Initiation of Polymerization by Ligand Displacement

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Summary Manganese(III) acetylacetonate, in the presence of a suitable electron donor such as dimethyl sulphoxide, is an active, selective, initiator of free-radical polymerization at 25°, the order for the monomers studied being acrylonitrile > methyl methacrylate > styrene: suggested mechanisms for selective and nonselective components of the reaction involve ligand displacement.

CONSIDERABLE interest has been shown in the behaviour of metal chelates as initiators of polymerization.[1-3] Manganese(III) chelates are amang the most active free-radical initiators of this type; we have shown[2] that at 80° manganese(III) acetylacetonate $[\mathrm{Mn^{III}}\,(\mathrm{acac})_3]$ initiates the polymerizations of bulk styrene and methyl methacrylate at similar rates. On the other hand, manganese(III) 1,1,1-trifluoroacetylacetonate $[\mathrm{Mn(facac)_3}]$, while seven times more active than $\mathrm{Mn(acac)_3}$ towards methyl methacrylate, is completely inactive towards styrene.[2] We now report that the rates of initiation by $\mathrm{Mn(acac)_3}$ at 25° (very low in bulk monomer) may be greatly increased (by a factor as large as 1000) by the presence of a suitable donor additive; further, under these conditions the type of selectivity shown by $\mathrm{Mn(facac)_3}$ makes its appearance.

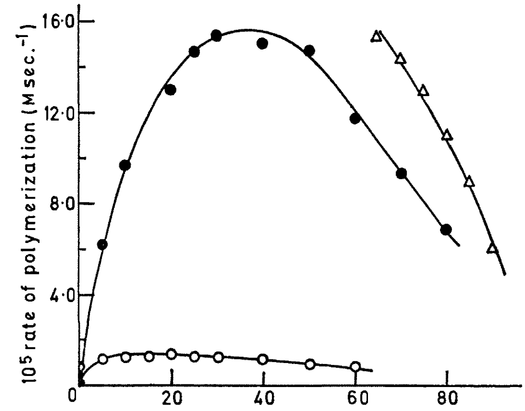


FIGURE 1. *Rates of polymerization of ST* (○), *MMA* (●) *and AN* (△) *in the presence of DMSO at* 25°. $[\mathrm{Mn(acac)_3}] = 5 \times 10^{-3}$ M.

Figure 1 illustrates the rates of polymerization obtained at 25° in dimethyl sulphoxide (DMSO) for styrene (ST) methyl methacrylate (MMA) and acrylonitrile (AN). It is immediately apparent that although the rates of polymerization are negligibly small in the bulk monomers, they can attain high values in the presence of DMSO; thus the maximum rate in Figure 1 for MMA is approximately 10% per hr. These polymerizations are undoubtedly free-radical processes; the rates are proportional to $[\mathrm{Mn(acac)_3}]^{\frac{1}{2}}$, and the values of $k_{\mathrm{p}}k_{\mathrm{t}}^{-\frac{1}{2}}$, determined experimentally for each point shown in Figure 1, were identical with those obtained with a conventional free-radical initiator $(k_{\mathrm{p}})k_{\mathrm{t}}$ are the velocity coefficients for propagation and termination, respectively). Since there are no storage problems associated with $\mathrm{Mn(acac)_3}$, these systems are convenient free-radical sources at room temperature.

Rates of initiation deduced from these data are shown in Figure 2. In their derivation account was taken of the variation of $k_{\mathrm{p}}k_{\mathrm{t}}^{-\frac{1}{2}}$ with reactant composition, which was found to be considerable; this arises from the inverse dependence of k_{t} upon viscosity[4] and partly from changes in k_{p}, in the case of MMA.[5] Selectivity in initiation is shown in Figure 2; the observed order AN > MMA > ST is the same as that encountered[2] in the bulk monomers with $\mathrm{Mn(facac)_3}$ at 80°, although it should be noted that the rate of initiation in styrene may be quite high in the present systems.

