Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Lissi, E. A.(1981) 'On the Use of a Modified Mayo Plot', Journal of Macromolecular Science, Part A, 15: 3, 447 — 456
To link to this Article: DOI: 10.1080/00222338108074384
URL: http://dx.doi.org/10.1080/00222338108074384

J. MACROMOL. SCI.–CHEM., A15(3), pp. 447-456 (1981)

On the Use of a Modified Mayo Plot

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ABSTRACT

The most usual procedure to estimate the chain transfer ratio in vinyl polymerization is to use a Mayo plot. This plot can only be applied directly when the polymerization rate is not modified by the chain transfer agent. In spite of this, the equation has been applied to several systems where this condition is not fulfilled. In the present work we present a slightly modified equation that can be employed irrespective of the changes in rate. This equation is applied to several systems reported in the literature. The improvement in the interpretation of the results in these systems is discussed.

INTRODUCTION

The chain transfer constant of a given sustrate S is usually determined from the slope of a Mayo plot [1]:

$$\frac{1}{\lambda} = \frac{1}{\lambda_0} + C_M + C_S \frac{S}{M} \qquad (1)$$

where λ_0 is the chain length in the absence of S, λ is the chain length at a given S, C_M is the monomer chain transfer constant, and C_S is the sustrate chain transfer constant.

This method can be used when:

1. The initiation rate is not modified by S
2. The radicals produced in the chain transfer step do not terminate the chain
3. The primary recombination is not important
4. The rate constants do not depend upon the mean size of the macroradicals or the concentration of S (i.e., due to changes in the viscosity of the solution or by complexing of the macroradicals and S

In spite of these shortcomings, the Mayo equation has been frequently employed under conditions where it cannot hold. Sometimes the data were extrapolated to limiting conditions [2]. In other cases the limitations mentioned above seem to have been overlooked [3-8]. We present in this article a slightly modified equation that allows the evaluation of C_S even when conditions 1 and 2 are not fulfilled.

THEORY

Let us assume the following scheme:

$$\mathrm{I} \longrightarrow 2\mathrm{R}\cdot \tag{2}$$

$$2\mathrm{R}\cdot \longrightarrow \mathrm{Z} \tag{3}$$

$$\mathrm{R}\cdot + \mathrm{M} \longrightarrow \mathrm{M}\cdot \tag{4}$$

$$\mathrm{M}\cdot + \mathrm{M} \longrightarrow \mathrm{M}\cdot \tag{5}$$

$$\mathrm{M}\cdot + \mathrm{M}\cdot \xrightarrow{k_t} \text{polymer} \tag{6}$$

$$\mathrm{M}\cdot + \mathrm{R}\cdot \xrightarrow{k_{pr}} \text{polymer} \tag{7}$$

$$\mathrm{M}\cdot + \mathrm{S} \xrightarrow{k_{tr}} \text{polymer} + \mathrm{S}\cdot \tag{8}$$

$$\mathrm{M}\cdot + \mathrm{S} \xrightarrow{k_d} \text{polymer} + \mathrm{Y}\cdot \tag{9}$$

$$S\cdot + M \longrightarrow M\cdot \tag{10}$$

$$Y\cdot + M \longrightarrow M\cdot \tag{11}$$

$$Y\cdot + M\cdot \longrightarrow \text{polymer} \tag{12}$$

$$Y\cdot + R\cdot \longrightarrow W \tag{13}$$

$$Y\cdot + Y\cdot \longrightarrow Q \tag{14}$$

$$M\cdot + M \xrightarrow{k_M} \text{polymer} + T\cdot \tag{15}$$

$$T\cdot + M \longrightarrow M\cdot \tag{16}$$

where S can be the solvent, the initiator, or any other added compound. The mean chain length λ, defined by

$$\lambda = v_p/v_C \tag{17}$$

can be evaluated from the rate of propagation (v_p) and the rate of macromolecules formation v_C. With the proposed reaction scheme

$$v_C = \alpha v_t + v_{tr} + \beta v_d + v_M + v_{pr} \tag{18}$$

where v_t, v_{tr}, v_d, v_M, and v_{pr} are the rates of Reactions (6), (8), (9), (15), and (17), respectively; α is determined by the combination to disproportionation ratio of M·; and the value of the parameter β depends upon the fate of radical Y·. If

$$v_{11} + v_{13} + v_{14} \gg v_{12}$$

then Reaction (9) forms only one chain end and the value of β approaches one. On the other hand, when

$$v_{11} + v_{13} + v_{14} \ll v_{12}$$

Reaction (9) is often followed by Reaction (12), thus causing two chain ends to be formed, and β approaches a value of two. The relevant point is that in any possible situation

