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

# Copolymerization with Depropagation. X

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**To cite this Article** Kang, B. K. and O'driscoll, K. F.(1973) 'Copolymerization with Depropagation. X', Journal of Macromolecular Science, Part A, 7: 6, 1197 — 1202

**To link to this Article: DOI:** 10.1080/10601327308060493

**URL:** http://dx.doi.org/10.1080/10601327308060493

J. MACROMOL. SCI.—CHEM., A7(6), pp. 1197-1202 (1973)

# Copolymerization with Depropagation. X.* Description of Reversible Copolymerizations by Irreversible Reactivity Ratios

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## ABSTRACT

It is shown that it is possible to interpret the physical significance of reactivity ratios obtained by applying the Mayo-Lewis equation to composition data from systems which are expected to polymerize with some depropagation.

## INTRODUCTION

Many workers have copolymerized monomer systems where one or more of the monomers was near or above its ceiling temperature, and then analyzed the composition data in terms of the ordinary reactivity ratios contained in the Mayo-Lewis equation. Since this equation (and

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extensions of it for terpolymerizations) was based on a kinetic model which does not consider depropagation, it is important to recognize that the physical significance of the reactivity ratios will be different if the experimental system actually does involve depropagation. Previous papers in this series as well as work from other laboratories [1, 2] have amply demonstrated that depropagation ought to be considered whenever a monomer is copolymerized under conditions of temperature of dilution that place it well above its homopolymerization ceiling temperature.

The purpose of this paper is to present an analysis of the physical significance of "irreversible" reactivity ratios which have been obtained by fitting the Mayo-Lewis equation to what are necessarily "reversible" copolymerization composition data. The analysis is based on the diad model for reversible copolymerization [3], which has been shown to be adequate to explain terpolymerization composition behavior as a function of temperature and dilution [4], and binary copolymerizations' composition [3], sequence distribution [5], rate, and molecular weight distributions [6, 2].

## THEORY

The nomenclature used below has been defined in an earlier paper [4], where we showed that the conditional probability, $P_{ij}$, of finding a monomer sequence $-M_iM_j-$ in a chain may be written

$$P_{ij} = f_{ij}^{a} M_j / \sum_j f_{ij}^{a} M_j \qquad (1)$$

where $f_{ij}^{a}$ is the apparent forward rate constant which ignores the possibility of depropagation. In actuality, if depropagation occurs, the apparent forward rate constant includes a contribution from the depropagation rate constant, $r_{ij}$, as well as the true propagation rate constant, $f_{ij}$:

$$f_{ij}^{a} = f_{ij}/(1 + r_{ij}x_j) \qquad (2)$$

The parameter $x_i$ in Eq. (2) may be determined as the solution of the set of equations having the form

$$\frac{1}{x_i} = \sum_j [f_{ij}M_j/(1 + r_{ij}x_j)] \qquad (3)$$

The parameter $x_i$ also has an explicit physical meaning in that it is defined as

$$x_i = \frac{\alpha_i}{a_i}\tau \qquad (4)$$

where $\alpha_i$ and $a_i$ define chain end monad probability and chain interior monad probability, respectively, while $\tau$ defines the average time to add one monomer unit. Obviously, all three parameters are dependent on the composition of the polymerizing system.

Equation (2) can be rewritten as

$$\frac{1}{f_{ij}^{a}} = \frac{1}{f_{ij}} + x_j \frac{1}{K_{ij}} \qquad (2')$$

where $K_{ij}$ is the equilibrium constant for the propagation-depropagation equilibrium. Since $\tau$ is necessarily a very small quantity when propagation predominates, the value of $x_i$ will also be small under such conditions. Equation (2') then serves to emphasize that $f_{ij}^{a}$ is the forward rate constant weighted by the amount of equilibrium contribution to the formation of the polymer chain.

