On the Use of the Mayo Equation in Cationic Polymerization

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Summary

With the help of some representative theoreti- cal Mayo plots it has been shown that when the concentration of active centers consisting of ions and ion pairs in a cationic polymerization system varies directly with monomer concentration, Mayo plots would be curved and there is every possibility that one would end up with an intercept at $1/\bar{P}$ axis even in the absence of monomer transfer.

Introduction

In a recent publication (MANDAL and KENNEDY, 1978) the applicability of Mayo equation in cationic polymerization systems has been discussed. For a system with free ions and ion pairs as active species the appropriate Mayo equation under impurity free conditions was deduced to be :

$$\frac{1}{\bar{P}_n} = \frac{\alpha k^+_{tr,M} + (1 - \alpha)\, k^{\pm}_{tr,M}}{\alpha k^+_p + (1 - \alpha)\, k^{\pm}_p}$$

$$+ \frac{(1 - \alpha)\, k^+_t K_d + (1 - \alpha)\, k^{\pm}_t}{\alpha k^+_p + (1 - \alpha)\, k^{\pm}_p} \cdot \frac{1}{[M]} \quad (1)$$

where k^+_p, k^+_t and $k^+_{tr,M}$ refer to the rate constants of propagation, termination and transfer to monomer respectively for the free ions, while $k^{\pm}_p$, $k^{\pm}_t$ and $k^{\pm}_{tr,M}$ represent those for the ion pairs. The degree of dissociation α is related to the dissociation constant K_d as follows :

$$M^+_n X^- \underset{}{\overset{K_d}{\rightleftharpoons}} M^+_n + X^- \quad \ldots \quad (2)$$
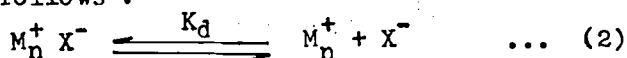
and

$$K_d = \alpha^2 \left[M^* \right] / (1 - \alpha) \qquad \ldots \quad (3)$$

where $\left[M^* \right]$ is the total active center concentration i.e.,

$$\left[M^* \right] = \sum_{n=1}^{\infty} \left[M_n^+ \right] + \sum_{n=1}^{\infty} \left[M_n^+ X^- \right] \qquad \ldots \quad (4)$$

In obtaining (3) the assumption has been made that K_d is independent of the degree of polymerization.

BIDDULPH et al (1965) and PLESCH (1968) pointed out the composite character of the slope and intercept of the Mayo plots because of the participation of both free ions and ion pairs in the polymerization. We not only supported this view (MANDAL and KENNEDY 1978) but also emphasized that the Mayo plots would be meaningful only if α remains independent of $[M]$ as would be evident from eq.(1). It was pointed out that if the rate of initiation R_i is dependent on $[M]$, the active center concentration will decrease and accordingly (eq.3) α will increase with decreasing $[M]$. The result is that an intercept may arise even in a monomer transfer-free system leading to erroneous conclusions.

In this paper we would like to show theoretically how the Mayo plots would look like in a monomer transfer free system, when the active center concentration varies directly as the monomer concentration in a cationic polymerization.

Discussion

Plesch (1971) concluded that in solvents of dielectric constants greater than 10 the contribution of ion pairs towards R_p is insignificant compared to that of the free ions in a cationic polymerization. R_p may be expressed as follows : (Mandal and Kennedy, 1978)

$$R_p = \left\{ \alpha k_p^+ + (1 - \alpha) k_p^{\pm} \right\} \left[M^* \right] \left[M \right] \qquad \ldots \quad (5)$$

If the contribution of ion pairs to R_p is negligible

$$\alpha k_p^+ \ggg (1 - \alpha) k_p^{\pm} \qquad \ldots \quad (6)$$

Applying the above inequality to eq.(1) we get

$$\frac{1}{P_n} = \frac{k^+_{tr,M}}{k^+_p} + \frac{(1-\alpha)}{\alpha} \cdot \frac{k^{\pm}_{tr,M}}{k^+_p}$$

$$+ \frac{(1-\alpha)}{\alpha} \cdot \frac{(k^+_t K_d + k^{\pm}_t)}{k^+_p} \cdot \frac{1}{[M]} \quad \dots (7)$$

This equation is simpler than eq.(1). But once again unless the constancy of α is assured, the Mayo plot would not be linear.

We shall now examine the variation of $(1-\alpha)/\alpha$ with $[M^*]$. Since in most cases the concentrations (C) of the active centers $[M^*]$ and their dissociation constants are unknown, we follow PLESCH (1971) in making some reasonable estimates of these two quantities. PLESCH considered the following ranges of K_d and C

$$10^{-5} \geqslant K_d \geqslant 10^{-7} M \text{ and } 10^{-5} \geqslant C \geqslant 10^{-10} M$$

so that C/K_d ranges between 10^2 and 10^{-5}.

From eq.(3) we have

$$\frac{C}{K_d} \alpha^2 + \alpha - 1 = 0 \quad \dots (8)$$

Thus for various values of C/K_d, α and hence $1-\alpha$ may be evaluated by solving the quadratic equation (8). Values so obtained are tabulated in Table-1. Table 1 also contains data for $R^+_p / R^{\pm}_p$ which were evaluated from the relation

$$R^+_p / R^{\pm}_p = \alpha k^+_p / (1-\alpha) k^{\pm}_p \quad \dots (9)$$

A value of 100 was used for the value of $k^+_p / k^{\pm}_p$ (PLESCH, 1971).