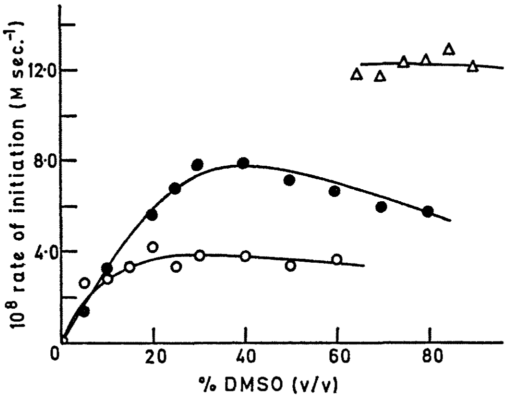


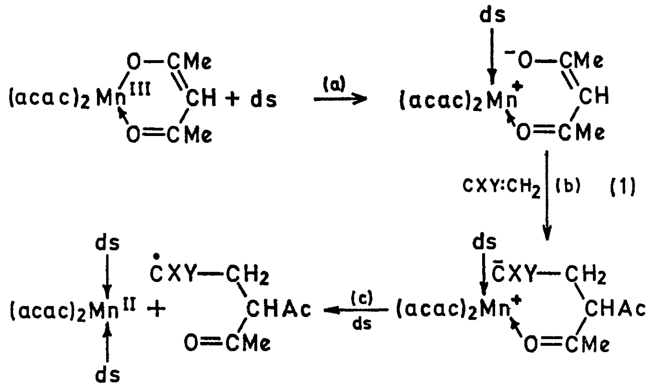
FIGURE 2. *Rates of initiation of polymerization of S* (○), *MMA* (●), *and AN* (△) *in the presence of DMSO at* 25°. $[\mathrm{Mn(acac)_3}] = 5 \times 10^{-3}$ M.

Rates of polymerization and initiation for MMA in the presence of some other additives are given in the Table, together with those in bulk monomer and in DMSO solution for comparison.

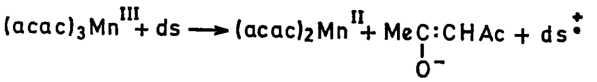
Polymerization of methyl methacrylate initiated by $\mathrm{Mn(acac)_3}$ *in* (5×10^{-3}M) *in the presence of additives* (*volume fraction* 0·1) *at* 25°

Additive	10^5 rate of polymerization Ms^{-1}	10^8 rate of initiation Ms^{-1}
1,2-Diaminopropane	23·6	19·9
Hexamethylphosphoramide ..	22·3	17·6
1,2-Diaminoethane	21·4	16·3
Dimethyl sulphoxide	9·8	3·4
NN-Dimethylformamide ..	4·3	0·66
None	0·8	0·02

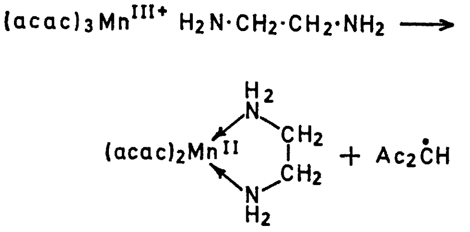
All the compounds listed in the Table are electron donors and hence capable of displacing the acetylacetonate ligand. If this occurs without a change in the oxidation state of the manganese atom, the observed selectivity may be explained in terms of a mechanism similar to that suggested[2] for $\mathrm{Mn(facac)_3}$ (Equation 1). Partial ligand displacement (1a) is followed by insertion of the monomer $\mathrm{CH_2{:}CXY}$ (1b) and electron transfer (1c) producing $\mathrm{Mn^{II}}$ and an initiating radical. Selectivity is imparted by (1b), which occurs most readily with monomers carrying electron-attracting groups and is negligible with styrene.



The non-selective component of initiation may arise in two ways. First, ligand displacement may occur with the simultaneous change $\mathrm{Mn^{III}} \rightarrow \mathrm{Mn^{II}}$. This seems most probable when the additive is itself a chelating agent; it would lead to the formation of a $\mathrm{Mn^{II}}$ heterochelate[6] and an acetylacetonyl radical [*e.g.* Equation (2)]. Secondly, after (1a) oxidation of the additive may occur, with formation of $\mathrm{Mn^{II}}$ and the radical cation $\mathrm{ds}^{+\bullet}$ [Equation (3)].[7]



$$(\mathrm{acac})_3\mathrm{Mn^{III}} + \mathrm{ds} \longrightarrow (\mathrm{acac})_2\mathrm{Mn^{II}} + \mathrm{Me}\underset{\mathrm{O^-}}{\underset{|}{\mathrm{C}}}\mathrm{:CHAc} + \mathrm{ds}^{\overset{+}{\bullet}} \quad (3)$$



(2)

These processes are being investigated. Early observations on the reactions in DMSO were carried out by D. J. Lind in this department.[8]

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