For a copolymerizing system, it has been shown [3] that the composition equation can always be written in the form first put forward by Goldfinger and Kane [7]:

$$\frac{dM_i}{dM_j} = \frac{P_{ji}}{P_{ij}} \qquad (i,j = 1,2) \qquad (5)$$

bearing in mind that the probabilities may be more complex than originally imagined. Substitution of Eqs. (1) and (2) into (5) gives for a binary copolymerization:

$$\frac{dM_1}{dM_2} = \frac{1 + R_{12}\left(\dfrac{1 + r_{12}x_2}{1 + r_{11}x_1}\right)\dfrac{M_1}{M_2}}{1 + R_{21}\left(\dfrac{1 + r_{21}x_1}{1 + r_{22}x_2}\right)\dfrac{M_2}{M_1}} \qquad (6)$$

where the true reactivity ratios $R_{ij}$ are the ratio of the true propagation rate constants $f_{ii}/f_{ij}$.

We now define an apparent reactivity ratio

$$R_{ij}{}^{a} = (f_{ii}/f_{ij})\left(\frac{1 + r_{ij}x_j}{1 + r_{ii}x_i}\right) \qquad (7)$$

which converts Eq. (6) to the form of the Mayo-Lewis equation:

$$\frac{dM_1}{dM_2} = \frac{1 + R_{12}{}^{a}\dfrac{M_1}{M_2}}{1 + R_{21}{}^{a}\dfrac{M_2}{M_1}} \qquad (6')$$

## DISCUSSION

There are two very different instances where reactivity ratios obtained by fitting the Mayo-Lewis equation to a potentially reversible copolymerization system can appear to be statistically precise descriptions of the composition data:

(a) Where the contribution of depropagation is so small as to be negligible in comparison with the scatter of experimental data.

(b) Where the compositional dependency of the function

$$\left(\frac{1 + r_{ij}x_j}{1 + r_{ii}x_i}\right)$$

is not too strong over the experimental range investigated.

Case (a) corresponds to both $x_1$ and $x_2$ of Eq. (6) being negligibly small. In such a case the physical significance of the numbers obtained as reactivity ratios from application of the Mayo-Lewis equation is real, and a complicated model, such as our diad model, is unnecessary. Such a case, for example, is that of the data of Rudin and Johnston [8] for styrene—α-methylstyrene at 60° C. For model discrimination in such a case, sequence distribution measurements are to be preferred [9] to composition measurements.

Case (b) is the more troublesome, in that a system such as styrene—α-methylstyrene cannot really be expected to be irreversible at 90 or 100°, even if it is at 60°. Therefore, Arrhenius plots of reactivity ratios have been shown to exhibit great curvature [10], or even a temperature dependency opposite to what might reasonably be expected [8]. The physical significance of the apparent reactivity ratios is not simple in such cases, and is, in terms of the diad model, that given by Eq. (7). It is easy to appreciate from Eq. (7) why apparent reactivity ratios may have an unusual temperature dependency.

Wittmer [10] had shown that the composition behavior of α-methylstyrene—methyl methacrylate copolymer system can be described in the temperature range 20-100°C using the Mayo-Lewis equation and the apparent reactivity ratios. Wittmer rejected this approach partly because these reactivity ratios have a strange temperature dependency. He also calculated the true reactivity ratios from his equation of Case 1, where he assumed $r_{22} = r_{12} = r_{21} = 0$. At the higher temperature range (100-150°C) his equations of Case 1 and Case 2 ($r_{12} = r_{21} = 0$) failed to describe this system and therefore additional parameters $q_i = r_{ij}/f_{ji}$ were needed.

As a support of the validity of our Eq. (6), we have derived Wittmer's equations of Case 1 and Case 2. (The derivations are rather long and available from the authors.)

In summary, while it is possible to represent composition data for a reversible copolymerization by the Mayo-Lewis equation, it is also possible to put a correct physical interpretation on the parameters derived from that equation. These parameters are not simple reactivity ratios, and should neither be reported nor used as such.

## ACKNOWLEDGMENT

Support of this research by the National Research Council of Canada is greatly appreciated.

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Accepted by editor January 31, 1973
Received for publication February 14, 1973