Kinetics of nonaqueous polymerization of methyl methacrylate by manganic laurate - n-hexanethiol redox system in carbon tetrachloride

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The polymerization of methyl methacrylate (MMA) has been studied in carbon tetrachloride with manganic laurate- n-hexanethiol as the initiator system. The rate of polymerization is proportional to [manganic ion]^{1/2} and [thiol]^{1/2}. The order in [monomer] is 1.5. A reaction scheme involving initial complex formation between manganic laurate and MMA and subsequent reaction of the complex with the thiol to produce the free radicals has been postulated to account for the observed results. The activation energy and different kinetic constants for the system have also been evaluated.

Metal ions such as Ce(IV), Fe(III), Mn(III) etc. in the presence of various organic reducing agents are known to form effective redox initiator systems in the polymerization of vinyl monomers, usually in aqueous systems only. We have successfully used metallic soaps (ferric laurate¹ and manganic laurate²,³) in combination with organic thiols for initiating polymerization in an organic medium. Title investigation is in continuation of our earlier work.

Experimental
The polymerization was carried out in sealed glass ampoules under vacuum. Polymers were isolated by precipitation from benzene solution and dried to constant weight at 50°C in an oven in vacuo. The molecular weight ($M_n$) of the polymers were determined by viscometric measurements in benzene at 35°C using the equation⁴, $[\eta] = 8.69 \times 10^{-5} M_n^{0.76}$ where $[\eta]$ is the intrinsic viscosity.

Results and discussion
A typical set of reaction curves showing the effect of varying $[n$-hexanethiol] on the polymerization of methyl methacrylate (MMA) in CCl₄ at 40°C at fixed [manganic laurate] is shown in Fig. 1. All the curves pass through the origin, indicating that there is no induction period involved. The rate of polymerization increases with increase in [thiol] and polymerization is completely inhibited by 2,2'-diphenyl-1-picrylhydrazyl indicating the free radical nature of the reaction. Manganic laurate or $n$-hexanethiol alone cannot initiate polymerization.

The rate of polymerization is proportional to [manganic ion]^{1/2} and [n-hexanethiol]^{1/2}, in accordance with free radical polymerization involving bimolecular termination of free radicals. The order in [monomer] is 1.5, similar to that observed earlier³ with Mn(III)-1-propanethiol and Mn(III)-2-propanethiol initiated systems, but the rate with manganic laurate- $n$-hexanethiol system is higher than that of the former and lower than that of the latter system under otherwise identical conditions.

Thiols are known to be easily oxidized to disulfides by various oxidizing agents. Wallace⁵ found that thiols and ferric octanoate undergo rapid oxidation-reduction reaction producing thiy radical (RS) which can be trapped by olefins. It is expected that in the present system a similar oxidation-reduction reaction will occur between Mn(III) ion and $n$-hexanethiol producing $n$-hexanethyl ($\text{C}_6\text{H}_{13}\text{S}$) radicals which initiate po
lymerization. The formation of a complex between manganic laurate and the monomer (MMA), was shown earlier on the basis of spectroscopic studies. Thus in analogy with the Mn(III)-propanethiol system, the following reaction mechanism may be visualized in the present system,

\[
\begin{align*}
\text{Mn(III)} + M &\rightarrow C \text{ (complex)} \\
C + \text{RSH} &\rightarrow RS + C^+ + H^+ \\
\text{RS} + M &\rightarrow M
\end{align*}
\]

followed by normal propagation, transfer and bimolecular termination of polymer radicals.

By applying steady-state assumptions to the above scheme, the rate of polymerization \( R_p \) is given by Eq. (1)

\[
R_p = \left( \frac{k_p}{k_t} \right) \left( k_d K_f \right) \frac{1}{2} \frac{[\text{Mn(III)}]}{[\text{M}]} \frac{1}{2} [T] \frac{1}{2} \ldots \ldots (1)
\]

and the average degree of polymerization \( \bar{DP} \) is given by Eq. (2)

\[
\frac{1}{\bar{DP}} = C_M + C_T [T]/[M] + C_M [S]/[M] + \frac{\delta^2}{[M]^2} R_p \ldots \ldots (2)
\]

where \( f \) is the initiator efficiency, \( K \) the equilibrium constant of the complex formation reaction, \( k_d \) the rate constant for the interaction between the complex \( C \) and the thiol \( \text{RS} \) or \( T \), and \( S \) the solvent (CCl4). All the other symbols have the usual meanings.

