Selective Initiation of Free-radical Polymerization by Metal Chelates

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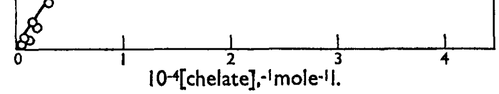
SEVERAL groups of workers have shown that certain metal acetylacetonates are capable of initiating the polymerization of vinyl monomers.[1-3] We have previously reported[3] the relatively high activity of manganic acetylacetonate in initiating free-radical polymerization at 80°, and suggested that the primary step involves the scission of the ligand as a free radical and the reduction $Mn^{III} \rightarrow Mn^{II}$. The latter process has subsequently been confirmed by measurements of magnetic susceptibility.[4]

Our studies have now been extended to $Mn(CF_3{\cdot}CO{:}CH{\cdot}CO{\cdot}CH_3)_3$ [$Mn(facac)_3$], and have revealed that the behaviour of this compound is novel in several respects. The chelate initiates the free-radical polymerization of methyl methacrylate at 80° over 7 times as fast as $Mn(acac)_3$ at the same concentration (see Table), the rate of polymerization, ω, being given by

$$\omega = 2{\cdot}63 \times 10^{-2}[Mn(facac)_3]^{\frac{1}{2}} \text{ mole l.}^{-1}\text{ sec.}^{-1} \quad (1)$$

The free-radical character of the reaction is indicated by (a) the square-root dependence of rate on concentration in (1); (b) the normal value of $k_pk_t^{-\frac{1}{2}}$ derived from measurements of rate and degrees of polymerization, (k_p,k_t are the velocity coefficients of propagation and termination, respectively); and (c) n.m.r. observations, which show that the tacticity of the polymer is identical with that of a polymer prepared at the same temperature with a conventional free-radical initiator.

In the presence of $Mn(facac)_3$, styrene polymerizes only very slowly at 80°, the rate being lower than that of the uncatalysed thermal reaction. The difference between $Mn(acac)_3$ and $Mn(facac)_3$ in their behaviour towards styrene is illustrated in the Table. The fluorinated chelate is a strong retarder of the free-radical polymerization of styrene (see Figure). This is not surprising since the metal atom in $Mn(facac)_3$ has a relatively high positive charge on account of the electron-withdrawing properties of the CF_3 group and styryl radicals are known[5] to react very rapidly with oxidizing ions of transition metals in non-aqueous solution *e.g.*, Fe^{III}. The results in the Figure are consistent with a conventional retardation mechanism, from which it follows that for



FIGURE

Retardation of styrene polymerization at 80° *by* $Mn(facac)_3$. *[Benzoyl peroxide]* = $2{\cdot}0 \times 10^{-3}$ *mole l.*$^{-1}$; ω_0, ω *are the rates of polymerization in the absence and presence of chelate, respectively.*

TABLE

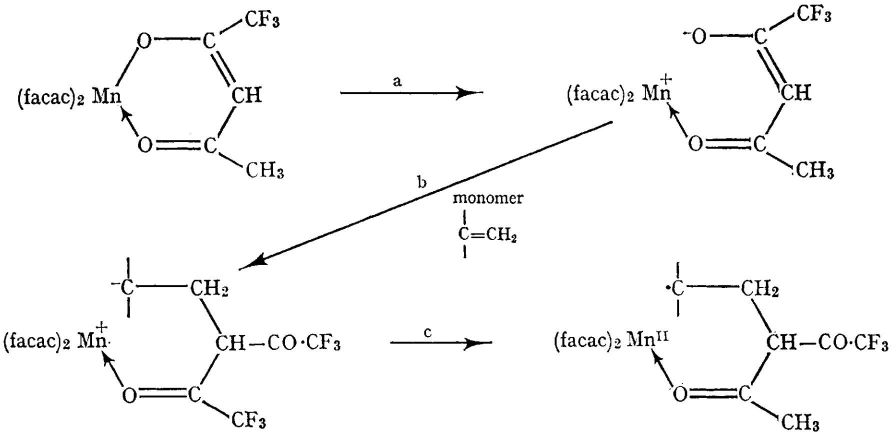
Comparison of Mn(acac)$_3$ *and* Mn(facac)$_3$

T°C	Monomer	Chelate; concentration (mole l.$^{-1}$) × 10^4	10^6 × Rate of polymerization (mole l.$^{-1}$ sec.$^{-1}$)
80	Styrene	Mn(acac)$_3$; 2·5	34
		Mn(facac)$_3$; 2·5	1·6
60	Vinyl acetate	Mn(acac)$_3$; 4·0	190
		Mn(facac)$_3$; 4·0	38
80	Methyl methacrylate	Mn(acac)$_3$; 4·0	210
		Mn(facac)$_3$; 4·0	530
60	Acrylonitrile	Mn(acac)$_3$; 5·8	15
		Mn(facac)$_3$; 5·8	1090

small values of $[C]^{-1}$ the plot should approximate to the straight line

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

Here C represents Mn(facac)$_3$, I is the rate of initiation by benzoyl peroxide, and a, b are the velocity coefficients for initiation and retardation by the chelate, respectively. The value of the intercept in the Figure, *i.e.*, $(a/b)(k_t/I)^{\frac{1}{2}}$ is close to zero, so that a is very small. Thus Mn(facac)$_3$ does not initiate the polymerization of styrene effectively. (If a had the value $3{\cdot}8 \times 10^{-4}$ sec.$^{-1}$, as with methyl methacrylate, the intercept on the ω/ω_0 axis would be 0·11; the observed value is $<10\%$ of this). We conclude, therefore, that initiation by Mn(facac)$_3$ is *selective*, and hence differs strikingly from that by Mn(acac)$_3$ which is non-selective, the polymerization of methyl methacrylate and styrene, for example, being indicated by Mn(acac)$_3$ at the same rate.



(3)

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 (3a), giving an anion, to which monomers with a sufficiently high electron-accepting capacity (*i.e.*, those susceptible to anionic polymerization) may add (3b). The resulting monomer anion is then oxidized by the Mn^{III} atom in the molecule (3c), to form a free radical, which initiates polymerization.

It is possible that steps (3a) and (3b), shown as separate, are combined in a single process, with a polar transition state in which the monomer accepts a negative charge. The proposed mechanism is consistent with the observed low frequency factor, 2×10^6 mole^{-1} l. sec.$^{-1}$, for the initiation of methyl methacrylate polymerization by Mn(facac)$_3$. The frequency factor for the corresponding process with Mn(acac)$_3$ is 8×10^{11} mole^{-1} l. sec.$^{-1}$

A brief comparison of the behaviour of Mn(acac)$_3$ and Mn(facac)$_3$ towards acrylonitrile and vinyl acetate has yielded results in conformity with these ideas. The Table shows that Mn(facac)$_3$ is a relatively ineffective initiator with vinyl acetate, but is extremely effective with acrylonitrile. However, the importance of retardation in the polymerization of these monomers has not yet been elucidated.

The phenomenon of selective 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.

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