$1 \leq \beta \leq 2$

If the primary radical, the v_{pr} term, is disregarded in Eq. (18), this equation can be rearranged to

$$\frac{1}{\lambda v_p} - \frac{C_M}{v_p} = \frac{\alpha k_t}{(k_p M)^2} + \frac{\beta k_d + k_{tr}}{kp} \frac{S}{Mv_p} \tag{19}$$

which reduces to Eq. (1) when v_p is constant. This equation predicts a linear relationship between $(\lambda v_p)^{-1} - (C_M/v_p)$ and $S/(Mv_p)$, provided that Conditions 3 and 4 are fulfilled and that β is independent of S/M. Several equations have been previously proposed to take into account the change in initiation rate with S, but they require a knowledgement of the rate law over all the concentration range [9] or they involve a rather complex analysis of the experimental results [10]. Equation (19), on the other hand, can be directly applied even if the initiation rate and/or the termination rate changes with the change in S/M. We can then handle results when S is at the same time an initiator, a chain transfer agent, and an inhibitor. Furthermore, it is interesting to consider that mutual termination by primary radicals (Reaction 2) and/or reactions of the primary radicals with the transfer agent will not invalidate the use of Eq. (19) if the radicals produced do not stop a growing chain. In the next sections we shall discuss some reported data whose interpretation can be improved with the aid of Eq. (19).

DISCUSSION

Polymerization in the Presence of Organometallics

Huff and Perry have carried out a study of the reactions of several macroradicals with organometallics [2]. Since in most of the systems investigated either acceleration or retardation was observed, different plots to evaluate C_S were employed. On the other hand, all the systems can be analyzed with the aid of Eq. (19). In this case the slopes would provide values of C_S limited only by the uncertainty in β. When some of the data reported are plotted according to this equation, no evidence of chain transfer to the organometallic compound could be detected. For example, for the acrylonitrile-triethyl indium system, Huff and Perry reported that C_S is 0.222 ± 0.167. When the same data are plotted according to Eq. (19), $(\lambda v_p)^{-1} - (C_M/v_p)$

decreases when $S/(Mv_p)$ increases. A similar result is obtained for the methyl methacrylate-triethyl indium system, in spite of the reported C_S value of 0.033 ± 0.0004. It can be concluded that the relatively high chain transfer constants obtained for these compounds are most likely an artifact of the method employed in their evaluation.

Solvent Effect in the Polymerization of Styrene

Kalaforov and Borsig have studied the transfer reactions in the radical polymerization of styrene in acetone and acetone-chloroform mixtures [5]. In this work it was found that the Mayo equation is not obeyed, and the curvature was explained by assuming a complexation phenomenon. We consider that most of the curvature can be accounted for by the change in polymerization rate associated with the monomer dilution.

1. When the data obtained in the styrene-acetone system were plotted according to the usual Mayo equation, a strong curvature was obtained and the initial slope was negative. C_S was then evaluated from the slope of the plot at high acetone/styrene. On the other hand, if Eq. (19) is applied, a positive slope is obtained, rendering a C_S value of the same order of magnitude as those previously reported [5].
2. The data obtained in the chloroform-styrene system gave a strongly curved Mayo plot, and only an "average" value of C_S could be obtained. The same data, plotted according to Eq. (19), are shown in Fig. 1. The plot obtained is fairly linear and gives a C_S value of 4.6×10^{-5}. This value is inside the range reported in the literature (3.6 to 7.8×10^{-5}) [5].
3. The data obtained in the acetone-chloroform-styrene system gave an S-shaped Mayo plot with a zero slope at a S/M approximately 3. The same data, plotted according to Eq. (19), give a much smaller curvature and provide a reasonable C_S value [11].