Equation (1) is in agreement with our experimental results indicating that the assumptions made are reasonably valid. Initiation by thiy radicals (RS) is confirmed by the incorporation of thiy end groups in the polymer (see ref. 2).

As expected from Eq. (1) the plot of \( R_p \) against \( [\text{Mn(III)}]/[\text{RSH}] \) at fixed [monomer] is linear passing through the origin. The slope gives \( \left( \frac{k_p}{k_t} \right) \left( k_d K_f \right) \frac{1}{2} \) \( [\text{M}] \frac{1}{2} \), from which \( k_d K_f \) is calculated to be \( 7.22 \times 10^{-3} \) dm\(^3\) mol\(^{-1}\) at 40°C, since [M] is known and the \( k_p/k_t \) has been obtained from literature. The \( k_d K_f \) values for 2-propanethiol and 1-propanethiol were determined earlier to be \( 7.91 \times 10^{-3} \) and \( 5.92 \times 10^{-3} \) respectively at 40°C. Thus the \( k_d K_f \) values for the three thiols follow the order 2-propanethiol > \( n \)-hexanethiol > 1-propanethiol, i.e., same as the order of \( R_p \) obtained with these thiols under otherwise identical conditions. This is also expected from Eq. (1) which indicates that \( R_p \) will be determined by \( k_d K_f \) or rather by \( k_d f \) since \( K \) is the same in all the cases. If we further assume that \( f \) is the same for all the thiols investigated so far, then the \( R_p \)'s for the different thiols will follow the order of their respective \( k_d \)'s. Now \( k_d \) refers to the reaction between the Mn(III)-monomer complex and thiol, and involves an electron transfer from thiol to the manganic ion. The reactivity of thiol will thus be dependent on electron-donating or electron-withdrawing influence of the attached groups. The relative activities of \( n \)-hexanethiol and 1-propanethiol can be explained on the basis of the electron-donating capabilities of their respective substituents. The highest rate observed with 2-propanethiol may be due to the presence of two electron-donating methyl groups.

The degree of polymerization \( \bar{DP} \) obtained in the present system is usually of the order of \( 10^3 \), and increases with increase in [monomer] and decreases with [manganic laurate] and \( [n \)-hexanethiol].
Thiols are known to be good chain transfer agents and transfer constant $(C_T)$ of $n$-hexanethiol can be determined with the help of Eq. (2). As expected, the plot of $1/DP - C_S[S]/[M] - \delta^2 \cdot R_p/[M]^2$ versus $[T]/[M]$ at fixed [manganic laurate] is linear, the slope giving $C_T$ and the intercept $C_M$, the chain transfer constant with respect to monomer. Literature values of $C_S$ (for CCl$_4$) ($= 3.09 \times 10^{-5}$ at 40°C) and $\delta = 10.6$ at 40°C were used for calculations. The value of $C_M$ for MMA at 40°C comes out to be $1.00 \times 10^{-5}$ agreeing with the literature value. The $C_T$ value for $n$-hexanethiol comes out to be 0.72. This is higher than those for 1-propanethiol (0.46) and 2-propanethiol (0.35). Transfer reaction with the thiols involves abstraction of a H-atom from the S–H bond. So normally electron-donating groups should increase and electron-withdrawing groups should decrease the transfer activity of a primary thiol. Thus the relative transfer activities of $n$-hexanethiol and 1-propanethiol may be explained as due to relative electron-donating capacity of the attached groups. As was explained earlier the lower activity of 2-propanethiol can be attributed to steric restriction due to methyl group substitution at the $\alpha$-carbon atom.

The value of $\delta$ can also be determined with the help of Eq. (2). The plot of $1/DP$ versus $R_p$ at fixed [monomer] and [thiol] is linear, the slope giving $\delta^2/[M]^2$. From this, the value of $\delta = 10.6$ at 40°C (ref. 6).

References
4. Fox T G, Kinsinger J B, Mason H F & Schuele E M, Poly- 

nym, 3 (1962) 71.