It is evident from Table 1 that for C/K_d values larger than 10^{-2} the population of ion pairs is not insignificant, although their contribution to the R_p is negligible. BOWYER et al (1971) showed for tropylium salt initiated cationic polymerization of N-vinyl carbazole in methylene chloride solvent that

although the ion pair contribution to R_p is negligible, their effect on monomer transfer and hence on DP is appreciable. Table 1 also shows how α changes with C/K_d. From these data it is possible to estimate the variation of α with C because for a given system of ion and ion pair K_d is constant.

TABLE 1

Relative population of Ion Pairs and Free Ions and the Degree of Dissociation α in Cationic Polymerization

C/K_d	α	$(1-\alpha)/\alpha$	$[M^+X^-]$ % of C	$R_p^+ / R_p^{\pm}$ *
10^2	0.095	9.53	90.5	10.5
10	0.270	2.70	73.0	37
1	0.618	0.62	38.0	161
10^{-1}	0.916	0.092	8.4	1087
10^{-2}	0.990	0.010	1.0	10^4
10^{-3}	0.999	0.001	0.1	10^5
10^{-4}	0.9999	0.0001	0.01	10^6

* In calculating $R_p^+ / R_p^{\pm}$ it has been assumed that $k_p^+ / k_p^{\pm} = 100$

So far as the applicability of the simplified general Mayo equation (eq.7) is concerned, we see from Table 1 that $(1-\alpha)/\alpha$ changes significantly with C at a fixed K_d. Thus if C varies with $[M]$, Mayo plot would not be linear. Therefore, conditions should be established to see that C, i.e. $[M^*]$ does not change with $[M]$.

For a monomer transfer free system the first and second term in the right hand side of eq.(7) would be zero. Therefore under such conditions

$$\frac{1}{\overline{P}_n} = \frac{(1-\alpha)}{\alpha} \cdot \frac{(k_t^+ K_d + k_t^{\pm})}{k_p^+} \cdot \frac{1}{[M]} \quad \ldots (10)$$

In figures 1a and 1b are shown two representative Mayo plots that would be obtained in a monomer transfer free system when the active center concentration varies directly with [M].
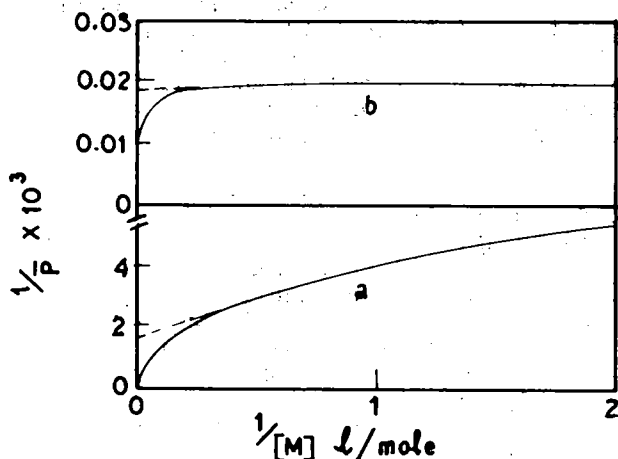

Fig.1. Mayo plot in absence of monomer transfer theoretically obtained from eq.(10) assuming

$$(k_t^+ K_d + k_t^{\pm})/k_p^+ = 10^{-3}$$

a: $[M^*] / K_d \propto [M]$ and = 100 for
$[M] = 5$ mole/l

b: $[M^*]/K_d \propto [M]$ and = 0.1 for
$[M] = 5$ mole/l

The figures were drawn theoretically using eq.(10) for which the values of $1 - \alpha/\alpha$ were obtained from Table 1 for any assumed value of C/K_d. The value[a] of $(k_t^+ K_d + k_t^{\pm})/k_p^+$ was arbitrarily chosen to be 10^{-3}.

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[a] The shape of the curves will be independent of this value. Any other value will only change the absolute values of $1/\bar{P}$.

It is evident from the figures that if C i.e., $[M]^*$ changes with $[M]$, Mayo plots would be curved. Since in an actual experiment one works in a monomer concentration range that excludes the initial portion of the curve, there is every possibility that one would end up with an intercept in the usual Mayo plots. This is evident from the extrapolation shown as the dotted lines in figures 1a and 1b. Thus Mayo plots show existence of monomer transfer, although we set out the condition that transfer to monomer is absent. For $C/K_d < 0.1$ a change in C at a fixed K_d will bring about a proportionate change in $1 - \alpha/\alpha$ (Table 1). Under such circumstances if C happens to be proportional to $[M]$, the Mayo plot for a monomer transfer-free system would be almost parallel to the $1/[M]$ axis (Figure 1b) in the experimentally accessible $[M]$ region. These perhaps explain why we obtained a Mayo plot with very little slope but large intercept in our earlier work (Mandal and Kennedy, 1978) on isobutylene polymerization using 3-chloro-1-butene initiator and aluminum trivinyl coinitiator even though monomer transfer was insignificant. For this particular system we argued that the rate of initiation would be dependent on $[M]$ and so also the active center concentration.

It should be kept in mind that the values in Table 1 are applicable in the absence of common ion effect. In the presence of common ion effect, however, α values would be lower than those quoted in Table 1 throughout the C/K_d range examined.

References

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