We can conclude that an appropriate treatment of the data eliminates most of the anomalies observed in these systems.

Chain Transfer to the Initiator

George and Ward studied the polymerization of styrene by poly(bisphenol A 4,4'-azobis-4-cyanopentanoate) in dimethylformamide as solvent [9]. The reaction mechanism was complex, and Eq. (20) and (21) were employed to obtain kinetic information on the elementary steps involved:

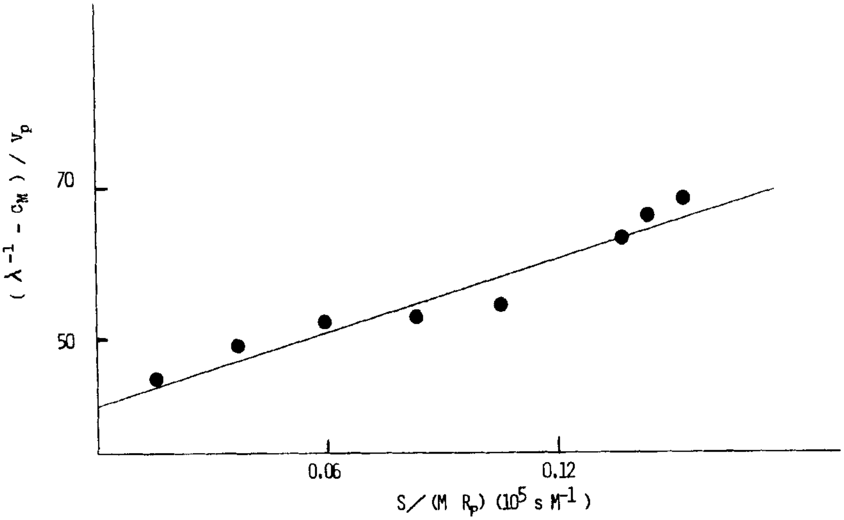

FIG. 1. Data obtained by Kalaforov and Borsig [5] for the polymerization of styrene in chloroform, plotted according to Eq. (19).

$$1/\lambda = (k_t v_p / k_p{}^2 M^2) + C_S(S/M) + C_M \tag{20}$$

$$(\lambda^{-1} - C_M)M = k_t f k_I (I)^{1/2} k_p{}^{-1} + C_S S \tag{21}$$

When λ^{-1} was plotted against v_p at constant S/M, an upward curvature was obtained. The authors state that the upward curvature could be due to attack on some parts of the bisphenol A units of the initiator molecule (a reaction disregarded to derive Eq. 20 or to primary radical termination). A plot of the data according to Eq. (19) is shown in Fig. 2. This plot indicates that the results can be explained assuming that $C_I = 0.15$.

Equation (21) was employed at constant initiator concentration to obtain values of the solvent chain transfer constant. The plot showed an unexplained upward curvature at high S/M. The same data plotted according to Eq. (19) are shown in Fig. 3. The plot is linear over the entire concentration range. The advantage of Eq. (19) over Eq. (21) is that neither a constancy in f nor a constant rate of initiator decomposition over the entire S/M range need be assumed.

Shahani and Indictor have studied the kinetics of tert-butyl-hydroperoxide initiated polymerization of methyl methacrylate in the presence of Cu(II) acetylacetonate [12]. The increase in rate and decrease in molecular weight of the polymer produced were analyzed in terms of an induced decomposition of the hydroperoxide. Treatment

