated the existence of complexes incorporating radicals and halogenated aromatic solvents³⁴. Bamford, Jenkins and Johnston³⁵ suggested that interaction between polyacrylonitrile radicals and salts such as LiCl gives complexes of the types



which have reactivities different from that of the simple radicals. Eaton³⁶ has recently studied complexing of metal ions with semiquinone radicals by ESR. There is thus considerable evidence of different kinds in the literature for radical complexing.

Changes in polymer microstructure brought about by additives have been attributed to complex formation by Rosen, Burleigh and Gillespie³⁷ (polyvinyl chloride radicals-butyr-aldehyde), by Kargin, Kabanov and Zubov³⁸ (polymethyl methacrylate radicals and zinc chloride) and by Bamford, Blackie and Finch³⁹ (polymethyl methacrylate radicals and metal carbonyls). Bovey and Tiers^{40, 41} could not find any NMR evidence for the structural changes postulated by Rosen *et al.* or by Kargin *et al.*, although they thought that complex formation may reduce the degree of branching in the polyvinyl chloride systems. The changes reported by Bamford, Blackie and Finch were not large and require further investigation. Work is in progress in our laboratories on this subject; possible structural changes as well as variations in velocity coefficients of component reactions are being sought. If radical complexing can be studied by physical techniques (*e.g.*, ESR) and correlated with changes in radical reactivity an interesting area for research will be opened up.

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