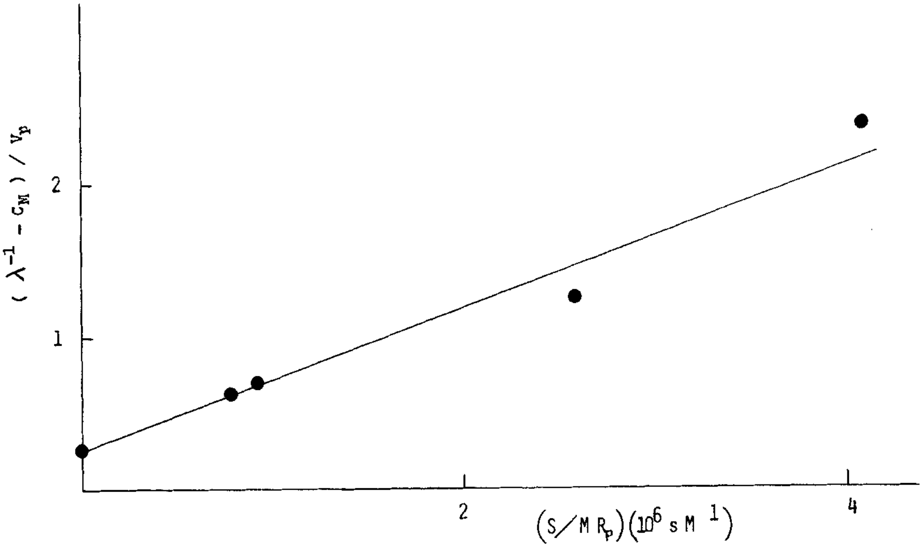

FIG. 2. Data obtained by George and Ward [6] for the polymerization of styrene initiated by poly(bisphenol A 4,4'-azobis-4-cyanopentanoate) in dimethylformamide plotted according to Eq. (19). S = poly(bisphenol A 4,4'-azobis-4-cyanopentanoate).

of the data obtained according to Eq. (19) shows that, if the proposed mechanism is accepted, chain transfer to the Cu(II) acetylacetonate must take place with $(\beta k_d + k_{tr})/k_p = 3.3$.

Ghosh, Mitra, and Banerjee have studied the photopolymerization of methyl methacrylate initiated by molecular bromine [4]. They observed that several solvents enhance the polymerization rate even when used in the range of catalytic concentrations. An initiation mechanism involving solvent molecules was proposed to account for this change in rate. In spite of this, a normal Mayo plot was employed to obtain chain transfer ratios to the solvent. The plots obtained, although lineal, extrapolate to different values when S approaches zero, and gave C_S values much higher than those obtained for the same solvents when other initiators were employed. The data obtained, when plotted according to Eq. (19), show that there is not a simple relationship between chain length and (S/M), clearly indicating that the change in chain length cannot be related to a chain transfer to the solvent and that the C_S values reported are not a measure of these processes.

Ghosh and Banerjee have studied the polymerization of methyl methacrylate with iodine and iodine monobromide as photoinitiators

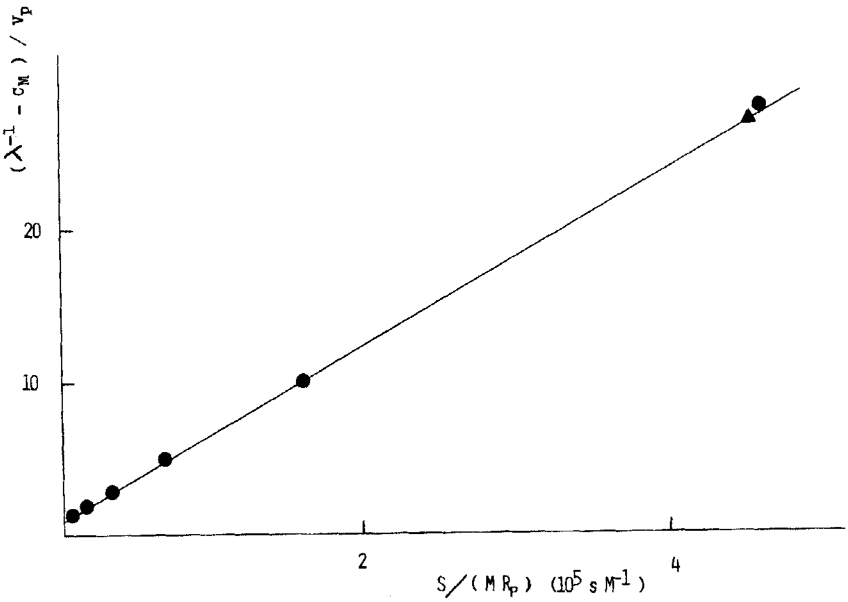

FIG. 3. Data obtained by George and Ward [6] for the chain transfer to dimethylformamide plotted according to Eq. (19). (▲) The values of $(\lambda R_p)^{-1} - (C_M/R_p)$ and $S/(M \times R_p)$ for this point have been divided by a factor of 5.

[3, 13]. The experimental data, plotted according to the usual Mayo's plot, show strong curvatures. This result was interpreted as due to two different processes: a chain transfer (predominant at low initiator concentrations) and a degradative chain transfer (predominant at high initiator concentrations). Equation (19) can be employed to test this hypothesis since it shows that, provided the same species is active in both processes (as assumed by Ghosh and Banerjee), linear plots must be obtained irrespective of the secondary reactions of the radical produced in the transfer reaction. Nevertheless, strong curvatures larger than those expected from a change in the value of β are still observed. This result indicates that another effect, different from a change in the fate of the radicals produced, is affecting the course of the reaction.

Kinetics of Polymerization in Presence of an Inhibitor

Bagdasaryan has derived an equation similar to that of Mayo that was assumed to be valid even when an inhibitor is considered [14]. Garina et al. [8] have applied this equation to a study of the effect of benzoquinone in the polymerization of methyl methacrylate in the

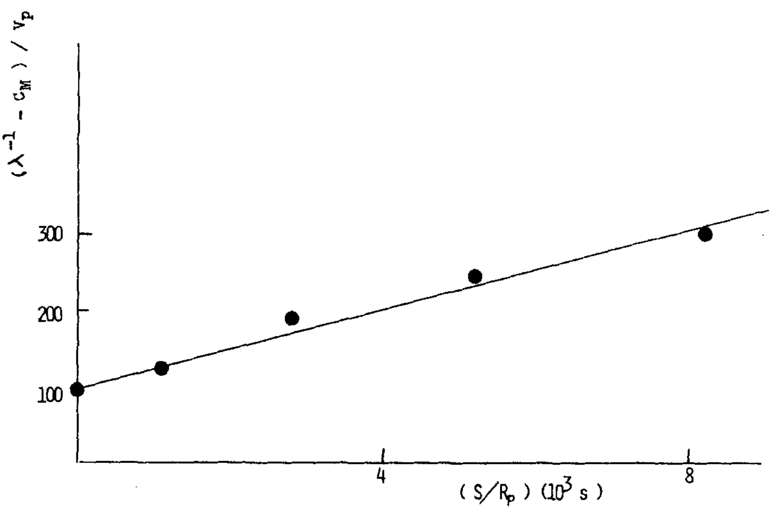

FIG. 4. Chain transfer to chromium(II) acetate in the polymerization of styrene in dimethylformamide. Data from Ref. 15 plotted according to Eq. (19).

presence of orthophosphoric acid. The use of the proposed equation seems incorrect, and Eq. (19) would have to be employed. Only under conditions such that

$$1/\lambda \gg 1/\lambda_0 \qquad (22)$$

will both treatments reduce to

$$1/\lambda = [(k_{tr}k_d)/k_p](S/M) \qquad (23)$$

and give similar results.

Trapping of the Primary Radicals by the Chain Transfer Agent

Lee and Minoura have studied the reactivity of chromium(II) acetate toward polymeric radicals in the AIBN-initiated polymerization of styrene in dimethylformamide [15]. The rate of interaction was deduced from the change in polymerization rate with the added salt concentration. In order to carry out this treatment, it has to be assumed that the salt did not influence the initiator decomposition nor did it trap the primary radicals. The treatment proposed in the present work can be applied even if these conditions are not fulfilled. Application of Eq. (19) to the data of Lee and Minoura is shown in Fig. 4. From this figure a reliable value of C_S can be obtained.

The above examples show how the use of Eq. (19) could improve the interpretation of the results in those systems where the polymerization rate changes when (S/M) changes. It is also interesting to note that in other systems (i.e., Ziegler-Nata type polymerization) where the Mayo equation do not hold [16], the use of an equation similar to Eq. (19) could be of aid in the interpretation of the results.

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Accepted by editor October 16, 1979
Received for publication November 13, 1979